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Lise Maisonneuve

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THÈSE

PRÉSENTÉE A

L'UNIVERSITÉ BORDEAUX 1

ÉCOLE DOCTORALE DES SCIENCES CHIMIQUES

Par **Lise MAISONNEUVE**

POUR OBTENIR LE GRADE DE

DOCTEUR

SPÉCIALITÉ : Polymères

**VEGETABLE OILS AS A PLATFORM
FOR THE DESIGN OF SUSTAINABLE AND NON-ISOCYANATE
THERMOPLASTIC POLYURETHANES.**

**Les huiles végétales comme plate-forme pour le « design » de polyuréthanes
thermoplastiques plus durables et sans isocyanates.**

Directeur de recherche : Pr. H. Cramail

Soutenance le : 17 décembre 2013

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*"In theory, theory and practice are the same.
In practice, they are not."
A. Einstein*

General Table of contents

Résumé en français	1
List of abbreviations and acronyms	9
List of publications	10
General introduction	11

PART I - Chapter 1: Literature - Toward vegetable oils-based thermoplastic polyurethanes via the isocyanate/alcohol route

<i>Introduction</i>	24
<i>1- Vegetable oils</i>	24
1.1- Vegetable oils composition	25
1.2- Reactive sites and common derivatives from vegetable oils	27
<i>2- Derivatization of fatty acid derivatives to thermoplastic PUs via the alcohol/isocyanate route</i>	28
2.1- Fatty acid-based diols	31
2.1.1- Diols containing ether and ester functions	31
2.1.2- Saturated and Unsaturated diols	35
2.1.3- Diols containing thioether linkages	36
2.2- Fatty acid-based diisocyanates	36
<i>Conclusion</i>	38
<i>References</i>	39

PART I - Chapter 2: Design of new diols from fatty acid methyl esters for the synthesis of poly(ester/amide urethane)s with versatile properties

Introduction	44
1- Monomer synthesis	44
1.2- Diol synthesis and characterizations	44
1.2.1- Transesterification step	45
1.2.2- Amidation step	47
1.2.3- Thiol-ene reaction on ester and amide-containing bis-unsaturated monomers	49
2- Polymerizations	50
2.1- Polyurethane synthesis	50
2.2- Molar masses and chemical structures	51
3- Thermal stability and thermo-mechanical properties	54
3.1- Thermal stability	54
3.2- Thermo-mechanical properties and crystallization	56
3.3- Crystalline structure	62
3.4- Mechanical properties	63
4- Organocatalysis for fatty acid-based diol and diisocyanate polyaddition	65
Conclusion	69
References	70
Experimental and supporting information	72

PART II - Chapter 1: Literature - Toward non-phosgene and non-isocyanates polyurethanes from vegetable oils

Introduction	87
1- Non-phosgene or non-isocyanate routes to PU	88
1.1- Non-phosgene isocyanate syntheses to PU	88
1.1.1- Reductive carbonylation of nitro compounds	88
1.1.2- Curtius, Hofmann and Lossen rearrangements	89
1.2- Phosgene non-isocyanate routes to PU	90
1.2.1- ROP of cyclic urethanes	90
1.2.2- From bis-(dialkyl carbonate)s	91
2- Non-phosgene and non-isocyanate routes to PUs	92
2.1- Transurethanization with non-phosgene-based bis-(dialkyl carbamate)s	92
2.1.1- Bis-(Dialkyl Carbamate)s from dimethylcarbonate	92
2.1.2- Bis-(Dialkyl Carbamate)s from ethylene carbonate	93
2.2- Thermoplastic polyhydroxyurethanes (PHUs)	94
2.2.1- Synthesis of cyclic carbonates	96
2.2.1.1- Synthesis of 5-membered cyclic carbonates (5CC)	96
2.2.1.2- Synthesis of 6- and 7-membered cyclic carbonates (6CC and 7CC)	99
2.2.1.3- Synthesis of bis-cyclic carbonates (bCC)	101
2.2.1.4- Reactivity of cyclic carbonates	102
2.2.2- Synthesis of amines	104
2.2.3- Studies on the model cyclic carbonate / amine reaction	106
2.2.3.1- Mechanism	107
2.2.3.2- Kinetic and reaction conditions	108
2.2.3.3- Effect of the chemical structure of the amine	111
2.2.3.4- Effect of the substituents and size of the cyclic carbonate	112
2.2.3.5- Selectivity of the reaction and by-products	114
2.2.4- Thermoplastic poly(hydroxyurethane)s (PHUs)	116
2.2.4.1- Reaction conditions, yield and kinetic	117
2.2.4.2- Molar masses	119
2.2.4.3- Selectivity and side reactions	120
2.2.4.4- Different reactivity for specific monomers	121
2.2.4.5- Thermo-mechanical properties and thermal stability	124
2.2.5- Additives and catalysts for the cyclic carbonate/amine reaction	125
2.2.6- Conclusion	128

3- Vegetable oils transformations to non-isocyanate and non-phosgene PUs	129
3.1- Transurethanization approach	129
3.1.1- Carbamate synthesis via Curtius rearrangement	129
3.1.2- Carbamate synthesis from ethylene carbonate	130
3.1.3- Carbamate synthesis via Lossen rearrangement	131
3.2- Vegetable oils-based 5-membered cyclic carbonates to poly(hydroxyurethane)s	131
3.2.1- Synthesis of poly(5-membered cyclic carbonates) from vegetable oil derivatives	131
3.2.2- Non-isocyanate PHU networks from vegetable oil derivatives	133
3.2.3- Fatty acid-based thermoplastic PHUs	136
3.3- Toward vegetable oils-based diamines	137
Conclusion	140
References	141

PART II - Chapter 2: Vegetable oils-based non-isocyanate PHUs via 5 membered cyclic carbonates

Introduction	150
1- Monomer synthesis	150
1.1- Bis epoxides intermediates	151
1.1.1- Transesterification and amidation	151
1.1.2- Epoxidation reaction	155
1.2- The bis 5-membered cyclic carbonate by carbonation with CO₂	155
2- Polymerization	159
2.1- Synthesis of PHUs and related molar masses	159
2.2- Thermo-mechanical properties	163
3- Catalysis of a model reaction	166
Conclusion and limitations	170
References	170
Experimental and supporting information	171

PART II - Chapter 3: Toward vegetable oil-based non-isocyanate PHUs from more reactive 6-membered cyclic carbonates

<i>Introduction</i>	182
<i>1- Bis 6-membered cyclic carbonate (b6CC) synthesis</i>	182
<i>1.1- Synthesis of the 6-membered cyclic carbonate (Und-6CC)</i>	183
<i>1.2- Coupling reactions</i>	187
<i>2- Comparison of different cyclic carbonates reactivity</i>	190
<i>3- Polymerization</i>	199
<i>3.1- Synthesis of PHUs and related molar masses</i>	199
<i>3.2- Thermal stability and thermo-mechanical properties</i>	206
<i>Conclusion</i>	207
<i>References</i>	208
<i>Experimental and supporting information</i>	209

PART II - Chapter 4: Vegetable oils-based diamines toward fully bio-based and non-isocyanate PHUs

Introduction	220
1-Diamine synthesis	220
1.1- Route via amide intermediates	221
1.1.1- Diacid precursors	221
1.1.2- Diamide synthesis	223
1.2- Route via nitrile intermediates	226
1.2.1- Diol precursors	226
1.2.2- Dinitriles synthesis	227
1.3- Diamines synthesis and comparison of the two routes	232
1.3.1- Reduction of primary diamides and dinitriles	232
1.3.2- Comparison of the two routes	235
2- Polymerizations to fully fatty acid-based PHUs	236
3- Thermal stability and thermo-mechanical properties	238
Conclusion	239
References	240
Experimental and supporting information	241
Conclusions and perspectives	251
Materials and Measurements	255
Appendix	261

RESUME EN FRANÇAIS :

Les huiles végétales comme plate-forme pour le « design » de polyuréthanes thermoplastiques plus durables et sans isocyanates.

Cette thèse porte sur la synthèse de polyuréthanes (PUs) thermoplastiques plus respectueux de l'environnement à partir d'huiles végétales, par voie organocatalysée et sans isocyanates. Elle s'inscrit dans le cadre de l'ANR POLYGREEN (CP2D-2009) en partenariat avec l'Iterg (Institut des corps gras) et l'ISM (Institut des Sciences Moléculaires). Les travaux de thèse ont été effectués au LCPO (Laboratoire de Chimie des Polymères Organiques) sous la direction du Prof. H. Cramail.

Introduction

Avec une production mondiale d'environ 20 millions de tonnes en 2011, les PUs représentent une classe importante de polymères. Ils sont traditionnellement synthétisés par polyaddition entre un diol (ou polyol) et un diisocyanate (ou polyisocyanate) (Schéma S-1). Les propriétés des PUs sont très variables en fonction de la nature chimique des monomères utilisés. Cependant, plusieurs points dans la synthèse de ces matériaux sont à améliorer pour engager un développement plus durable de ces derniers, et notamment l'utilisation de ressources renouvelables et de voies de synthèse sans phosgène et sans isocyanates.

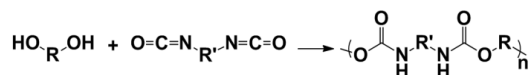


Schéma S-1- Synthèse de polyuréthanes thermoplastiques à partir d'un diol et d'un diisocyanate.

Le cycle du carbone des produits chimiques et des polymères issus des ressources fossiles est déséquilibré. (Figure S-1) En effet, le temps nécessaire pour leur consommation et leur dégradation en dioxyde de carbone est bien plus court que celui requis pour la régénération des réserves fossiles. De ce fait, la grande majorité de la matière de ce cycle du carbone sera un jour sous forme de dioxyde de carbone, et donc indisponible. Au contraire, le temps de régénération de la biomasse est comparable au temps d'utilisation et de retour à l'état de dioxyde de carbone. Compte tenu de ce simple constat, et de la volatilité des prix du pétrole,

l'utilisation de la biomasse pour la préparation de produits chimiques et de polymères est une perspective évidente et nécessaire pour un développement durable à long terme.

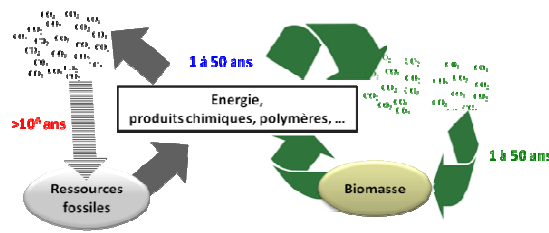


Figure S-1- Cycle du carbone et temps de régénération des ressources fossiles et de la biomasse.

Durant cette dernière décennie, de nombreuses initiatives pour valoriser la biomasse se sont développées. Parmi les ressources renouvelables disponibles, les huiles végétales présentent un large potentiel pour substituer les monomères issus du pétrole, du fait de leur variabilité, disponibilité, durabilité et biodégradabilité.^{1, 2} Ce manuscrit de thèse est divisé en deux parties. Dans ces deux parties, une étude bibliographique est présentée dans un premier temps, puis les résultats expérimentaux y sont développés. (Schéma S-2)

Dans la première partie de cette thèse, l'utilisation des huiles végétales pour la préparation de PUs thermoplastiques suivant la voie alcool/isocyanate est proposée. Par ailleurs, compte tenu de la volonté de proscrire les catalyseurs métalliques toxiques, l'utilisation de catalyseurs organiques a été étudiée sur cette approche. Aussi, du fait de la toxicité des isocyanates et du phosgène, ces composés doivent être remplacés dans la préparation de PUs. La seconde partie de cette thèse vise donc à décrire les alternatives possibles pour la synthèse de PUs sans phosgène et/ou sans isocyanates, via la synthèse à partir de dérivés d'huiles végétales, de carbonates cycliques à 5 et 6 chaînons, ainsi que de diamines.

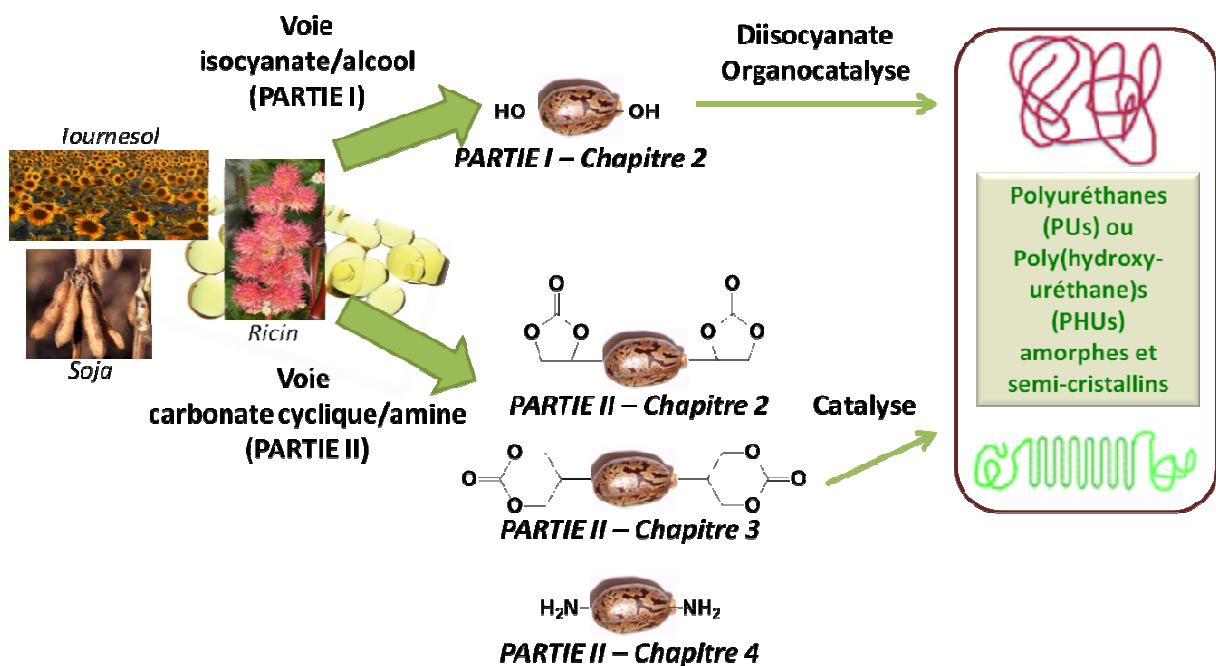


Schéma S-2- Organisation du manuscrit.

PARTIE I : Vers des PUs thermoplastiques à partir d'huiles végétales suivant la voie isocyanate/alcool

Tout comme d'autres ressources renouvelables telles que la cellulose, l'hémicellulose, l'amidon, la lignine, ..., les huiles végétales ont attiré l'attention des chercheurs pour remplacer les ressources fossiles actuelles. Les triglycérides, composant des huiles, présentent des sites réactifs notamment des fonctions ester et des doubles liaisons, permettant des modifications chimiques et donc le « design » de nouveaux monomères. Le premier chapitre de cette partie expose plus particulièrement la littérature concernant les PUs issus des huiles végétales par la voie isocyanate/alcool. Les huiles végétales sont tout d'abord décrites en termes de composition chimique et de marché. Les précurseurs commercialement disponibles pouvant en être issus et qui seront exploités dans cette thèse sont également présentés. L'huile de ricin, qui présente un caractère non alimentaire, et plus précisément un de ces dérivés, l'undécénoate de méthyle, sont principalement utilisés dans ces travaux. Dans un second temps, les différentes réactions chimiques conduisant à la synthèse de polyols et de polyisocyanates directement à partir des triglycérides sont brièvement exposées. Enfin, la littérature concernant la préparation de PUs thermoplastiques à partir de dérivés d'huiles végétales (acides gras, esters méthyliques d'acides gras) par la voie isocyanate/alcool est proposée. Cette dernière étude a fait l'objet d'une revue dans *Polymer Chemistry*.³ Les résultats développés dans cette étude ont conduit à la préparation de PUs thermoplastiques amorphes à haute température de transition vitreuse voire semi-cristallins à partir de dérivés des huiles végétales.

« Design » de nouveaux diols à partir d'esters méthyliques d'acides gras pour la synthèse d'une large gamme de poly(ester/amide uréthane)s thermoplastiques.

Dans un premier temps, des diols ont été synthétisés à partir de l'undécénoate de méthyle et de l'oléate de méthyle, par transesterification/amidification puis addition thiol-ène. Du fait de la structure aliphatique inhérente aux dérivés des huiles végétales, des PUs amorphes ayant des températures de transition vitreuse relativement basses sont classiquement décrits dans la littérature. L'objectif était donc l'obtention, à partir des huiles végétales, de PUs amorphes à haute température de transition vitreuse voire de PUs semi-cristallins. Pour cela, l'incorporation de liaisons amide très cohésives par liaisons hydrogène a notamment

été réalisée. Une série de diols bio-sourcés contenant les liaisons ester et/ou amide a été préparée. Ces monomères ont été caractérisés par spectroscopies infrarouge (IR) et de résonance magnétique nucléaire (RMN) ainsi que par chromatographie en phase gaz (GC), puis ont été utilisés en polyaddition. Une large gamme de PUs thermoplastiques ayant des propriétés thermo-mécaniques modulables a été préparée par réaction de ces différents diols avec deux diisocyanates : le diisocyanate d'isophorone (IPDI) et le 4,4'-diisocyanate de diphenylméthylène (MDI). Les PUs obtenus ont notamment été caractérisés par calorimétrie différentielle à balayage (DSC), analyse thermo-gravimétrique (TGA), analyse mécanique dynamique (DMA) et par des tests de traction. Les PUs obtenus étaient amorphes ou semi-cristallins en fonction de la nature chimique du diol et du diisocyanate utilisé. La DSC modulée a révélé des températures de transition vitreuse dans la gamme -27 °C à 63 °C, ainsi que la présence de phases cristallines métastables. La présence de ces phases métastables a été confirmée par microscopie de force atomique et par des analyses aux rayons X. Grâce à l'incorporation des liaisons amide, une augmentation significative du module de Young de 287 MPa à 775 MPa a pu être obtenue. Ces travaux ont permis la rédaction d'un brevet ⁴ et d'une publication dans *Polymer Chemistry* ⁵. Dans un second temps, la catalyse organique de la réaction entre un diol issu des huiles végétales et un diisocyanate a été étudiée. Elle a démontré que des catalyseurs organiques tels que la guanidine MTBD permettent d'obtenir des PUs ayant des masses molaires similaires avec des temps de polymérisation convenables.

PARTIE II : Vers des PHUs thermoplastiques sans isocyanates et sans phosgène à partir d'huiles végétales

Dans un contexte de développement durable, l'utilisation de diisocyanates et de phosgène pour la préparation des PUs doit être bannie du fait de leur toxicité mais aussi des nouvelles réglementations REACH. La deuxième partie de cette thèse présente donc les différentes voies de synthèse de PUs sans phosgène ou/et sans isocyanates. L'accent est mis sur une voie prometteuse de synthèse sans isocyanates et sans phosgène de poly(hydroxyuréthane)s (PHUs) qui consiste en la réaction d'un bis carbonate cyclique (ou polycarbonate cyclique) et d'une diamine (ou polyamine). ² (Schéma S-3)

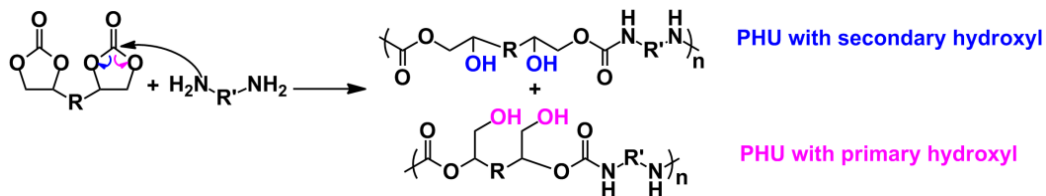


Schéma 5-3- Synthèse de polyuréthanes thermoplastiques sans isocyanates ni phosgène à partir d'un bis carbonate cyclique et d'une diamine.

Dans la littérature, différents précurseurs bis carbonates cycliques, ainsi que les PHUs correspondants ont été synthétisés à partir des huiles végétales. Aussi, les mécanismes de polyaddition et les différents catalyseurs permettant la catalyse des PHUs sont brièvement exposés. La littérature concernant les PHUs et/ou leurs précurseurs (carbonates cycliques et amines) issus des huiles végétales est également présentée. Dans les chapitres suivant de cette deuxième partie (chapitres 2, 3 et 4), les différents résultats expérimentaux liés à la voie bis carbonate cyclique/diamine sont présentés. L'intérêt s'est porté sur la synthèse de bis carbonates cycliques à 5 et 6 chaînons et sur le développement de voies prometteuses pour l'obtention de diamines à partir d'huiles végétales.

Bis carbonates cycliques à 5 chaînons issus de l'undécénoate de méthyle pour la synthèse de PHUs thermoplastiques sans isocyanates et sans phosgène.

Ce second chapitre est consacré à la synthèse de bis carbonates cycliques à 5 chaînons, présentant des liaisons ester ou amide, par transesterification ou amidification, époxydation puis carbonation, ainsi qu'à la préparation des PHUs en découlant. L'intérêt d'utiliser des groupements amide, plus stables, plutôt que des esters est principalement de limiter les réactions secondaires possibles d'amidification, déjà rapportées lors de la polymérisation de carbonates cycliques à 5 chaînons peu réactifs avec des diamines. Différents bis carbonates cycliques à 5 chaînons, ayant des blocs centraux variables, ont été préparés à partir de l'undécénoate de méthyle. Les monomères synthétisés ont été caractérisés par spectroscopies IR et de RMN, ainsi que par GC quand la solubilité le permettait. Ils ont ensuite été utilisés en polyaddition avec des diamines telles que l'isophorone diamine (IPDA), la butane-1,4-diamine (4DA), la diamine CRODA et la Jeffamine 400. Des masses molaires relativement élevées ($11\ 000\ \text{g}\cdot\text{mol}^{-1}$ - $31\ 000\ \text{g}\cdot\text{mol}^{-1}$) ont été atteintes. Les PHUs ont ensuite été caractérisés par DSC et TGA. Ces derniers présentent une large gamme de propriétés thermo-mécaniques, qui ont pu être corrélées à la structure chimique des

monomères utilisés. Les PHUs sans isocyanates obtenus étaient amorphes ou semi-cristallins avec des températures de transition vitreuse comprises entre -21°C et 55°C .

Cependant, les polyadditions ont nécessité des températures et des temps de polymérisation élevés. De plus, la polymérisation sans solvant a été nécessaire. La faible réactivité des bis carbonates cycliques à 5 chaînons peut s'expliquer par l'effet inductif +I des longues chaînes alkyle qui désactivent le carbonate cyclique. Les deux possibilités pour améliorer ce système sont la catalyse et la synthèse de carbonates cycliques plus réactifs. La catalyse de la réaction entre le carbonate de propylène et l'hexylamine a été étudiée. Elle a démontré l'efficacité du catalyseur de Schreiner. Cependant il est efficace uniquement jusqu'à une certaine conversion après quoi son action par doubles liaisons hydrogène semble inhibée par le réseau de plus en plus dense de liaisons hydrogène issues des hydroxyuréthanes formés.

Vers des bis carbonates cycliques plus réactifs à partir de l'undécénoate de méthyle: synthèse de bis carbonates cycliques à 6 chaînons et des PHUs correspondants

La synthèse de carbonates cycliques, plus réactifs que ceux pouvant être classiquement obtenus à partir des huiles par époxydation et carbonation, a été effectuée. Dans un premier temps, un carbonate cyclique à 6 chaînons est préparé à partir de l'undécénoate de méthyle via deux intermédiaires : un malonate et un 1,3-diol. Ce carbonate cyclique à 6 chaînons est ensuite couplé en conditions douces soit par métathèse, soit par réaction thiol-ène, pour obtenir deux bis carbonates cycliques à 6 chaînons. Les (bis) carbonates cycliques synthétisés sont alors utilisés en réactions modèles avec l'hexylamine, ainsi que dans la synthèse de PHUs avec la dodecane-1,12-diamine (12DA). L'amélioration de la réactivité des carbonates cycliques à 6 chaînons vis-à-vis de ceux à 5 chaînons est démontrée. Les constantes de vitesse de réaction de plusieurs carbonates cycliques avec l'hexylamine ont été calculées sur la base d'une réaction d'ordre 2, qui corrèle finement les valeurs expérimentales. Les constantes de vitesse de réaction du carbonate de triméthylène et du carbonate d'éthylène avec l'hexylamine sont respectivement de $1.42 \text{ L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ et $0.55 \text{ L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ dans les conditions étudiées. Pour la réaction entre le carbonate cyclique à 6 chaînons issu des huiles végétales et l'hexylamine, l'énergie d'activation a pu être calculée via des réactions modèles à différentes températures, et est estimée à $20.7 \text{ kJ}\cdot\text{mol}^{-1}$. Les bis carbonates cycliques à 6 chaînons se sont avérés plus réactifs que leurs homologues à 5 chaînons. Les PHUs obtenus ont des masses molaires allant jusqu'à $23\,000 \text{ g}\cdot\text{mol}^{-1}$ (dispersité de 1.7) après un jour de

polymérisation en solvant. Avec des analyses MALDI-TOF MS, la formation non désirée d'urée au cours d'une trempe chimique a pu être mise en évidence. Des températures de transition vitreuse entre -20°C et 0°C ont été observées. La plus grande réactivité des carbonates cycliques à 6 chaînons permet la polymérisation en solution et l'obtention rapide de conversions élevées.

Synthèses de diamines à partir d'huiles végétales pour la préparation de PHUs sans isocyanates entièrement bio-sourcés

Dans la littérature, très peu de diamines à partir d'acides gras ont été développées. Dans la dernière partie de ce manuscrit de thèse, la synthèse de diamines à partir de l'undécénoate de méthyle et de l'acide sébacique, tous deux issus du ricinoléate de méthyle a été réalisée. Deux voies de synthèse sont envisagées pour préparer des diamines à partir de ces dérivés des huiles végétales. La première méthode fait intervenir la préparation de chlorures d'acyle puis de diamides primaires à partir de diacides. La seconde approche nécessite la synthèse de dinitriles à partir de diols. Une procédure, utilisant le dioxygène comme oxydant et un complexe catalytique à base de cuivre pour la synthèse, à partir d'alcools primaires, de nitriles en conditions douces, est adaptée aux dérivés aliphatiques issus des huiles. Suivant les deux stratégies, une dernière étape de réduction est nécessaire pour l'obtention des diamines. Cette dernière s'est avérée délicate à mettre en œuvre pour les diamides primaires du fait de leur faible solubilité. Aussi, la voie nitrile s'est avérée plus prometteuse du fait des conversions élevées obtenues. Des PHUs sans isocyanates et potentiellement entièrement bio-sourcés ont été synthétisés. L'utilisation de différents carbonates cycliques à 5 et 6 chaînons dans les mêmes conditions de polymérisation a également permis une comparaison directe de leur réactivité en polyaddition.

Conclusion

Les huiles végétales ont permis la préparation d'une plateforme de précurseurs de PUs : diols, bis carbonates cycliques à 5 et 6 chaînons, ainsi que diamines. Les propriétés thermo-mécaniques ont pu être ajustées via le « design » de la structure chimique des précurseurs issus des huiles végétales. La voie de synthèse de PUs sans isocyanates basée sur la réaction entre des bis carbonates cycliques et des diamines a été étudiée en détails et a été appliquée aux ressources renouvelables telles que les huiles végétales.

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List of abbreviations and acronyms

Monomers:

(b)nCC=(bis) n-membered cyclic carbonate (n=5,6,7)
HDI=1,6-hexamethylene diisocyanate
HPMDI=1,7-heptamethylene diisocyanate
IPDA=isophorone diamine
IPDI=isophorone diisocyanate
MDI=4,4'-methylene diphenyl diisocyanate
TDI=toluene-2,4-diisocyanate
4DA=butane-1,4-diamine
12DA=decane-1,10-diamine

Reactants:

LiAlH₄=lithium aluminium hydride
m-CPBA=meta-chloroperbenzoic acid
NaH=sodium hydride
TCB= 1,2,4-trichlorobenzene
UndME=methyl 10-undecenoate
5CC=ethylene carbonate
5CChydroxyl=glycerol carbonate
5CCMe=propylene carbonate
5CCvinyl=vinyl ethylene carbonate
6CC=trimethylene carbonate

Solvents:

DCM=dichloromethane
DEC=diethylcarbonate
DMAc=dimethylacetamide
DMC=dimethylcarbonate
DMF=N,N-dimethylformamide
DMSO=dimethylsulfoxide
NMP=N-methyl-2-pyrrolidone
THF=tetrahydrofuran

Techniques:

AFM=Atomic Force Microscopy
COSY=Homonuclear correlation Spectroscopy
DMA=Dynamic Mechanical Analysis
(Mod)DSC=Modulated Differential Scanning Calorimetry
ESI-TOF MS=Time-of-flight Mass Spectrometer with ElectroSpray Ionization
FTIR-ATR=Fourier Transformed Infrared-Attenuated Total Reflection
GC-FID=Gas chromatography with Flame Ionization Detectors
HSQC=Heteronuclear single quantum coherence
MALDI-TOF MS=Time-of-flight Mass Spectrometer with Matrix-Assisted Laser Desorption/Ionization
NMR=Nuclear Magnetic Resonance
SEC=Size Exclusion Chromatography
TGA= Thermogravimetric Analysis
WAXS=X-ray diffraction patterns at wide angles

Catalysts/initiators:

AIBN=azobisisobutyronitrile
DABCO=diazabicyclooctane
DBTDL=dibutyltin dilaurate
DBU=1,8-diazabicyclo[5.4.0]undec-7-ene
BnTBO=6-benzyl-1,4,6-triazabicyclo-[3.3.0]oct-4-ene
DMAP=4-dimethylaminopyridine
DMPA=2,2-Dimethoxy-2-phenylacetophenone
MMII=1-methyl-3-methylimidazolium iodide
MTBD=7-methyl-1,5,7-triazabicyclo-[4.4.0]dec-5-ene
MTBN=7-methyl-1,5,7-triazabicyclo-[4.3.0]non-5-ene
TBABr=tetra-n-butylammonium bromide
TBD=1,5,7-triazabicyclo-[4.4.0]dec-5-ene
TBD.HBr=1,5,7-triaza-bicyclo[4.4.0]dec-5-enium bromide
TEA=triethylamine
ZnAc=zinc acetate

Polymers:

PU(s)=polyurethane(s)
PHU(s)=poly(hydroxyurethane)(s)
TPE-U(s)=thermoplastic elastomer polyurethane(s) or segmented polyurethane(s)
TPU(s)=thermoplastic polyurethane(s)
IPN(s)= interpenetrated network(s)
PA=polyamide
PEG=polyethylene glycol
PTMO= poly(tetramethyleneoxide)
PMMA=polymethylmethacrylate
PS=polystyrene
NIPU(s)=non isocyanate polyurethane(s)

Miscellaneous:

ADMET=Acyclic diene metathesis
CMR=Carcinogenic Mutagenic Reprotoxic
DFT= Density Functional Theory
ROP=Ring Opening Polymerization
RT=Room temperature
T_c=Crystallization temperature
T_g=Glass transition temperature
T_m=Melting temperature

Publications, patents and communications

Publications

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More, A. S.; Lebarbé, T.; Maisonneuve, L.; Gadenne, B.; Alfos, C.; Cramail, H., Novel fatty acid based di-isocyanates towards the synthesis of thermoplastic polyurethanes. *European Polymer Journal* **2013**, 49 (4), 823–833.

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Lebarbé, T.; Maisonneuve, L.; Nguyen, N.; Gadenne, B.; Alfos, C.; Cramail, H., Methyl 10-undecenoate as raw material for the synthesis of renewable semi-crystalline polyesters and poly(ester-amide)s. *Polymer Chemistry* **2012**, 3 (10), 2842-2851.

Maisonneuve, L.; Lebarbé, T.; Nguyen, N.; Cloutet, E.; Gadenne, B.; Alfos, C.; Cramail, H., Hydroxy-telechelic building blocks from fatty acid methyl esters for the synthesis of poly(ester/amide urethane)s with versatile properties. *Polymer Chemistry* **2012**, 3 (9), 2583-2595.

Foltran, S.; Maisonneuve, L.; Cloutet, E.; Gadenne, B.; Alfos, C.; Tassaing, T.; Cramail, H., Solubility in CO₂ and swelling studies by in situ IR spectroscopy of vegetable-based epoxidized oils as polyurethane precursors. *Polymer Chemistry* **2012**, 3 (2), 525-532.

Patents

WO 2013072436 A1 (**2013**), EP 13 306735 (**2013**), EP 13 306736 (**2013**) and EP 13 306737 (**2013**).

Communications

246th ACS National Meeting (Indianapolis, USA, **2013**) – Oral presentation «*Building blocks from fatty acid methyl esters for the synthesis of renewable polyurethanes*».

40^{ème} JEPO (Anduze, France, **2012**) – Oral presentation «*Building blocks from fatty acid methyl esters for the synthesis of renewable polyurethanes*».

MacroGroup UK International Conference on Polymer Synthesis & UKPCF International Conference on Polymer Colloids (Warwick, Grande-Bretagne, **2012**) – Poster.

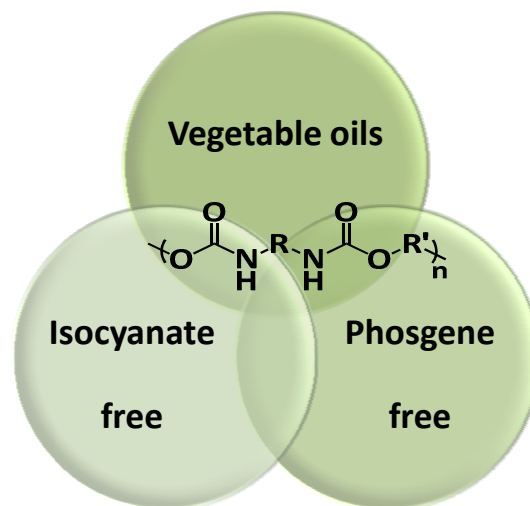
5th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry (Karlsruhe, Allemagne, **2012**) – Poster.

3rd Aquitaine Conference on Polymers (Arcachon, France, **2011**) – Poster.

3rd International Conference on Biodegradable and Biobased Polymers BIOPOL (Strasbourg, France, **2011**) – Poster.

4th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry (Karlsruhe, Allemagne, **2011**) – Poster.

General introduction

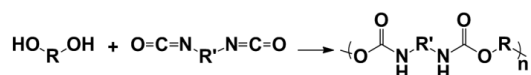


Mots clés : polyuréthanes thermoplastiques, poly(hydroxyuréthane)s, bio-sourcé, huiles végétales, acide gras, sans isocyanates, sans phosgène, catalyse organique, diol, diisocyanate, (bis) carbonate cyclique, (di)amine.

Keywords : thermoplastic polyurethanes (TPUs), poly(hydroxyurethane)s, bio-based, vegetable oils, fatty acid, isocyanate free, phosgene free, organocatalysis, diol, diisocyanate, (bis) cyclic carbonate, (di)amine.

Polymers are widely present in our daily life for numerous applications. Currently, most of the commercially available polymers are derived from non-renewable resources. Worldwide, approximately 7% of the total consumption of fossil oil and gas are used by the polymer industry.¹ The world's annual production of polymers has significantly increased from less than 2 million tons in 1950 to more than 280 million tons in 2011.^{2,3}

Among the various polymers, polyurethanes (PUs) are likely the most versatile polymers and take part of the important class of specialty polymers⁴ with a worldwide production of about 20 million tons in 2011 according to *PlasticsEurope*.³ They were first synthesized by Dr Otto Bayer, in 1947.^{5,6} Then, PU products were introduced on the market in the late 1940s and in slightly more than 70 years of existence, the PUs growth has been constant. It is well-known that the conventional and indisputable route for the preparation of PUs is the reaction of a polyol or a diol, with a polyisocyanate or a diisocyanate. The Scheme I-1 illustrates the formation of thermoplastic PUs from a diisocyanate and a diol. This AA+BB route leads to [n,m]-PUs, but with other methods such as reacting AB monomers or ring opening polymerization of cyclic urethanes, [n]-PUs are achievable.



Scheme I-1-Synthesis of thermoplastic polyurethanes from a diol and a diisocyanate.

One of the remarkable point about PUs lies in their ability to be shaped into different forms like flexible or rigid foams, thermoplastics (TPUs), thermoplastic elastomer PUs or segmented PUs (TPE-U), interpenetrated networks (IPNs), ... As can be seen in Figure I-1, PUs are mostly used in the form of flexible and rigid foams, with 29% and 26% respectively of the PUs market. They are also used in coatings, adhesives, sealants, biomedical materials and elastomers.⁴ The flexible foams are used in automotive seating and sofas, while the rigid foams are used in automotives, construction and building insulations.⁷

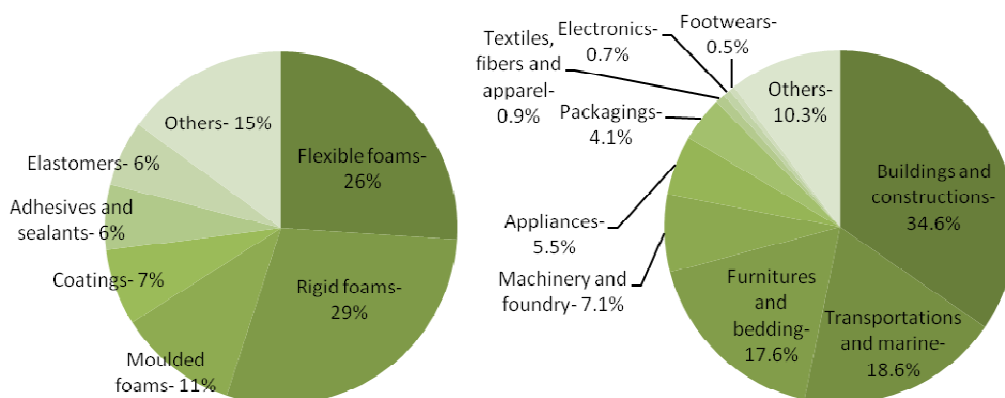


Figure I-1- PUs market sectors^a and applications^b (in 2003, in 2010).^{7,8}

In order to develop more sustainable polymers, a point to consider is the use of green chemistry, which is guided by the “12 Principles of Green Chemistry” introduced in 1998 by Anastas and Warner.⁹ The 12 principles can be classified into four main categories: 1/ the use of safer chemicals, solvents and syntheses, 2/ the use of renewable feedstocks, 3/ the circumvention of pollution and waste, and 4/ the optimization of the syntheses efficiency by the atom economy, the reduction of intermediates, the energy efficiency and the use of catalytic systems instead of stoichiometric amount of chemicals. In order to synthesize more sustainable PUs, we focus on two main aspects: the preparation of renewable bio-based PU precursors and the use of a non-phosgene / non-isocyanate route.

Indeed, there is nowadays an effort to replace petroleum-based resources with renewable ones to improve PUs sustainability. At the beginning of the 19th century, the demand for basic chemicals was satisfied entirely by renewable raw materials, but progressively it has been replaced by coal then petrol. At the beginning of the 21st century, in both a context of limited and so uncertain supply and costs of fossil resources, and meanwhile due to the environmental impacts of the consumptions of non-renewable resources, a renaissance and a growing interest for bio-based polymers is evident. The use of renewable resources is a first step toward a sustainable development.

Concerning the market, as can be seen in Figure I-2, the global production capacity of bio-based and biodegradable polymers in terms of biomass content is expected to increase by 500% by 2016.¹⁰

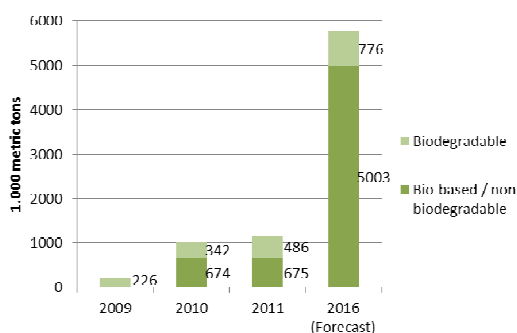


Figure I-2- Global production capacity of bio-based and biodegradable polymers in terms of biomass content (2012).¹⁰

Vegetable oils are one of the most promising renewable resources to prepare monomers for polymer synthesis. By taking advantage of the wide possibilities for chemical modification onto their active sites, vegetable oils can be efficiently converted into new tailored bio-based PU precursors. In the last decade, tremendous efforts have been made to develop a broad range of strategies to functionalize vegetable oils with hydroxyl groups and in a much smaller contribution with isocyanate, cyclic carbonate and amine functions. The large

majority of the research on vegetable oil-based PUs focuses on the synthesis of cross-linked systems, and limited attention has been paid to thermoplastic fatty acid-based PUs.

Synthesizing bio-based PUs is only one part of the answer to more sustainable PUs, but one major drawback in PUs synthesis is the inherent toxicity of diisocyanates. Indeed, they are produced from an even more toxic compound, the phosgene, which in the context of REACH becomes more and more problematic.¹¹ Isocyanate compounds are very harmful and some of them are CMR substances (such as MDI and TDI). Besides, the exposure to isocyanates can result in health issues such as skin irritation and asthma.¹² Due to these hazard concerns, non-phosgene and/or non-isocyanate routes to PUs are being considered. Among them, one of the most promising is the reaction between bis- or poly-functional cyclic carbonates and amine compounds, which gives poly(hydroxyurethane)s (PHUs). Numerous reviews and book chapters have been published on the synthesis of non-isocyanate PHUs¹³⁻¹⁷ and on vegetable oil-based cross-linked and thermoplastic polymers.¹⁸⁻²² Finally, the reader can find numerous reviews on vegetable oils-based PUs.^{2, 23-27}

In this context, this thesis takes part of the ANR POLYGREEN (2009-CP2D) project in collaboration with the *Institut des Sciences Moléculaires (ISM)* and the technical center *ITERG*. The objective of this thesis is the synthesis of vegetable oils-based thermoplastic PUs with organocatalysis following the isocyanate route as well as non-isocyanate routes. Both alcohol/isocyanate (Part I) and cyclic carbonate/amine (Part II) approaches have been developed during this study.

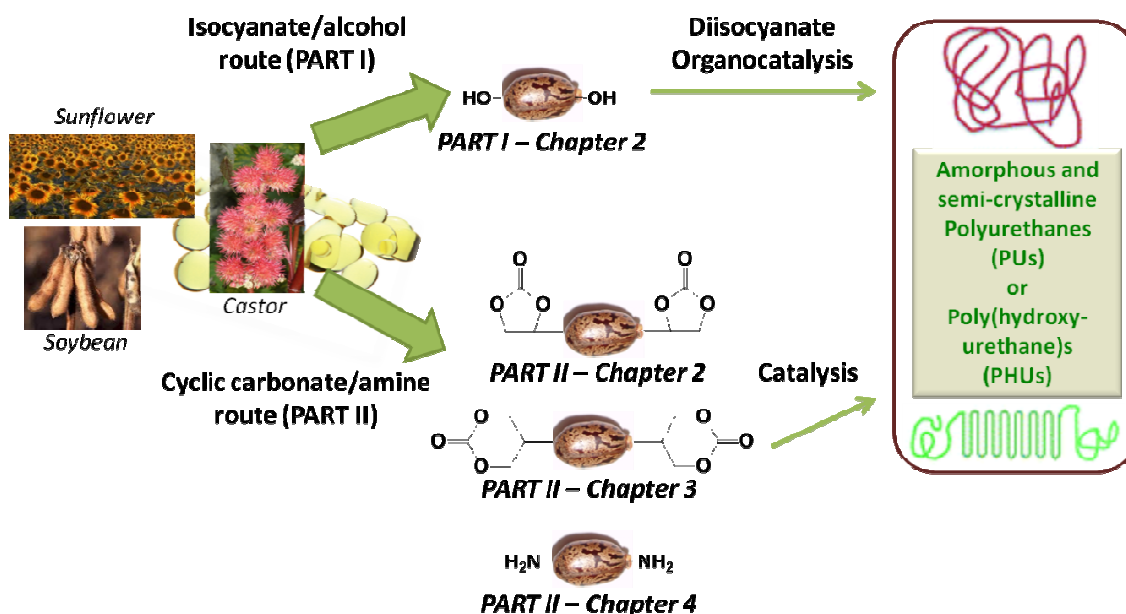
The first chapters of each part attempt to illustrate the state of art of more sustainable PUs through a panoramic overview of vegetable oil-based monomers to PUs, as well as non-isocyanate and/or non-phosgene PUs. (See Scheme I-2) However, the aim of these chapters is neither a comprehensive review on non-isocyanate and non-phosgene chemistry, nor a complete description of all vegetable oil PUs. It is dedicated to provide the reader the basics to better understand the objectives and the achievements of this work.

The first part of this study covers the achievements related to the synthesis of vegetable oil-based PU precursors for the isocyanate/alcohol route. In the first chapter of this part, the contributions of the literature are collected as a function of the different synthetic routes used and the nature of the PUs formed (cross-linked or thermoplastic). The second chapter (Part I - Chapter 2) then exposes the experimental results of the synthesis of vegetable oils-based thermoplastic PUs with a large range of thermo-mechanical properties following this alcohol/isocyanate approach. For this intent, a series of bio-based diols has been prepared

from fatty acid methyl esters by transesterification and/or amidation followed by thiol-ene addition. The catalysis of the polyaddition of a fatty acid-based-diol and a diisocyanate has also been investigated.

The second part of this thesis deals with non-phosgene or/and non-isocyanate routes to vegetable-based PUs. In the first chapter of this second part, an overview of non-isocyanate and/or non-phosgene PUs is briefly provided. The cyclic carbonate/amine route is then exposed in details, underlining notably the mechanisms and the catalysis of PHUs syntheses. Outlines of the PHUs applications and the various methods to synthesize 5- and 6-membered cyclic carbonates and amines are also described. The cyclic carbonate/amine model reactions and corresponding polymerizations are presented as well. Finally the literature about vegetable oil-based cyclic carbonates and amines is developed.

The subsequent chapters (Part II - Chapters 2, 3 and 4) expose the experimental data regarding the cyclic carbonate/amine route. Non-isocyanate and bio-based poly(hydroxyurethane)s with various thermo-mechanical properties have been synthesized. For that purpose, ester and amide-based bis 5-membered cyclic carbonates have first (Part II - Chapter 2) been prepared from methyl undecenoate. Then (Part II - Chapter 3) with the target to reach higher reactivity, bis 6-membered cyclic carbonates have been synthesized via fatty acid-based malonate, 1,3-diol and 6-membered cyclic carbonate intermediates. The differences in reactivity between cyclic carbonates of different chemical structures have been quantified. Finally, with the aim to achieve fully vegetable oil-based and non-isocyanate polyurethanes, a promising route to diamines have been studied from methyl undecenoate, via nitrile intermediates.

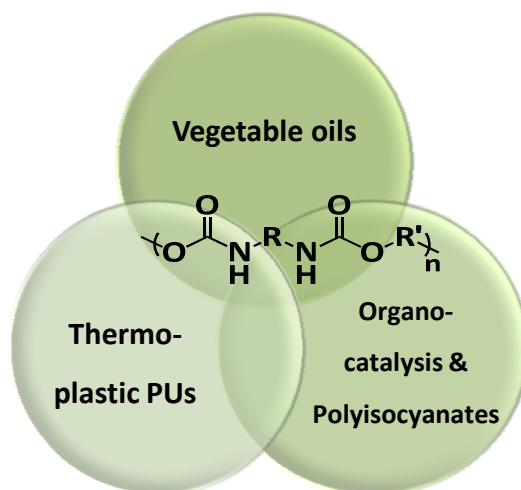


Scheme I-2- Organization of the manuscript.

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PART I



Mots clés : polyuréthanes thermoplastiques, bio-sourcé, huiles végétales, acide gras, voie isocyanate/alcool, diol, diisocyanate, catalyse organique.

Keywords : thermoplastic polyurethanes (TPUs), bio-based, vegetable oils, fatty acid, isocyanate/alcohol route, diol, diisocyanate, organocatalysis.

PART I - Chapter 1: Literature

Toward vegetable oils-based thermoplastic polyurethanes via the isocyanate/alcohol route

*Part of this Chapter has been published in a review article in Polymer Chemistry.*¹

Table of contents

Introduction	24
1- Vegetable oils	24
1.1-Vegetable oils composition	25
1.2- Reactive sites and common derivatives from vegetable oils	27
2- Derivatization of fatty acid derivatives to thermoplastic PUs via the alcohol/isocyanate route	28
2.1- Fatty acid-based diols	31
2.1.1- Diols containing ether and ester functions	31
2.1.2- Saturated and Unsaturated diols	35
2.1.3- Diols containing thioether linkages	36
2.2- Fatty acid-based diisocyanates	36
Conclusion	38
References	39

Introduction

This chapter is dedicated to the literature on thermoplastic vegetable oil-based polyurethanes via the isocyanate/alcohol route. A lot of efforts have been made to replace petroleum-based resources. Among renewable resources, vegetable oils present various advantages going from their availability to the large range of possible chemical modifications. Firstly, the vegetable oil chemical composition and market as well as the main commercially available vegetable oil precursors are exposed. Concerning vegetable oils-based polyurethanes, research groups first focused on cross-linked systems directly from triglycerides then on thermoplastic ones from fatty acids or fatty acid methyl esters. The second part of this chapter focuses on thermoplastic PUs and underlines the literature about the introduction of hydroxyl groups and isocyanate functions onto triglyceride derivatives. Besides, in a view to the isocyanate/alcohol approach, vegetable oil-based thermoplastic PUs and corresponding diols and diisocyanates are described in details.

1- Vegetable oils

Various renewable resources (cellulose, hemicellulose, starch, lignin, natural oils, chitosan,...) have gathered a lot of attention as potential substitute for fossil resources in the polymer science field. Three ways have been studied to obtain renewable polymers. The first and second are respectively the fermentation of the biomass and the chemical degradation and transformation of natural polymers. The third route, which is followed in this thesis, consists in using the biomass obtained from nature with or without chemical transformation.

Why choosing vegetable oils as renewable resources? Vegetable oils are among the most promising renewable resources thanks to various advantages. Indeed, vegetable oils present different chemical structures and various reactive sites that can be straightforward chemically modified into a large range of tailor-made monomers with variable functionalities. Moreover, they are available and annually renewable, regenerated by photosynthesis year after year. The inherent biodegradability of vegetable oils is also an attractive characteristic in the growing environmental concerns context.

One question, which returns continuously, is the competition with the feed and food industry. The scientist's opinions are split on this question. On one hand, some support that

conventional crops is only a part of the solution and underline the serious competition between the production of food and feed, with the bio-based products (chemical and polymers) and the transportation biofuels (bioethanol and biodiesel). They recommend the use of agricultural wastes and the development of both new crops grown on marginal land, and fast-growing vegetative biomass such as grass, wood, ...² On the other hand, it has been shown that biomass can be produced in a sufficient volume for industrial utilization without compromising the food supply for the increasing global population.³ Besides, the needs of raw materials for bio-based products will always be very modest compared to the food and feed requirements.⁴ Indeed, the bio-based and biodegradable plastics rely on only 0.006% of the global agricultural area of 5 billion ha in 2011, and is predicted to be 0.022% in 2016.⁵ To replace fossil resources in polymer science, different strategies need to be studied at the same time such as the use of wastes (agricultural and others), the use of inedible resources, the improvement of biomass growing and the use of various renewable resources (vegetable oils but also others) to satisfy the requirement of sustainability.

Another key issue up to date is the high cost involved in processing renewable resources into chemicals compared with their synthesis from fossil resources. The difference is that processes from fossil resources have been continuously improved during more than one century resulting in a very high degree of technical and cost optimization, whereas methods to obtain chemicals from biomass are comparatively in their infancy. Therefore, wide research and development efforts in biotechnology, chemistry and engineering are required to reduce processing cost by valorizing co-products and by-products and optimizing the inputs (feedstock supply, water management) and outputs (energy and product recovery, treatment of waste).² The life cycle analysis of the synthesized product is also a crucial tool to take into account in order to validate whether the use of biomass in such or such application is relevant or not.

In the last decades, numerous studies and reviews have emerged using fats and oils for the polymer field.^{3, 6-10}

1.1-Vegetable oils composition

The main constituents of vegetable oils are triglycerides which are the esterification product of glycerol with three fatty acids. The fatty acids account for 95% of the total weight of triglycerides.⁷ Each vegetable oil contains different triglycerides with various fatty acid

chains. Fatty acids and fatty acid methyl esters can be recovered and purified from vegetable oil respectively by saponification and transesterification with methanol.¹¹ The common fatty acids that can be obtained vary from 14 to 20 carbons in length, with 0 to 3 double bonds per fatty acid. Soybean and sunflower oils, for instance, consist of largely linoleic acid (C18:2) and oleic acid (C18:1). The fatty acid structure and the compositions of few common oils are given in Figure I-1-1.

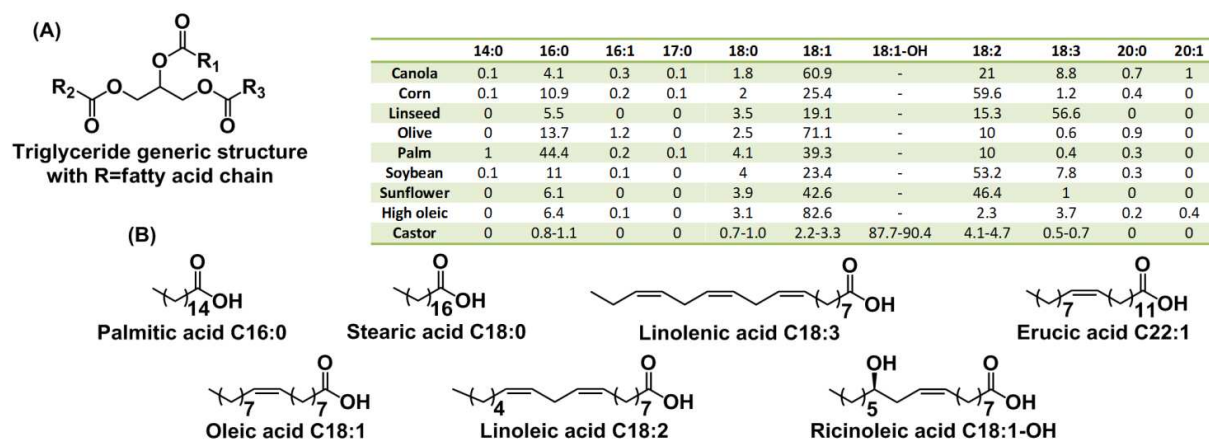


Figure I-1-1- (A) General triglyceride structure and the proportion of the different fatty acid chains in vegetable oils. (B) Common fatty acids found in vegetable oils. (In C_x:_y, the x=chain carbon atoms and y=number of C-C double bonds).^{7, 12}

The fatty acid composition in vegetable oils varies depending on the plant, the crop, the season, the growing conditions, the year and the location of crops.¹³ The annual world supply and distribution of the major vegetable oils in 2009/10 amounted to 141 Million tons (Mt), increasing in 2010/11 to 148 Mt and to 156 Mt in 2011/12.¹⁴ On the Figure I-1-2, the evolution of the world supply and distribution of the major vegetable oils, as well as the compared proportion of each vegetable oil are represented.

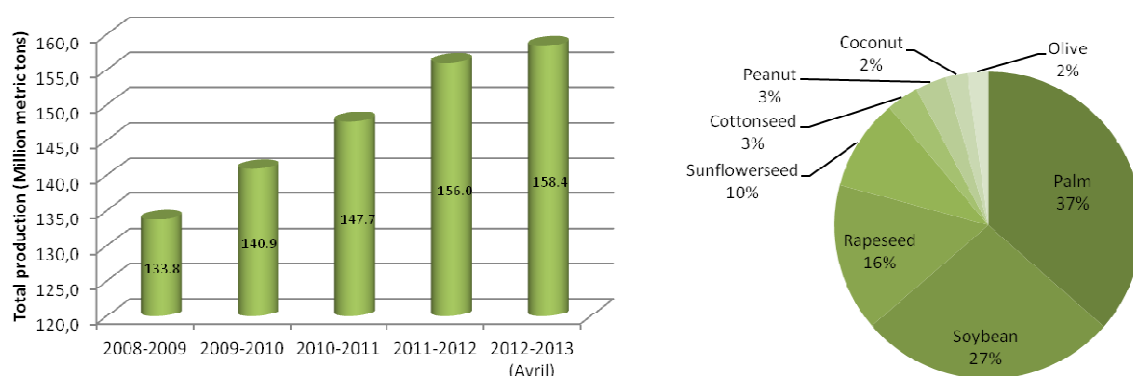
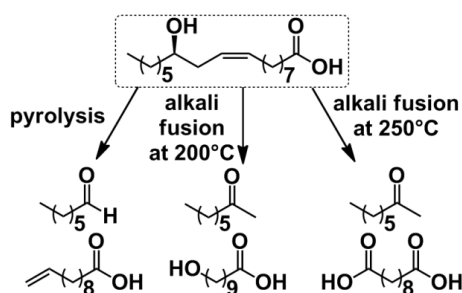


Figure I-1-2- World supply and distribution of the major vegetable oils and their proportions in 2011-2012.¹⁴

1.2- Reactive sites and common derivatives from vegetable oils

Two main approaches are followed to synthesize polymers from vegetable oils. The first way is the direct use of triglycerides taking advantages of the naturally occurring functional groups or after chemical modifications, to end up with cross-linked materials. The second route is the use of purified fatty acids or fatty acid methyl esters to design well defined thermoplastic polymers and to better control the relationship between the chemical structures of the monomers and the final polymer properties. The reactive sites in triglycerides and fatty acids available for chemical modifications are the carbon-carbon double bonds, the allylic carbons, the ester groups, the alpha carbons to the ester group, and in some cases, the hydroxyl and epoxide moieties.

Castor oil is a unique vegetable oil because it is an inedible oil, owing to the presence of ricine in it, which is a toxic protein. Moreover, it contains up to 90% of ricinoleic acid; a mono-unsaturated fatty acid with 18 carbons bearing a hydroxyl function. Other advantages that can be noticed is that the plant itself requires relatively less fertilizers, pesticides, water and maintenance than most other cultivated crops.¹⁵ Those properties make castor oil a veritable interesting renewable precursor for chemical and polymer syntheses. Castor oil is extracted from the seeds of the castor bean plant *Ricinus communis* (Euphorbiaceae), which grows in tropical and subtropical areas.¹⁶ Two main platform molecules, which will be used in this thesis study, can be derived from castor oil: the methyl 10-undecenoate¹⁶⁻¹⁸ and the sebacic acid^{12, 19}, as can be illustrated in Scheme I-1-1.



*Scheme I-1-1- Castor oil as a platform precursor.*¹²

Nowadays, some of the most widely used renewable resources in the chemical industry for non-fuel applications include vegetable oils and polysaccharides. The vegetable oils have effectively been applied for a long time in the production of surfactants^{2, 20}, lubricants²¹⁻²⁴, agrochemicals, coatings, inks and plasticizers. While talking about industrial application of

vegetable oils, the biodiesel (fatty acid methyl/ethyl esters) production has also to be mentioned.²⁵⁻²⁷

Considering the expected growth of biodiesel market in the near future, glycerol as a co-product of bio-diesel production, becomes a base chemical. Currently, glycerol has various different applications in numerous fields but new outlets for glycerol need to be found to optimize the overall process effectiveness and sustainability of the biodiesel production. Nowadays, the main utilization of glycerol is the production of glycerol esters, used as emulsifiers, surfactants and lubricants. Besides, among the various chemicals that can be obtained from glycerol, some of them, which are interesting for PUs preparation, can be listed: the 1,3-propanediol and the glycerol carbonate.^{23, 26} In terms of the added value provided, glycerol and glycerol carbonate take part of the top 30 chemicals for the chemical industry.²⁸

2- Derivatization of fatty acid derivatives to thermoplastic PUs via the alcohol/isocyanate route

Industrially a broad range of polyols are available whereas only few diisocyanates are commonly prepared from petrochemical resources. This wide range of polyols brings PUs a plethora of different properties, making them suitable in many fields of applications.²⁹ Around 75% of the polyols used for PU synthesis are polyether polyols, which are produced by the addition of cyclic ethers, especially propylene oxide or ethylene oxide, to diol initiators.³⁰ Concerning the isocyanate part, the difference is made between aliphatic and aromatic diisocyanates. Frequently used aromatic diisocyanates are 4,4'-methylene diphenyl diisocyanate (MDI) and toluene-2,4-diisocyanate (TDI), whereas aliphatic isocyanates are for example 1,6-hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI). (See Figure I-1-3)

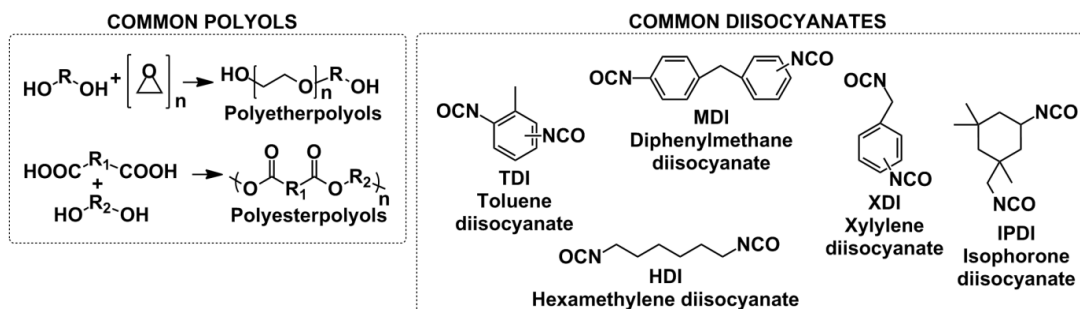
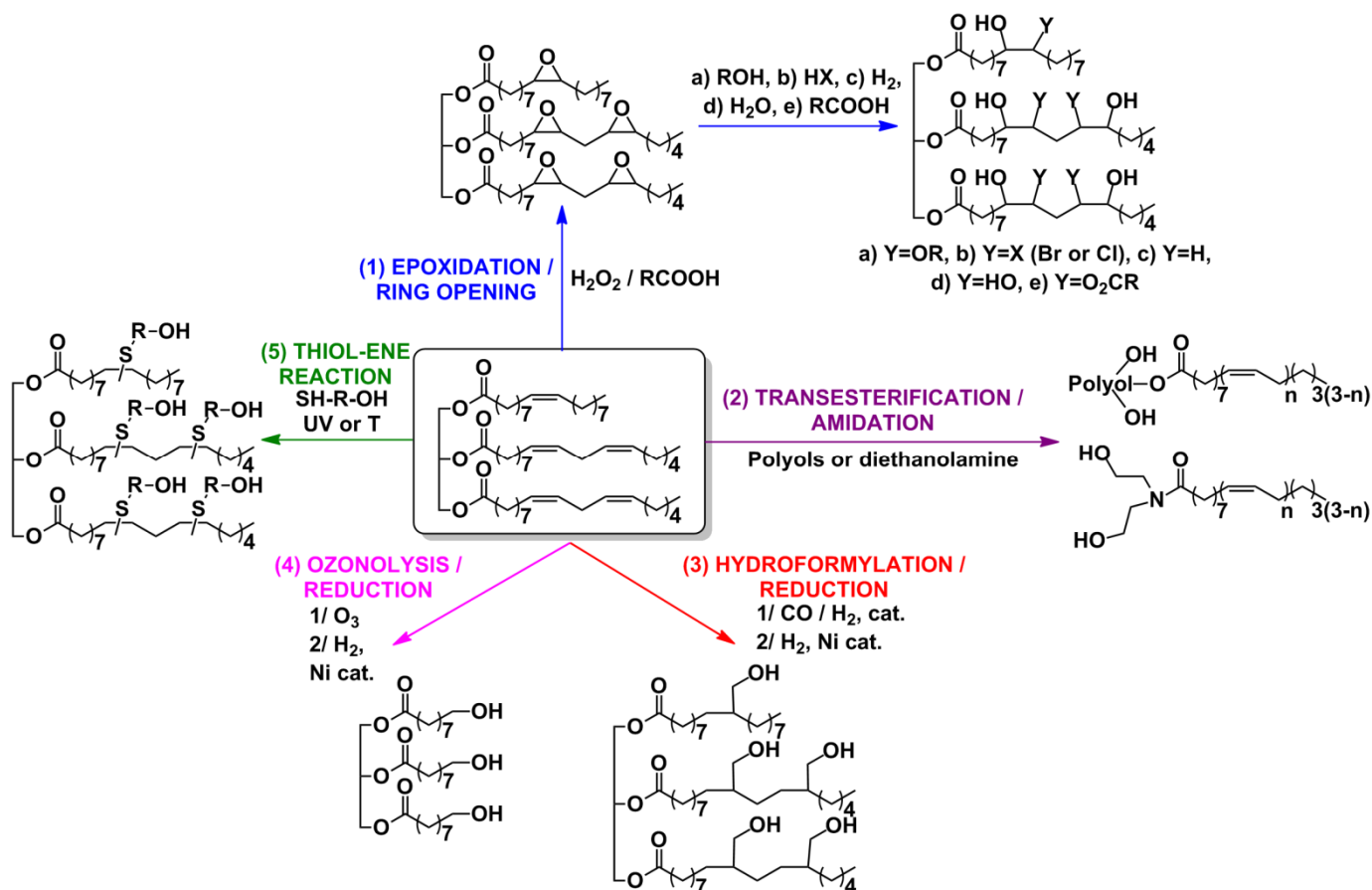


Figure I-1-3- Common diols and diisocyanates.

A lot of efforts have been done to develop alternatives from vegetable oils. The synthesis of polyols and corresponding PU networks from vegetable oils has been already well reviewed in the literature.^{8-10, 31-33} Castor oil is an exception in vegetable oils with its naturally occurring hydroxyl groups and thus was studied in priority in PU synthesis.^{12, 17} Different methods (See Scheme I-1-2) have been followed such as (1) epoxidation / ring opening of the epoxide, (2) transesterification or amidation, (3) hydroformylation / reduction, (4) ozonolysis / reduction and (5) thiol-ene addition. Nowadays, the commercialization of vegetable oils-based polyols and corresponding PUs is growing. (See Table I-1-1)



Scheme I-1-2- Commonly used strategies to introduce OH groups into triglycerides and thus prepare polyols.^{33, 34}

Vegetable oil-based polyisocyanates have been studied to a much lesser extent compared to vegetable oil-based polyols. Two strategies have been followed to bring isocyanate groups onto triglycerides; they both use the very expensive silver isocyanate salt AgNCO , prepared from NaOCN , and AgNO_3 . The silver counter ion in AgNCO ensures that the isocyanate reacts on the nitrogen end, and not on the oxygen end of the group.^{35, 36}

Table I-1-1- Raw material, trade names and major producers of vegetable oil-based polyols and PUs in 2009. ^{30, 32}

^a CASE: Coatings, Adhesives, Sealants and Elastomers; ^b For Bayer's flexible PU foams, SoyOyl polyols from Urethane Soy System are used; ^{c,d} Estimation; ^e Projected data for the next 2-4 years by the company.

Bio-based raw material	Product type	Trade name	PUs applications	Company	Capacity p.a.
Soybean oil	Polyol	BiOH™	Flexible foams	Cargill	~10 kt ^c
	Polyol	Renuva™	Flexible foams and CASE ^a	Dow	n/a
	Polyol	SoyOyl®	Flexible and rigid foams, PUR spray foam, elastomers	Urethane Soy System	23-34 kt
	Polyol	Agrol®	CASE, moulded foams	Bio-based Technologies	n/a
	PU	Bio-based®			
	PU	Baydur® SOVERMOL®	Rigid and flexible foams ^b	Bayer (COGNIS)	n/a
Castor oil	Polyol	Lupranol® BALANCE	Rigid foams /mattresses	BASF	n/a
	Polyol	POLYCIN®	Coating	Vertellus	n/a
	Polyol		Flexible and rigid foams	Mitsui Chemicals	n/a
	PU				
Rapeseed oil	Polyol		Rigid foams / refrigerator insulation	IFS Chemicals	~1kt ^d
Sunflower oil	PU	RUBEX NAWARO®	Flexible foams / mattresses	Metzeler Schaum	n/a
	Polyol	Edenor®, Emersol®, Emery®	Foams, coatings, adhesives	Emery OleoChemicals	n/a
Vegetable oil	Polyol	RADIA®	Flexible and rigid foams	OLEON - SOFIPROTEOL	n/a
	Polyol	PRIPLAST™	Coatings, adhesives	CRODA	n/a

A remarkable large series of papers and reviews investigated the functionalization of triglycerides to get interesting multifunctional PU precursors. The main problem encountered in such cases is the heterogeneity of the monomers due to the distribution of double bonds per triglyceride. This has a negative effect on the mechanical properties and the correlation between the final polymer properties and the monomer structures is more complicated. In light of this, the following part covers the advances made in the synthesis of vegetable oil-based well defined difunctional PU precursors, collecting the literature data of

the different synthetic routes used. In appendix, the Table A-1 summarized the literature concerning fatty acid-based precursors for thermoplastic PUs. In order to synthesize fatty acid-based thermoplastic PUs following the classical route, both diols and diisocyanates are requested.

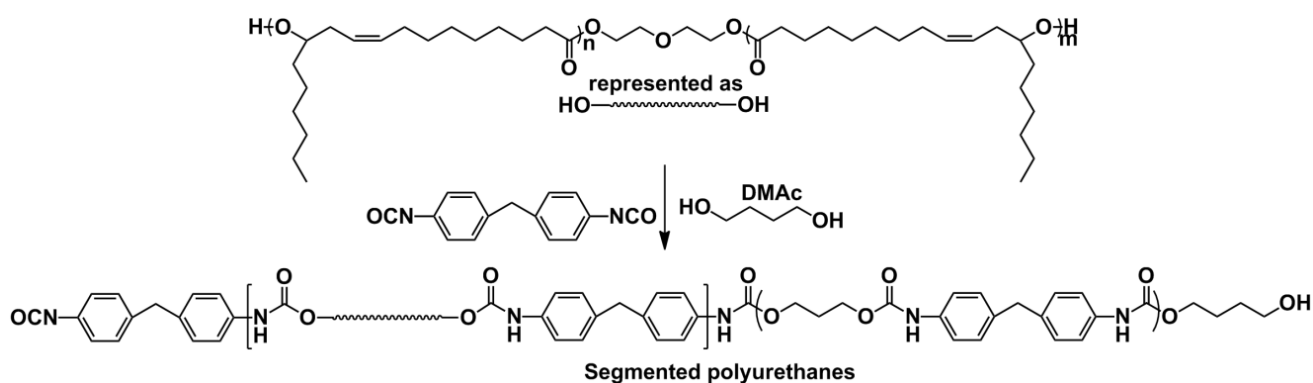
2.1- Fatty acid-based diols

2.1.1- Diols containing ether and ester functions

Segmented thermoplastic elastomer PUs or TPE-Us are commonly used because of their excellent properties, such as good transparency, tunable stiffness, good wear resistance, excellent biocompatibility, etc. These properties are obtained thanks to the alternating of soft and hard segments in the structure of the polymer. Soft segments are usually flexible low glass transition polyether or polyester chains with molar masses between 1 and 4 kg.mol⁻¹, and can be easily obtained from fatty acid derivatives. Hard domains are usually crystalline with high melting points. For polyether diol, only one example of TPUs was reported from vegetable oil derivatives.³⁷ This polyether diol containing ester pendant groups was obtained by the acid-catalyzed ROP of epoxidized methyl oleate and partial reduction with lithium aluminum hydride (LiAlH₄). Polyols with various hydroxyl functionality degrees were obtained depending on the conversion of the reduction step, and PUs were synthesized with MDI. The TPU obtained with the polyether diol (f=2) presented a low glass transition temperature of -15°C and an interesting degradation temperature at 5% weight loss of 307°C.

Polyester diols, diols containing ester and/or amide linkages, dimer diols, linear saturated or unsaturated diols and diols containing thioether linkages are referenced using fatty acids or fatty acid methyl esters as starting materials. The synthesis of diols containing ester group have been much more widely explored due to the initial presence of ester or acid function in vegetable oil derivatives. Few research groups have prepared low Tg polyester diols from vegetable oil derivatives to use them in TPE-Us. The fatty acid-based polyester diols were synthesized either by transesterification of methyl ricinoleate with diethylene glycol as an initiator, or by transesterification of diesters with diols in excess.

Petrovic and coll. have used a poly(ricinoleic acid) diol of 2580 g.mol^{-1} as soft segment to prepare a series of TPE-Us by reacting MDI and 1,4-butanediol with various soft segment weight concentrations ranging from 40% to 70%.³⁸ (Scheme I-1-3) The TPE-Us obtained display a microphase separation and two glass transition temperatures at around -50°C and 100°C . Interestingly, “spherulitic-like” superstructures that are believed to arise from the nucleation and crystallization of the hard segments were noticed in these polymers. Melting points in the range 170°C to 220°C were observed depending on the soft segment content. The mechanical and thermal features of these bio-based PUs suggest that they could be used in conventional TPE-Us applications. Very recently, the same group has studied the phase structure of such segmented PUs using DMA, AFM and USAXS.³⁹ A co-continuous morphology with domains around 15 nm was obtained in the case of the TPE-Us with 50% of soft segment weight concentrations. However in the sample of TPE-Us with 70% of soft segment weight concentrations, dispersed hard domains were observed in the soft matrix. The biodegradation of these TPUs has been investigated by respirometry.⁴⁰ These TPE-Us with poly(ricinoleic acid) as soft segments have been found to exhibit faster degradation rates than the corresponding petrochemical poly(ester urethane)s, even if this rate is relatively slow. The authors observed that TPE-Us with a co-continuous morphology demonstrated a slightly slower biodegradation than those with dispersed hard domains in the soft phase.



Scheme I-1-3- Thermoplastic elastomer polyurethane prepared from poly(ricinoleic acid).³⁸

Using the same methodology, a polyesterpolyol was prepared by transesterification of methyl 12-hydroxy stearate with 1,6-hexanediol catalyzed by titanium isopropoxide.⁴¹ This precursor of 1552 g.mol^{-1} was used in segmented PU with MDI and 1,4-butanediol with 50% and 70% of soft segment content. Glass transition temperatures of -40°C and 100°C were obtained for the soft segments and hard segments respectively. Besides, T_m of -18°C to -14°C and 175°C to 180°C were observed for the soft segments and hard segments respectively.

More recently, polyester diols have been synthesized by transesterification of diesters with diols in excess. Using this strategy, Koning and coll. have prepared partially fatty acid-based aliphatic polyester diols from dimethyl sebacate using TBD as a catalyst.⁴² Moreover, Corcuera and coll. have used similar polyester diols from dimethyl sebacate with molar mass from 1 320 g.mol⁻¹ to 3 500 g.mol⁻¹ to prepare TPE-Us with HMDI and 1,3-propanediol as chain extender. The TPE-Us obtained by a two-step bulk polymerization without catalyst exhibited a molar mass in the range of 52.1 kg.mol⁻¹ to 138.9 kg.mol⁻¹. The authors have studied the effect of the soft segment molar mass on the morphology and the final properties.⁴³ A decrease in the polyester diol molar mass leads to a better phase mixing between hard and soft domains, giving higher T_g for the soft segments than the one for the pre-polyester diol. The same approach has also been used to synthesize polyester diols from azelaic acid and 1,9-nonanediol using titanium (IV) butoxide, with molar masses ranging from 500 to 1 500 g.mol⁻¹. The effect of the polyester diol have then been studied in aliphatic thermoplastic poly(ester urethane)s with fatty acid based HPMDI (1,7-heptamethylene diisocyanate).⁴⁴ The use of polyester diols with various lengths into the TPUs enabled to control the crystalline morphology, the chain dynamics, and eventually the strength of the polymer. The crystal structure and the physical properties are directly linked to the polyester chain length and can be explained by the interplay between polyester dipole-dipole intermolecular forces, as well as by the Van der Waals and hydrogen bonding attractive interactions.

Another effective strategy developed by Cádiz and coll. was to prepare polyester diols.⁴⁵ These telechelic macrodiols with a molar mass of 3.1 kg.mol⁻¹ have been synthesized through two one-pot thiol-ene reactions; first a step growth polymerization using 3,6-dioxo-1,8-octanedithiol and then an end-group postpolymerization modification with 2-mercaptoethanol. Then TPE-Us have been prepared with MDI and 1,4-butanediol. A low T_g and T_m at -45°C and -9°C respectively were observed, which correlate well with the thermal properties of the polyester diol precursor. The phase separated morphology has been confirmed by the hard segment transitions: a second T_g at 55°C and a broad melting endotherm at 190°C.

An alternative to synthesize TPE-Us with a fatty acid-based diol as soft segment, is to use the CRODA polyester diol synthesized by transesterification between dimerized fatty acids (obtained by Diels-Alder reaction) and an excess of linear diol. Averous and coll. have synthesized bio-based TPE-Us from this diol having dangling chains of 3 kg.mol⁻¹, MDI and 1,4-butanediol, with several hard segment contents from 10% to 40%.^{46, 47} Molar masses of

14.7 kg.mol⁻¹ to 38.0 kg.mol⁻¹ with dispersity from 2.17 to 5.52 have been reached. Only one glass transition temperature at -47.0°C was noticed for the PU with 10% of hard segments. Otherwise two glass transition temperatures were obtained; one for the soft segments (-51.3°C to -47.8°C) and one for the hard segments (118.1°C to 122.8°C). Melting points around 200°C are observed for PUs with hard segment content of 30% and 40%. By selecting the appropriate hard segment concentration, different thermo-mechanical properties were achieved and could fulfill some industrial requirements in diverse fields.^{46, 47} To obtain well defined monomers, several research groups have synthesized bis-unsaturated compounds with one or two ester functions from methyl oleate and methyl undecenoate or from the corresponding acid derivatives. Afterwards, the hydroxyl moieties were introduced on the double bonds by thiol-ene reaction or ring opening of epoxy. By using the thiol-ene addition method, asymmetric ester diols have been prepared from oleic and undecenoic acids by esterification with allyl alcohol and thiol-ene reaction with 2-mercaptoethanol.⁴⁸ (See Figure I-1-4) Polymerizations with MDI and using tin (II) 2-ethylhexanoate as catalyst, have led to TPUs with molar masses from 50 to 70 kg.mol⁻¹ and dispersity in the range 1.6-1.9. Amorphous (T_g=8°C to 20°C) to semi-crystalline PUs (T_m=124°C) were obtained depending on the fatty derivative used. These TPUs revealed both good thermal and mechanical properties as well as no cytotoxic response, which make them possible candidates for biomedical purposes.

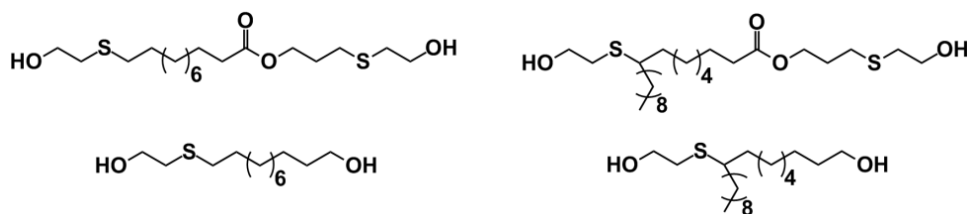


Figure I-1-4- Examples of diols synthesized from undecenoic and oleic acids.⁴⁸

Boutevin and coll. have used a similar strategy to prepare symmetrical diester diols by transesterification of methyl oleate with ethylene glycol followed by a grafting of 2-mercaptoethanol onto the double bonds using thiol-ene click chemistry.⁴⁹ The diester diols appeared not pure enough to synthesize TPUs. Finally, PU networks with interesting thermal properties were obtained by step growth polyaddition with MDI.

To further explore the potential of such diester diols, Cramail and coll. have synthesized a plethora of diester diols by transesterification of methyl oleate or methyl undecenoate with various central diol blocks followed by either thiol-ene reaction with 2-mercaptoethanol, or ring opening of epoxidized double bonds.⁵⁰⁻⁵² Diols containing ether linkages were also synthesized in this work. These diester diols have been polymerized with IPDI in the

presence of dibutyl tin dilaurate (DBTDL) as catalyst. The behavior of the PUs was correlated to the purity and to the chemical structure of the starting ester-containing diols. As expected, the reactivity of primary diols obtained by thiol-ene reaction was found to be higher than the one of secondary diols synthesized by ring opening of the epoxide, yielding higher molar mass TPU up to $35 \text{ kg}\cdot\text{mol}^{-1}$. The rheological properties were also impacted by the monomer structure and the purity. Glass transitions below room temperature were observed due to the pendant alkyl chains along the PU backbone.

Cramail and coll. also prepared sugar-based fatty ester polyols by selective transesterification of epoxidized methyl or ethyl oleate with unprotected methyl α -D-glucopyranoside and sucrose respectively, followed by hydrolysis of the epoxide moiety.⁵³ The polyols were then used in PUs with IPDI in the presence of dibutyl tin dilaurate (DBTDL) as catalyst. The authors noticed that the reactivity of the hydroxyl functions attached to the sugar and to the fatty ester chain moieties respectively could be discriminated with respect to the solvent used, enabling the synthesis of either linear or cross-linked PUs.

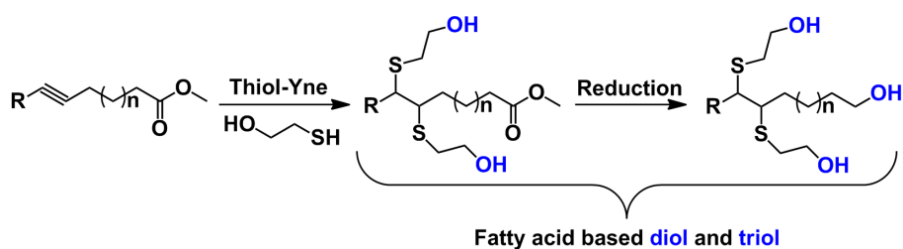
2.1.2- Saturated and Unsaturated diols

By taking advantage of the prominent metathesis reaction, Narine and coll. have synthesized 1,18-octadec-9-endiol, a long chain diol from oleic acid, by self-metathesis followed by reduction to the diol (Y=58%).⁵⁴ Alternatively, a saturated shorter terminal diol, 1,9-nonanediol, has been synthesized from oleic acid with a purity of 99% (Y=72%). These diols were reacted with different diisocyanates namely HMDI and the fatty acid-based HPMDI to give TPUs. The properties of such aliphatic TPUs will be described in the fatty acid-based diisocyanate section.

Cationic dimerization of oleic and linoleic acids could also be done to synthesize saturated diols with pendant chains. This complex reaction is realized at high temperature with homogeneous catalysts such as ionic salts of alkali metals, or heterogeneous catalysts such as clays (montmorillonite or bentonite) or aluminosilicates. The synthesized diacids are reduced to yield fatty acid-based diols. This methodology was initially introduced, in the 1950s, by General Mills Chemicals and Emery (became Cognis Corp. acquired by BASF).^{55, 56} These fatty acid dimer diols are commercially available and used in TPUs providing biocompatibility, high hydrophobicity, stretching and chemical stability properties.⁵⁷

2.1.3- Diols containing thioether linkages

Using efficient functionalization techniques such as thiol-ene and thiol-yne reactions, fatty acid-based diols containing thioether linkages have been synthesized. Diols by thiol-ene reaction of methyl oleate and methyl undecenoate with 2-mercaptoethanol followed by reduction of the ester group using LiAlH_4 have been reported.⁴⁸ Afterwards TPUs having molar masses from 40 to 80 $\text{kg}\cdot\text{mol}^{-1}$ and dispersities in the range 2.1-2.2 were done with MDI. Only semi-crystalline PUs were obtained with glass transition temperature from 28°C to 56°C and melting temperatures around 110°C. No cytotoxic response was observed for these TPUs suitable in the medical field. In a significant contribution, the same group demonstrated the use of thiol-yne reaction for the synthesis of polyols and in particular diols for PUs.⁵⁸ These diols were synthesized in two steps, the first being an alkyne derivatization of fatty acids by bromination and dehydrobromation of the double bond, and the second being a thiol-yne addition with 2-mercaptoethanol. (Scheme I-1-4) The TPUs obtained with MDI as comonomer were amorphous ($T_g=15$ to 20°C). Based on the analyses of biocompatibility, in terms of cell attachment of an osteoblastic cell line, the authors have suggested using these PUs as polymeric scaffolds for tissue engineering. Although the literature above proved the contribution of research groups to the synthesis of fatty acid-based diols to TPUs, a lack of papers on fatty acid-based diisocyanates is unfortunately observable.



Scheme I-1-4- Use of the thiol-yne reaction to prepare diol and triol.⁵⁸

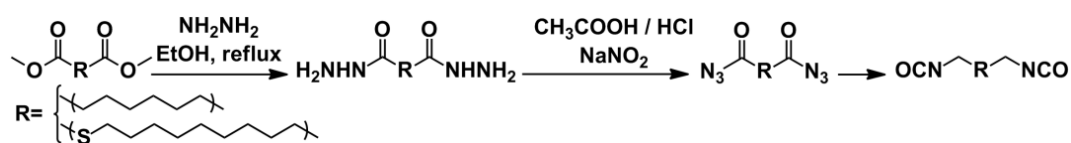
2.2- Fatty acid-based diisocyanates

Vegetable oil-based diisocyanates have been studied in a much lesser extent perhaps as a consequence of the inherent aliphatic structure of the isocyanate that could be prepared and their lower reactivity compared to aromatic ones, as well as due to the intrinsic toxicity of isocyanates. Indeed the most commonly diisocyanates used industrially are aromatic namely MDI and TDI due to their high reactivity required to produce foams. Thus, the uses of

aliphatic diisocyanates are limited to coatings in which the absence of unsaturation is profitable. In industry, isocyanates are synthesized from primary amines by phosgenation. As primary amines are not easily introduced into vegetable oils, other strategies have been developed on vegetable oils and their derivatives.

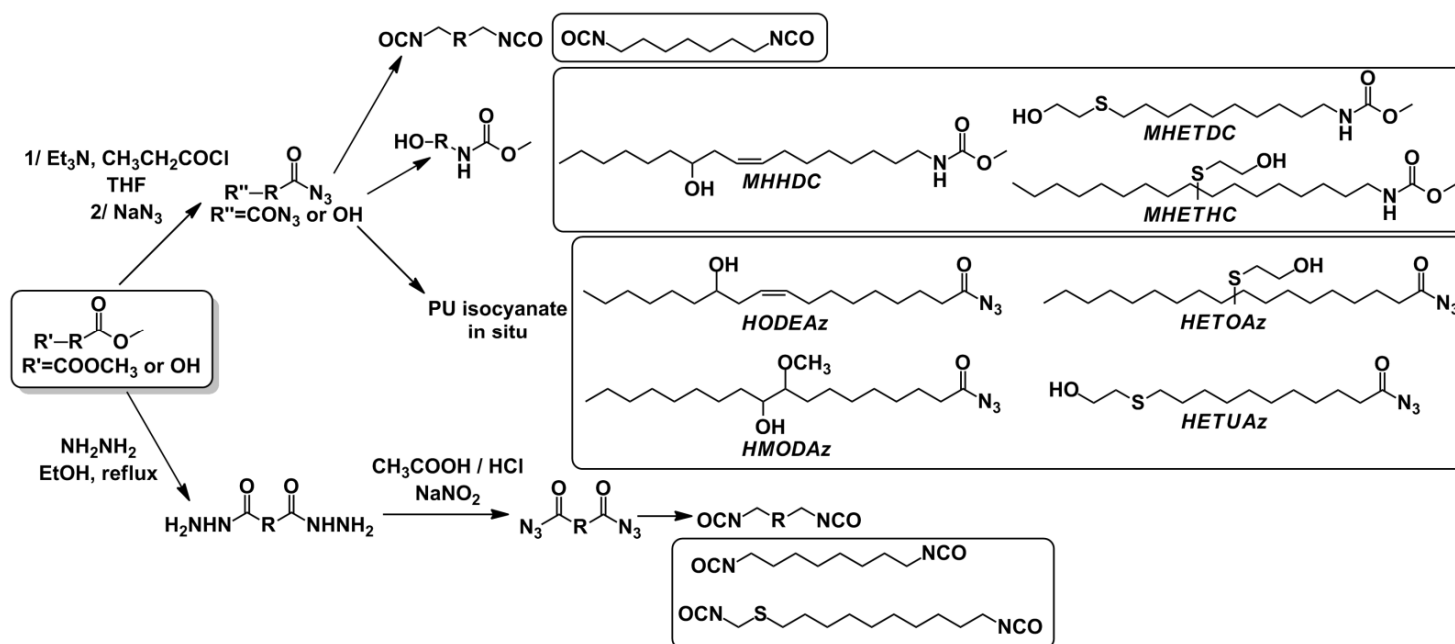
Isocyanates can be synthesized by taking the advantage of the Curtius, Hoffman and Lossen rearrangements, which involve nitrene intermediates (See Part II - Chapter 1 - Scheme II-1-2). In an effort to access fatty acid-based diisocyanates, Narine and coll. used the Curtius rearrangement to prepare oleic acid-based linear diisocyanates, both saturated and unsaturated.^{59, 60} Two linear diacids were first synthesized by methods reported earlier in this chapter, then converted to acyl azides by the reaction with sodium azide and, upon heating, had decomposed to isocyanates. The fatty acid-based HPMDI was used to prepare TPUs and compared with HMDI.⁵⁴ The odd number of methylene groups in HPMDI-based TPUs affected the thermo-mechanical properties, because the crystal structure was less ordered and the strength of the hydrogen bonding was weaker. Indeed lower T_g and T_m were obtained for HPMDI-based TPUs than for HMDI-based TPUs. Still the authors claim that HPMDI-based TPUs exhibit comparable properties that HMDI-based TPUs within acceptable tolerances considering the impacts on physical properties.

A recent paper from our group reports the synthesis of fatty acid-based diisocyanates using the Curtius rearrangement through acyl hydrazide fatty acid-based derivatives without the use of harmful sodium azide (Scheme I-1-5).⁶¹ Diesters were first synthesized and then reacted with hydrazine hydrate to form diacyl hydrazides in quantitative yields. Afterwards, these diacyl hydrazides were converted into diacyl azides then into diisocyanates via the Curtius rearrangement. A series of partially and fully vegetable oil-based TPUs were synthesized and a large range of thermo-mechanical properties were achieved. Relatively good thermal behaviors were observed with decomposition temperatures at 5 wt% loss from 230°C to 280°C. For some PUs, a close resemblance to HDPE was obtained in terms of solubility and thermal transitions with melting points close to 145°C.



*Scheme I-1-5- Fatty acid-based diisocyanates using hydrazine hydrate.*⁶¹

In the Scheme I-1-6, the different routes to isocyanates or equivalents are summarized. The acyl azide and methyl carbamate precursors will be developed in the Part II - Chapter 1.



Scheme I-1-6- Summary of the different routes to fatty acid based-isocyanates or equivalents via the Curtius rearrangement. ^{59, 62, 63}

Conclusion

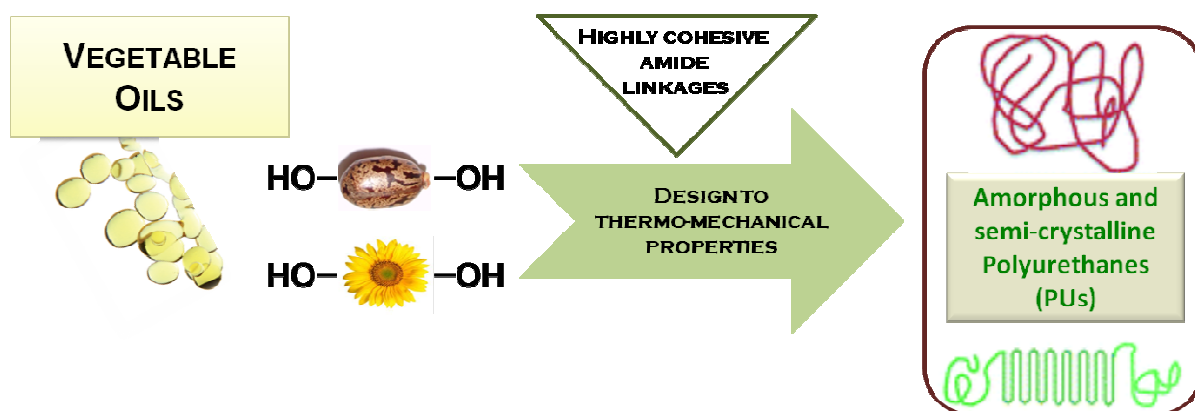
Vegetable oils represent an interesting substitute to fossil resources. This Part I - Chapter 1 highlights the tremendous research efforts that have been made and are still currently made on the synthesis of fatty acid-based polyurethanes following the isocyanate / alcohol route with a focus on thermoplastic PUs. In most cases, the use of vegetable oil derivatives in thermoplastic polyurethanes leads to the preparation of low glass transition temperature materials due to the inherent aliphatic structure and the presence of dangling chains. In this context, as exposed in the next chapter (Part I - Chapter 2), novel fatty acid methyl ester-based diols containing ester and/or amide linkages have been synthesized with a view to obtain high glass transition and/or semi-crystalline PUs.

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PART I - Chapter 2: Design of new diols from fatty acid methyl esters for the synthesis of poly(ester/amide urethane)s with versatile properties



Part of this Chapter has been patented¹ and published in Polymer Chemistry².

Table of contents

Introduction	44
1- Monomer synthesis	44
1.2- Diol synthesis and characterizations	44
1.2.1- Transesterification step	45
1.2.2- Amidation step	47
1.2.3- Thiol-ene reaction on ester and amide-containing bis-unsaturated monomers	49
2- Polymerizations	50
2.1- Polyurethane synthesis	50
2.2- Molar masses and chemical structures	51
3- Thermal stability and thermo-mechanical properties	54
3.1- Thermal stability	54
3.2- Thermo-mechanical properties and crystallization	56
3.3- Crystalline structure	62
3.4- Mechanical properties	63
4- Organocatalysis for fatty acid-based diol and diisocyanate polyaddition	65
Conclusion	69
References	70
Experimental and supporting information	72

Introduction

The present work extends the design of fatty acid-based bifunctional precursors with the idea of obtaining amorphous to semi-crystalline TPU with high glass transition temperatures. To that purpose, methyl undecenoate and methyl oleate were used as precursors to design new diols through a sequence of transesterification and/or amidation reactions followed with thiol-ene additions. The selected co-reactants, 1,3-propanediol, isosorbide and butane-1,4-diamine can all be issued from bio-based raw materials such as glycerol,³ starch⁴ and glutamic acid,⁵ respectively. The so-formed ester diols, amide diols and esteramide diols were characterized with FTIR-ATR, NMR and GC. In a second part, the correlation between the diol structures and the tailor-made bio-based thermoplastic PUs properties will be discussed as a function of the fatty acid building blocks (monomer symmetry, presence of dangling chains or cyclic structures and ester and/or amide linkages). Various characterizations such as FTIR-ATR, SEC, DSC, TGA, DMA, tensile-test experiments and WAXS were performed to investigate PUs thermo-mechanical properties, thermal stability and crystalline structure. Finally, with the interest of replacing metallic catalyst by organic ones, investigations on organocatalysis of the polyaddition between a fatty acid diol and isophorone diisocyanate are presented.

1- Monomer synthesis

1.2- Diol synthesis and characterizations

In order to obtain tunable TPUs based on fatty acid methyl esters, a series of well-defined diols were synthesized starting from methyl undecenoate and methyl oleate by transesterification and/or amidation followed by thiol-ene reaction. To bring the hydroxyl groups, the atom efficient and high efficiency of thiol-ene reaction was preferred over other strategies. Moreover, more reactive primary hydroxyl groups are thus incorporated.

To tune the end-properties of the TPUs, the diols were composed of linear or cyclic central blocks with one or two ester linkages (UndPdE-diol, UndIdE-diol, OIPdE-diol and UndPmE-diol), one or two amide linkages (UndBdA-diol and UndPmA-diol) or both ester and amide linkages (UndPEA-diol), as reported in Figure I-2-1. Methyl undecenoate was chosen

to obtain well-defined linear diols leading to polymer without dangling chains. Owing to the ability of strong hydrogen bonding formation, amide functions were introduced into the diols to achieve semi-crystalline TPUs with high glass transition temperatures and Young's modulus. The chemical structure of the synthesized diols and intermediates was assessed by NMR and FTIR-ATR spectroscopies. The purity of the final diols and their melting points were determined by GC and Kofler bench, respectively. These diols were also of interest as potential precursors for the synthesis of polyesters⁶; only the results of PU syntheses will be described in this manuscript.

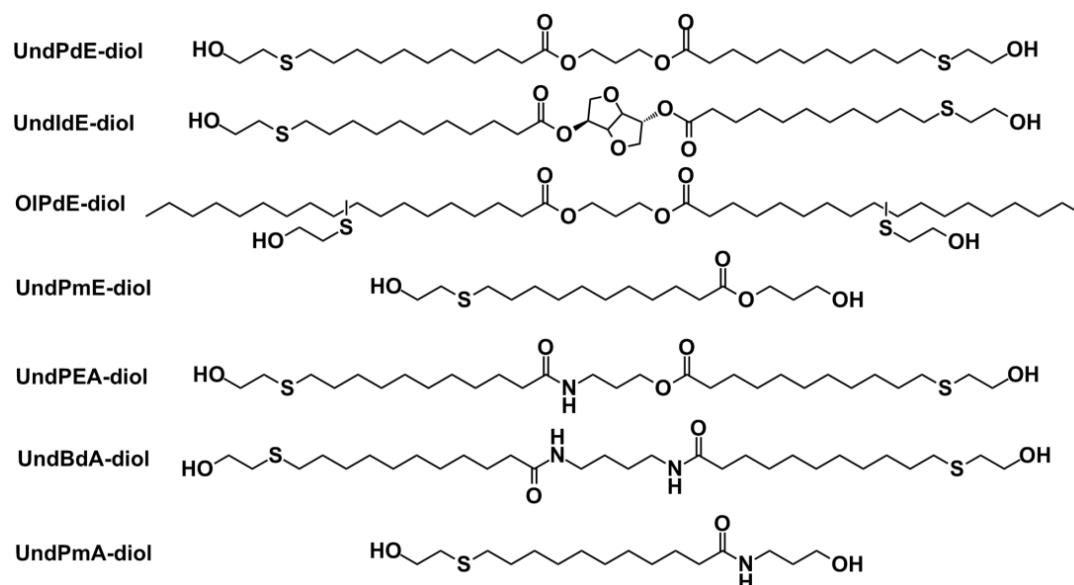
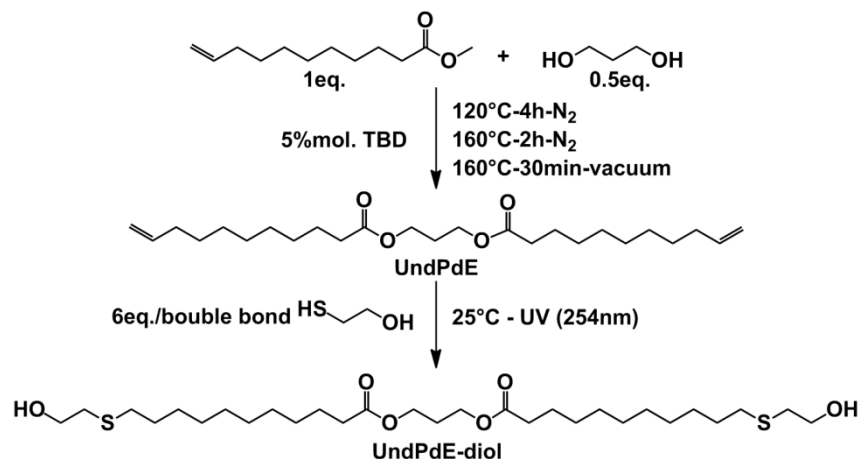


Figure I-2-1- Synthesized diols. Abbreviations used are as follows: [Und = from methyl undecenoate, Ol = from methyl oleate]; [P = propyl, I = from isosorbide, B = butyl]; [d = di-, m = mono-] and [E = ester, A = amide, EA = ester-amide].

1.2.1- Transesterification step

Scheme I-2-1 illustrates the synthesis of UndPdE-diol starting from methyl undecenoate. The synthesis involved a transesterification step with 5 mol% of TBD as an organocatalyst followed by the thiol-ene addition. The transesterification reactions were performed in two stages, at 120 °C - 160°C under nitrogen atmosphere and then at 160 °C under vacuum. The progress of the transesterification reactions was monitored by ¹H NMR spectroscopy. The ester linkage methyl protons in methyl undecenoate (See Figure I-2-2-(1), H9 protons at 3.6 ppm) or in methyl oleate disappeared as a function of time. After transesterification, a triplet corresponding to the methylene protons nearby the ester oxygen appeared at 4.1 ppm for the diesters (UndPdE and OIPdE), as well as for the ester-amide (UndPEA) and at 4.2 ppm for the monoester (UndPmE). (See H9 protons in Figure I-2-2-(2) for UndPdE)



Scheme I-2-1- Synthetic pathway to diols containing ester linkages: UndPdE-diol (Undecenoate Propyl diEster-diol).

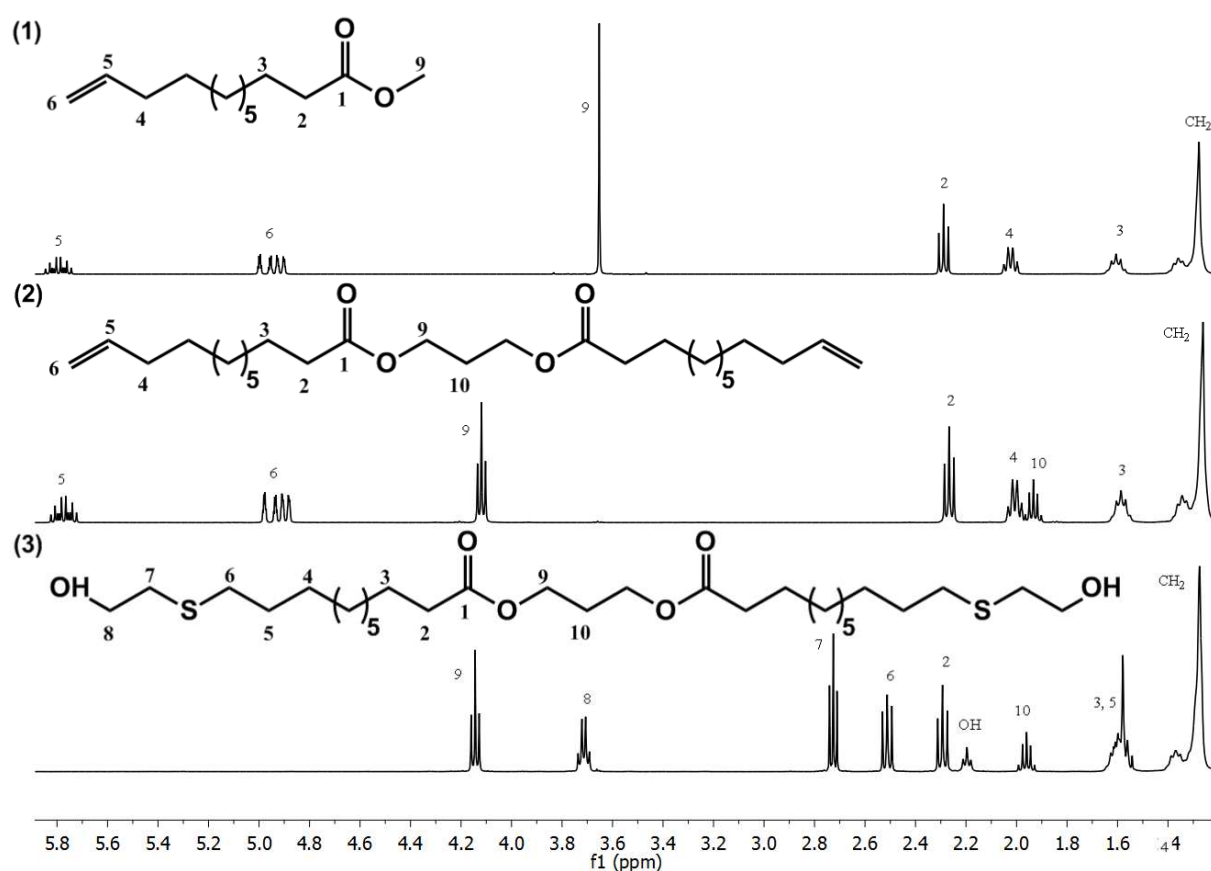


Figure I-2-2- Stacked ¹H NMR spectra of (1) Methyl undecenoate, (2) UndPdE and (3) UndPdE-diol. (Analyses in CDCl₃)

For isosorbide-containing diol (UndIdE), the appearance of two signals at 5.2 ppm and 5.1 ppm (See Figure I-2-3-(2), H9 and H12 protons) confirmed the diester formation between methyl undecenoate and isosorbide and not the monoester one (for which the protons nearby the ester are at 5.1-5.2 ppm). The percentages of side products and remaining methyl undecenoate (or methyl oleate) were determined through SEC assuming similar $\delta n/\delta C$. For UndPdE, only 0.7% of methyl undecenoate was left. However, side products and

unreacted methyl oleate were remaining in UndIdE (34% of monoester), OIPdE (6% of methyl oleate) and UndPmE (30% of diesters). To isolate selectively either the diester or the monoester, purifications by column chromatography were carried out on UndIdE, OIPdE and UndPmE (See the experimental methods section). After purification, the proton number ratios were in agreement with the resonance intensity ratios.

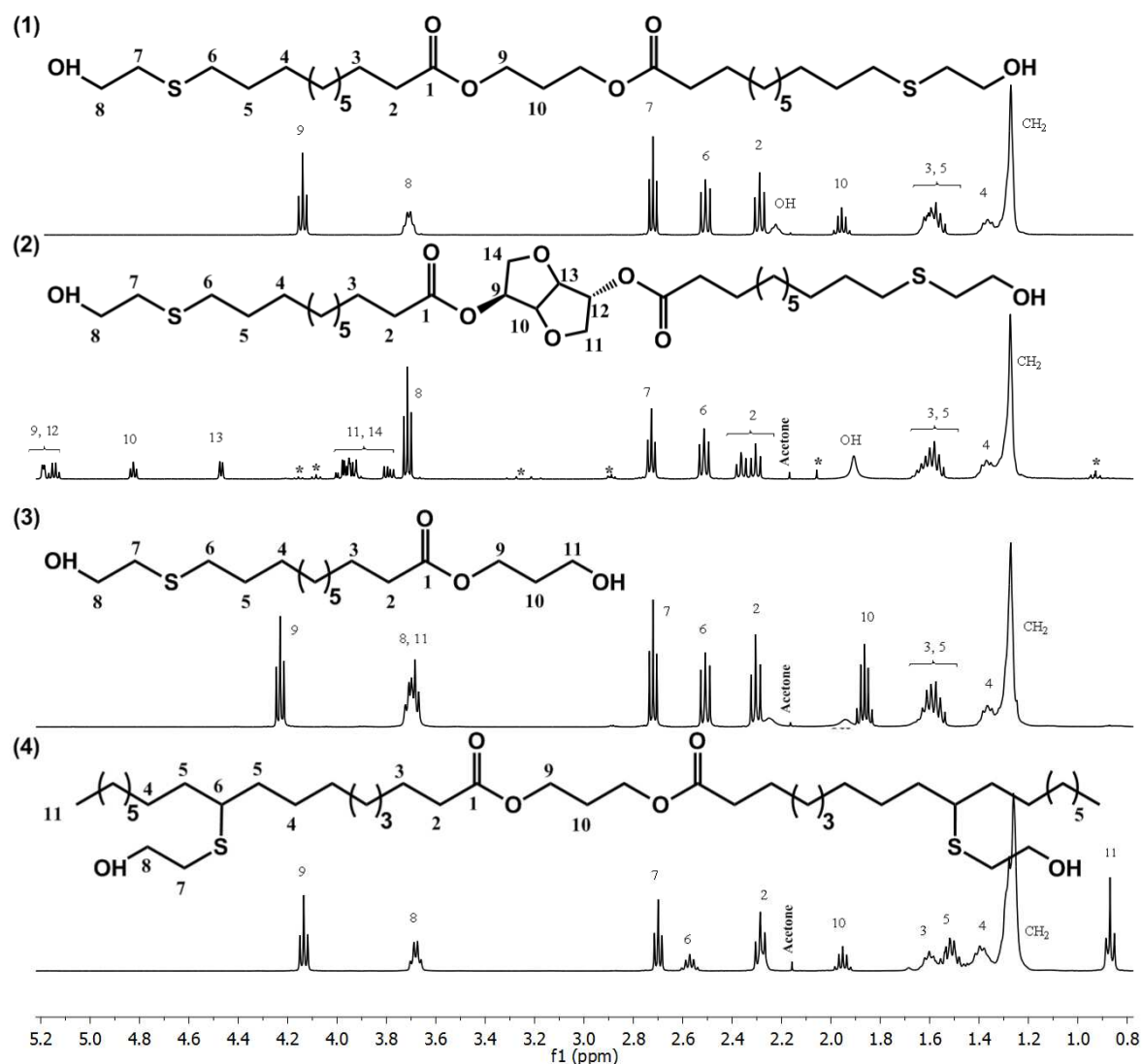


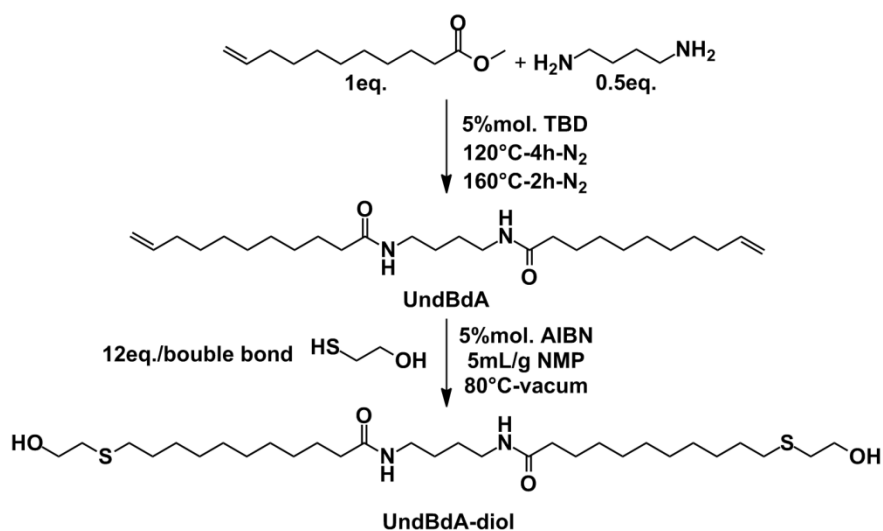
Figure I-2-3- Stacked ¹H NMR spectra of (1) UndPdE-diol, (2) UndIdE-diol, (3) UndPmE-diol and (4) OIPdE-diol.

(*) Impurities. (Analyses in CDCl₃)

1.2.2- Amidation step

As an illustration, Scheme I-2-2 shows the synthesis of the diamide diol UndBdA-diol. The amidation reactions of UndBdA and UndPEA were performed at 120 °C followed by 160°C under nitrogen atmosphere using TBD with quantitative conversion.⁷ For the diamide UndBdA synthesis, potentially bio-based butane-1,4-diamine was preferred over propane-

1,3-diamine. In the particular case of UndPmA, no catalyst was used to avoid the formation of ester function and the amidation step was performed at 150 °C - 160 °C.⁸ In all cases, the amidation reactions were monitored by means of FTIR-ATR, ¹H NMR spectroscopy and SEC (when the samples were soluble).



Scheme I-2-2- Synthetic pathway to Undecenoic Butyl diAmide-diol (UndBdA-diol).

FTIR-ATR spectra of UndPdE-diol, UndPEA-diol, UndBdA-diol and UndPmA-diol are presented in Figure I-2-4. The FTIR-ATR of UndPEA, UndBdA and UndPmA showed two absorption bands at 1632 cm⁻¹ and 1540 cm⁻¹ characteristic of the amide carbonyl stretching vibration (O=C-NH) and the deformation vibration (C-N-H) respectively. Ester carbonyl stretching (O=C-O) band at 1720 cm⁻¹ decreased for UndPEA, UndBdA and UndPmA during the reaction. Diols with amide linkages display also a band at 3290 cm⁻¹ specific of N-H stretching vibrations.

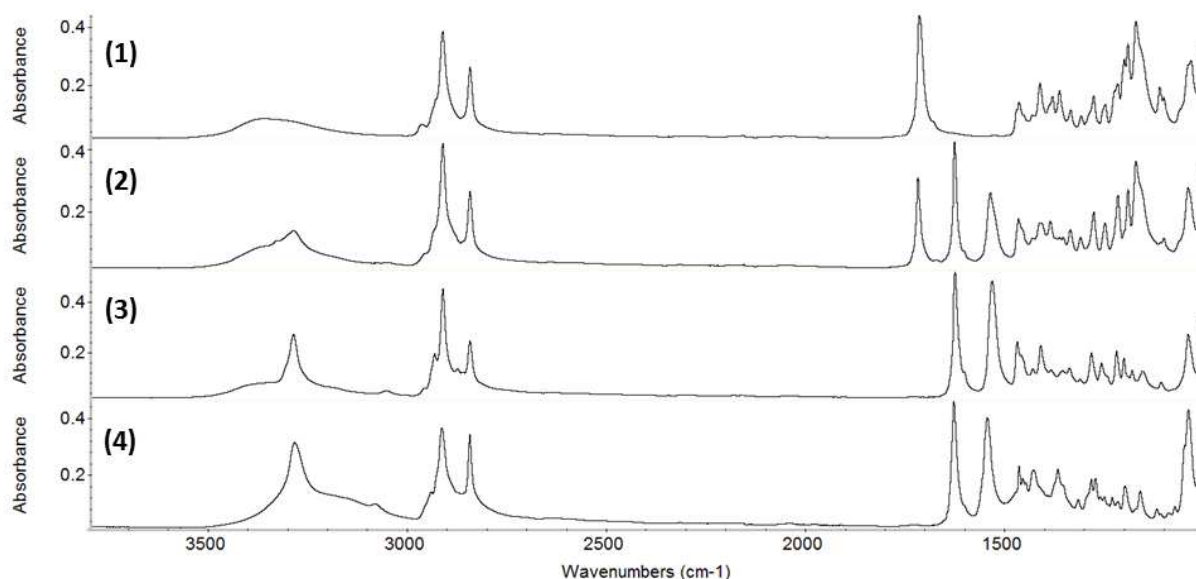


Figure I-2-4- Stacked FTIR-ATR spectra of (1) UndPdE-diol, (2) UndPEA-diol, (3) UndBdA-diol and (4) UndPmA-diol.

The disappearance of ester methyl group protons of methyl undecenoate was also monitored by means of ^1H NMR. A multiplet corresponding to the H9 protons in the formed amide linkages appeared at respectively 3.0 ppm (for UndBdA), 3.2 ppm (for UndPEA) and 3.4 ppm (for UndPmA) (See Figure I-2-5). The ^1H NMR revealed the formation of 11% monoamide for UndPEA and 7% ester-amide during UndPmA synthesis. Due to the presence of these side products, purifications by column chromatography were performed. In the case of UndBdA which was insoluble in any solvent at room temperature, a filtration method was employed.

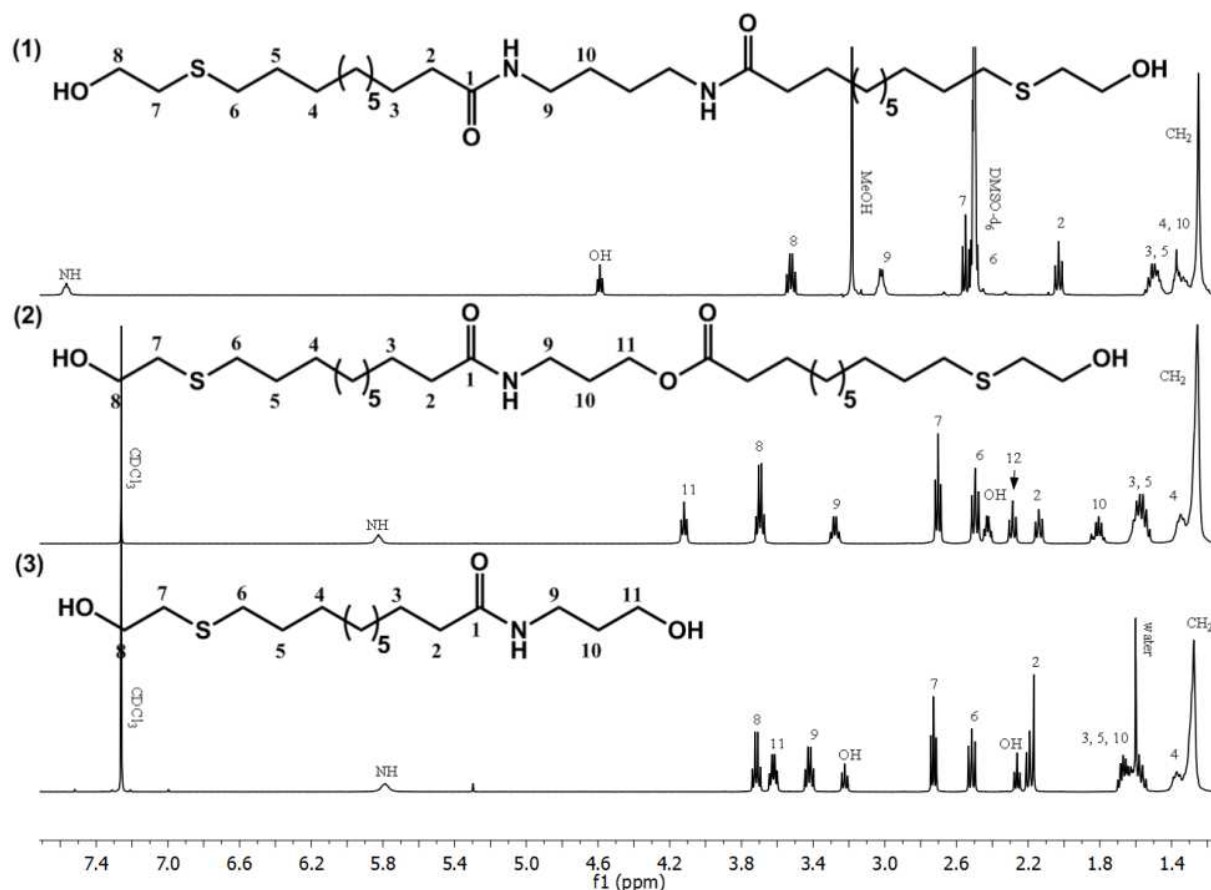


Figure I-2-5- Stacked ^1H NMR spectra of (1) UndBdA-diol (in DMSO- d_6), (2) UndPEA-diol and (3) UndPmA-diol (latter two in CDCl_3).

1.2.3- Thiol-ene reaction on ester and amide-containing bis-unsaturated monomers

Thiol-ene reactions were then carried out using an excess of mercaptoethanol, in different experimental conditions depending on the bis-unsaturated compound (solvent and initiator were not necessarily used, see experimental part). The reaction progress was followed by the disappearance of double bond protons by ^1H NMR spectroscopy (See Figure I-2-2-(2) and Figure I-2-2-(3) for UndPdE-diol, H5 and H6 protons at 5.73 ppm and 4.88 ppm). Full conversion was attained in all cases, except for OIPdE-diol because of the internal double

bonds, which are generally less reactive than the terminal ones. Thereof, the OIPdE-diol was purified by column chromatography. In the ^1H NMR spectra of ester- (See Figure I-2-3) and amide- (See Figure I-2-5) containing diols, protons H5, H6, H7 and H8 confirm the addition of mercaptoethanol onto the double bonds. SEC analyses indicated no coupling reaction such as disulfides formation, during the thiol-ene addition, as illustrated in supporting information for UndPdE-diol (See SI Figure I-2-1). Besides, the FTIR-ATR spectra showed signal between 3000 cm^{-1} and 3500 cm^{-1} , corresponding to the hydroxyl groups.

The melting points and purities of the final monomers, as well as an example of 2D NMR analyses are given in the supporting information (See SI Table I-2-1 and SI Figures I-2-2 for UndePEA-diol). Amide-containing diols showed higher melting points than diols with ester linkages ($T_m=70^\circ\text{C}$ compared to $T_m=145^\circ\text{C}$). Asymmetric diols (UndPmE-diol and UndPmA-diol) and diol containing isosorbide as central block (UndIdE-diol) exhibited lower melting points. As expected, the diester diol from methyl oleate (OIPdE-diol) displayed the lowest melting point ($T_m=-43^\circ\text{C}$) due to the presence of the side chains.

2- Polymerizations

2.1- Polyurethane synthesis

These various diols were used with two diisocyanates, cycloaliphatic (isophorone diisocyanate, IPDI) and aromatic (methylene diphenyl diisocyanate, MDI) ones, to synthesize a wide range of TPUs. IPDI was used owing to its lower toxicity compared to the other diisocyanates. Moreover, due to its cyclic and asymmetric structure, IPDI is known to enhance the solubility of the PUs by increasing the free volume between polymer chains. Due to its aromatic and symmetric structure, MDI can lead to linear high T_g and semi-crystalline PUs.

Such novel bio-sourced PUs were then analyzed, in terms of thermal stability and thermo-mechanical behavior.

Table I-2-1- gives the experimental details along with the abbreviations used for PUs and the polymerizations results. The equimolecular ratio between the fatty acid diol and the diisocyanate was essential to achieve high molar masses PUs. Polymerizations were carried out in bulk when IPDI was used as a comonomer and with diols having a melting point

temperature below 80°C. For MDI as comonomer and diols with higher melting temperature, PU syntheses were carried out in anhydrous DMF. Specifically in the case of UndBdA-diol based PU (with IPDI and MDI), 4 wt% LiCl was added to maintain the reaction homogeneous. LiCl is known to impart the solubility of the polymer.⁹⁻¹¹ PUs based on IPDI were yellow to transparent and viscous to solid in nature, except PU-dA-1 that was isolated as a white fibrous material. With MDI, white fibrous PUs were obtained, except PU-dE-6 and PU-mE-2 recovered as yellow viscous solids. The SI Table I-2-2 gives all the details concerning the solubility properties for each polymer in DMF, THF and chloroform. The insolubility behaviors of the amide-based PUs can be explained by the tightly packed chains thanks to hydrogen bonds. Further evidences of the polymer chains packing are given in DSC.

2.2- Molar masses and chemical structures

The progress of the polyaddition was monitored by FTIR-ATR. The intensity of NCO band at 2243-2260 cm^{-1} with time was followed to determine the reaction conversions. FTIR-ATR spectra confirmed the expected chemical structures of the PUs. As shown in Figure I-2-6, characteristic absorption bands of urethane linkage appeared at 1680-1730 cm^{-1} and 1522-1538 cm^{-1} . In MDI-based PUs (PU-dE-2, PU-dE-4, PU-dE-6, PU-mE-2, PU-EA-2, PUdA-2 and PU-mA-2), absorption bands at 1414 cm^{-1} and 1600 cm^{-1} were detected due to the aromatic rings. Besides, the specific absorption bands from the diol precursors containing ester and/or amide linkages were kept. In the NH region, the distribution of the NH stretching was narrower for PU-dE-1 to PU-dE-2 and to PU-dA-1. Moreover, for MDI-based PUs, the absorption band for urethane carbonyl was splitted into two bands. The band at lower wavelength was the consequence of H bonds as it is commonly attributed.¹²

Furthermore, evidence of PUs formation was proved by ^1H NMR spectroscopy as shown in Figure I-2-7 for PU-dE-1 and PU-dE-2. For IPDI-based PUs, protons corresponding to the cyclic IPDI were identified (See Figure I-2-7-(1), H11 to H14 protons). Besides, aromatic protons and a singlet for the methylene protons between the two aromatic rings were observed for MDI-based PUs. (See Figure I-2-7-(2), H11 protons)

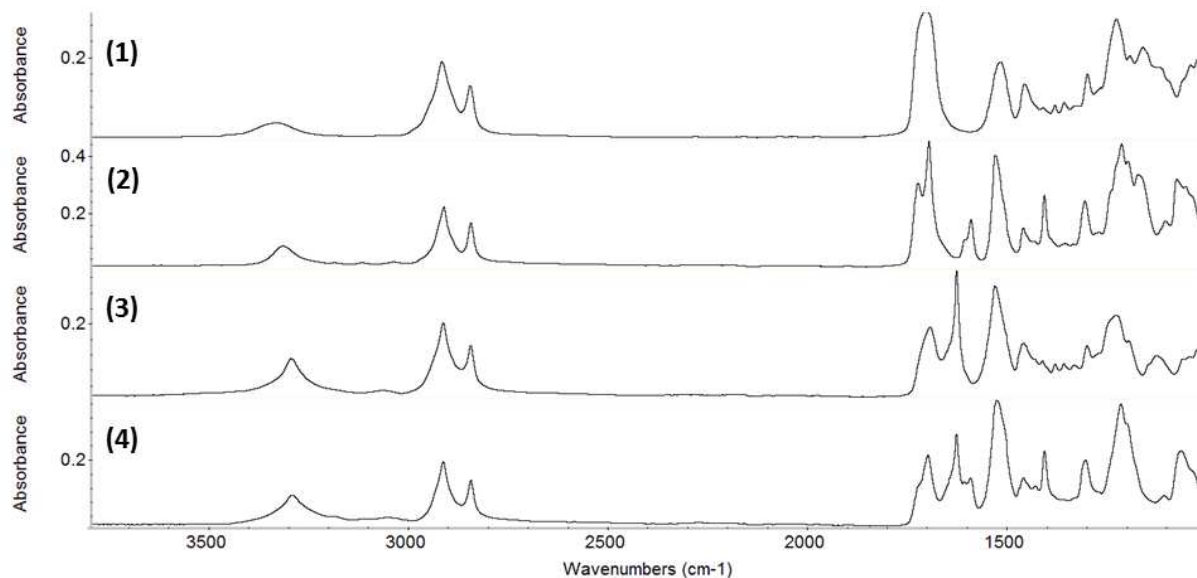


Figure I-2-6- Stacked FTIR-ATR spectra of (1) PU-dE-1 : UndPdE-diol + IPDI ; (2) PU-dE-2 : UndPdE-diol + MDI ; (3) PU-dA-1 : UndBdA-diol + IPDI and (4) PU-dA-2 : UndBdA-diol + MDI.

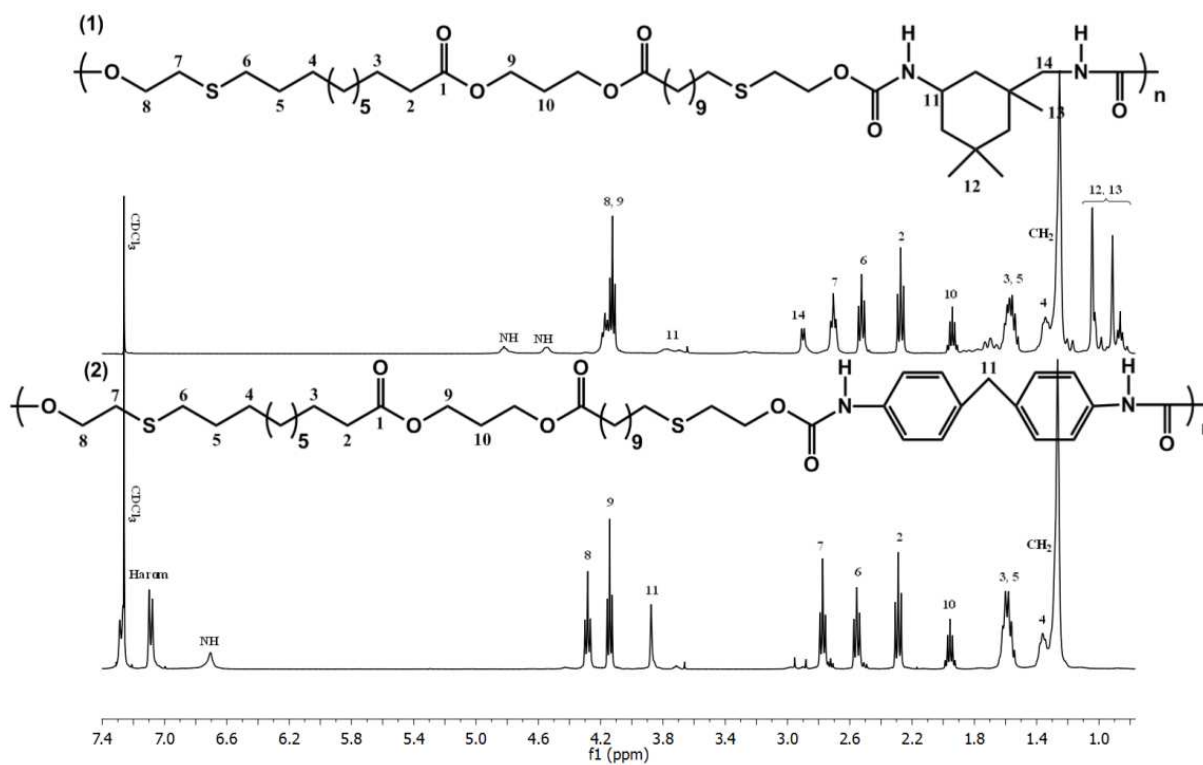


Figure I-2-7- Stacked ^1H NMR spectra of (1) PU-dE-1 : UndPdE-diol + IPDI and (2) PU-dE-2 : UndPdE-diol + MDI. (Analyses in CDCl_3)

SEC data (See Table I-2-1) indicate the formation of reasonably high molar mass polymers. Molar masses around 60 000 g.mol⁻¹ were obtained for PU-dE-1, PU-dE-4 and PU-mE-1. In this study, relatively lower molar masses were obtained for MDI-based PUs compared to IPDI ones. Usually higher molar masses are expected with MDI due to the higher reactivity of its isocyanate functions. The molar mass dispersities were in the range 1.3 to 1.9. Such novel bio-sourced PUs were then analyzed, in terms of thermal stability and thermo-mechanical behavior.

Table I-2-1- Molar masses and dispersity of the poly(ester urethane)s, poly(ester/amide urethane)s and poly(amide urethane)s.

Sample	Used diol	Diisocyanate	\bar{M}_n (g.mol ⁻¹)	\bar{M}_w (g.mol ⁻¹)	Dispersity
Poly(ester urethane)s					
PU-dE-1	UndPdE-diol	IPDI	50 000	100 000	1.9
PU-dE-2 ¹		MDI	30 000	50 000	1.6
PU-dE-3	UndIdE-diol	IPDI	60 000	110 000	1.7
PU-dE-4		MDI	50 000	70 000	1.5
PU-dE-5	OIPdE-diol	IPDI	30 000	45 000	1.6
PU-dE-6		MDI	35 000	60 000	1.7
PU-mE-1	UndPmE-diol	IPDI	70 000	130 000	1.9
PU-mE-2 ¹		MDI	30 000	45 000	1.5
Poly(esteramide urethane)s and Poly(amide urethane)s					
PU-EA-1	UndPEA-diol	IPDI	40 000	50 000	1.4
PU-EA-2		MDI	60 000	95 000	1.6
PU-dA-1	UndBdA-diol	IPDI	ns	ns	ns
PU-dA-2		MDI	ns	ns	ns
PU-mA-1	UndPmA-diol	IPDI	30 000	40 000	1.3
PU-mA-2		MDI	40 000	60 000	1.5

(1) The analyses were performed on the soluble fraction after recovery of the PU, following the purification method described in the experimental section. Abbreviations used are as follows: [Und=from methyl undecenoate, Ol=from methyl oleate], [P=propyl, I=from isosorbide, B=butyl]; [d=di-, m=mono-] and [E=ester, A=amide, EA=ester-amide], ns=not soluble. (SEC in DMF with 1 wt% LiBr - Calibration with PS standards)

3- Thermal stability and thermo-mechanical properties

3.1- Thermal stability

Thermal stability of PUs was investigated by TGA under nitrogen stream at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and the data are summarized in Table I-2-2 and depicted in Figure I-2-8. In general, PUs present low heat resistance due to the presence of thermo-labile urethane linkages compared to amide/ester bonds. By chemical modification of their structure with thermally stable ester and amide moieties, the thermal stability of PUs can be improved.¹³ In this study, thermal stabilities up to 280°C were obtained for the synthesized poly(ester/amide urethane)s. Overall, the PUs were found to have a typical complex decomposition behavior as clearly displayed by the TGA derivatives of the weight loss as a function of the temperature (See Figure I-2-8(2)). Multiple degradation steps were detected possibly due to the decomposition of both the urethane functions¹⁴, thiocarbon chains, ester and/or amide linkages. The first weight loss stage may be correlated to the decomposition of urethane moieties. Studies of the urethane bond decomposition indicated three pathways for the initial cleavage of the urethane bond: dissociation to isocyanate and alcohol, formation of primary amine, olefin and carbon dioxide and finally elimination of carbon dioxide, leading to the formation of a secondary amine. Besides, the decomposition initial temperature of the urethane bonds depends on the diol and diisocyanate chemical structures.¹⁵

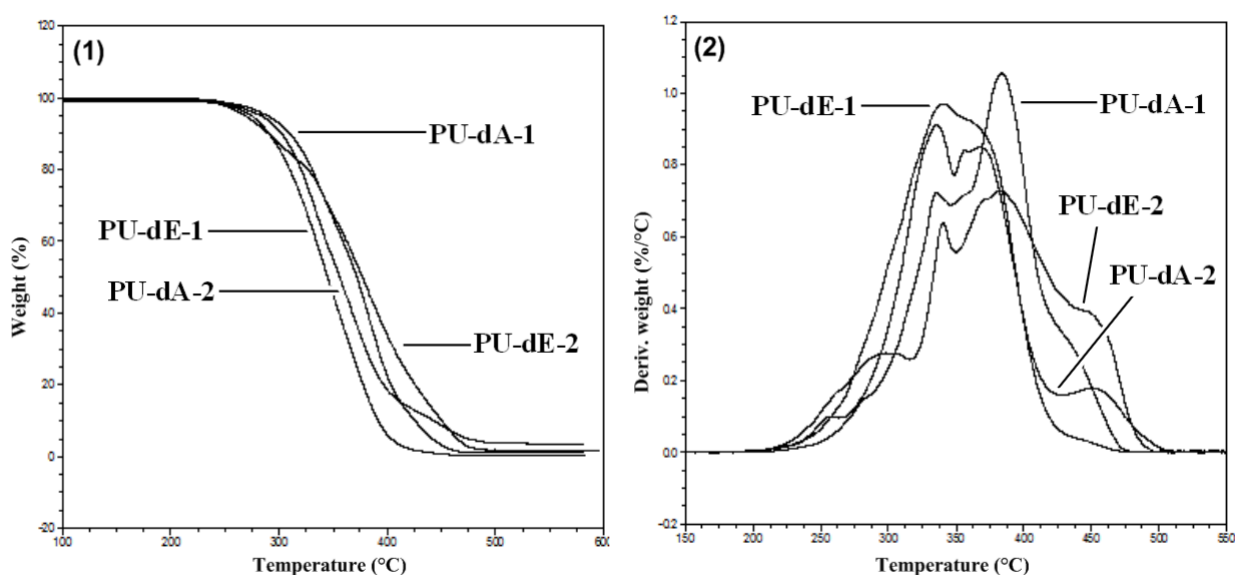


Figure I-2-8- (1) Weight loss as a function of temperature (2) Derivative of weight loss with temperature for PU-dE-1, PU-dE-2, PU-dA-1 and PU-dA-2 obtained from TGA experiment at $10^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere.

As can be seen, PUs containing isosorbide and MDI moieties (PU-dE-3 and PU-dE-4) displayed fair thermal stability. PUs containing pendant alkyl chains (PU-dE-5 and PU-dE-6) showed comparable thermal stability to the one without dangling chains (PU-dE-1 and PU-dE-2). This could be explained by the high ratio of linear methylene units vs pendant alkyl chains in the repeat unit. In this study, the insertion of amide and ester linkages in the polyurethane chains has a moderate effect on the thermal stability of the corresponding PUs. According to the maximum degradation temperature, PUs containing two amide linkages were more thermo-stable among all. No clear trend can be reached for the stability differences between IPDI and MDI-based PUs. All PUs based on IPDI, except PU-EA-1 and PU-dA-1, showed negligible weight residue at 600°C (less than 1 wt%) signifying a complete thermal degradation of these PUs.

Table I-2-2- Thermal and thermo-mechanical properties for the synthesized PUs.

Sample	DSC		TGA		DMA	
	T _g (°C)	T _m (°C)	T _{c heating} (°C) ¹	T _{5%} / T _{max} (°C)	Tan δ _{max}	T (tan δ _{max}) (°C)
Poly(ester urethane)s						
PU-dE-1	-6	-	-	275 / 462	1.36	5.7
PU-dE-2	-2	82 / 106 / 116	83	283 / 551	0.20 / 0.21 / 0.15	22.3 / 81.2 / 107.0
PU-dE-3	13	-	-	293 / 471	1.31	26.8
PU-dE-4	30	-	-	278 / 532	1.28	41.3
PU-dE-5	-27	-	-	299 / 454	0.66	-8.8
PU-dE-6	-23	-	-	312 / 526	0.93	9.8
PU-mE-1	44	-	-	285 / 480	1.13	63.3
PU-mE-2	51	-	-	297 / 575	1.05	68.3
Poly(ester/amide urethane)s and Poly(amide urethane)s						
PU-EA-1	17	-	-	302 / 475	0.71	23.8
PU-EA-2	22	108 / 132	80 / 117	284 / 503	0.29 / 0.20 / 0.46	40.7 / 103.0 / 125.6
PU-dA-1	47	117	-	289 / 579	0.87 / 0.16 / 0.60	48.1 / 74.5 / 116.7
PU-dA-2	47	155 / 172 / 178 / 183	158	269 / 596	0.58 / 0.44	46.6 / 173.9
PU-mA-1	46	-	-	292 / 456	0.75	49.2
PU-mA-2	63	161 / 169 ²	-	255 / 501	0.92 / 0.84 / 0.91	68.9 / 121.8 / 185.4

(1) T_{c heating} corresponds to the crystallization temperatures upon heating; cold crystallization or melt crystallization (2) PU-mA-2 DSC and ModDSC were performed after annealing at 130°C during 2h.

3.2- Thermo-mechanical properties and crystallization

To better understand the relationship between the diol structure and the PU properties in terms of ester / amide moieties density, cyclic central block, symmetry of the diol and presence of dangling chains, the thermal behavior of PUs was further analyzed by DSC experiments. Glass transition temperatures and melting points were obtained from the second heating scan of PUs performed at $10^{\circ}\text{C}\cdot\text{min}^{-1}$. Results are given in Table I-2-2. Most of the PUs derived from IPDI as a comonomer (except with UndBdA-diol) were amorphous in nature and hence displayed well-defined Tg ranging from -27°C to 51°C as illustrated in Figure I-2-9. Among all systems, PUs containing pendant alkyl chains displayed the lowest glass transition temperature below room temperature (-27°C for PU-dE-5 and -23°C for PU-dE-6). This result is very reasonable and can be attributed to the pendant alkyl chains along the polymer backbone, which act as internal plasticizer, increase the free volume and thereby the segmental mobility. Isosorbide provided rigidity to the PU with the two five membered cyclic structures, which resulted in the increase of the glass transition temperature (13°C for PU-dE-3 and 30°C for PU-dE-4).

PUs based on ester-amide and amide-containing diols with IPDI led to amorphous PUs with glass transition temperatures of 17°C and 47°C for PU-EA-1 and PU-mA-1 respectively. Indeed the presence of hydrogen bonds in these poly(ester/amide urethane)s and poly(amide urethane)s increase the rigidity and thus contribute drastically to prevent the mobility of the polymer chains. Besides, PUs from monoester and monoamide diols displayed higher glass transition temperature than their homologues diester and diamide diols-based PUs. This observation is explained by the higher urethane density in the polymer chains that can be correlated with a lower contribution of the fatty acid segments.

With MDI as a comonomer, PUs derived from isosorbide-based diol (UndIdE-diol), oleate-based diol (OIPdE-diol) and asymmetric monoester diol (UndPmE-diol) displayed an amorphous behavior. Due to the aromatic and symmetric structure, an obvious increase in glass transition temperature is observed in MDI-based PUs compared to IPDI-based ones. As expected, the presence of cycloaliphatic ring, pendant alkyl chains or asymmetry of the monomer enhance the free volume and hence hinder the packing of the polymer chains. In contrast, PUs from the linear symmetric diester diol (UndPdEdiol), symmetric amide-containing diol (UndBdA-diol) and asymmetric amide diols (UndPEA-diol and UndPmA-diol), with MDI as a comonomer, were semi-crystalline. The presence of highly

symmetric structure, the formation of hydrogen bonds and the higher ratio of amide linkages in comparison with the methylene segments resulted in packed polymer chains.

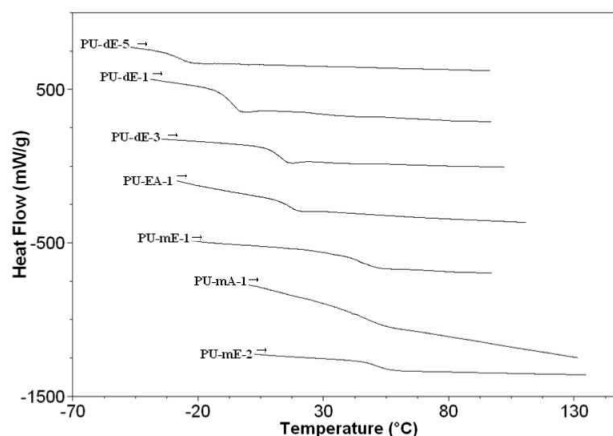


Figure I-2-9- DSC traces of amorphous PUs. PU-dE-1 : UndPdE-diol + IPDI ; PU-dE-3 : UndIdE-diol + IPDI ; PU-dE-5 : OIPdE-diol + IPDI ; PU-mE-1 : UndPmE-diol + IPDI ; PU-mE-2 : UndPmE-diol + MDI ; PU-EA-1 : UndPEA-diol + IPDI and PU-mA-1 : UndPmA-diol + IPDI.

Thermo-mechanical properties of the so-formed semi-crystalline PUs were investigated by DSC showing more complex behaviors. Data are summarized in Table I-2-2. Upon heating, polymers exhibit a glass transition temperature, a first exothermic peak (in case of PU-EA-2), a melting endotherm, followed immediately by a second exothermic peak, and then other endotherms. Upon cooling at $10^{\circ}\text{C}\cdot\text{min}^{-1}$, the thermograms obtained displayed none (in case of PU-EA-2 and PU-mA-2), one (PU-dE-2 and PU-dA-1) or two (PU-dA-2) exothermic peaks, characteristic of the crystallization of the sample.

The crystallization is more difficult for PU-EA-2 and PU-mA-2 due to the asymmetric structure of the diol. Indeed, no crystallization during cooling cycle is observed in PU-EA-2. However, during heating scan, a crystallization of the sample could be seen. In this particular case, chains gained mobility after the glass transition and a cold crystallization was observed. Besides, PU-mA-2 can crystallize only upon annealing.

For PU-dE-2, two phases crystallize upon cooling under the same exothermic peak. Indeed, if the sample was rapidly cooled from the melt with liquid nitrogen and then subsequently heated up, two corresponding exothermic peaks were observed (See Figure I-2-10). ModDSC was performed on semi-crystalline PUs in order to decorrelate the signals. All PU thermograms from classic DSC at $10^{\circ}\text{C}\cdot\text{min}^{-1}$ and from ModDSC at $2^{\circ}\text{C}\cdot\text{min}^{-1}$ are presented in SI Figures I-2-3 to I-2-6. Glass transition temperatures, melting and melt-crystallization temperatures obtained from the second cycle are listed in Table I-2-2 and illustrated in Figure I-2-11. Several authors have already observed this thermal behavior on different polymeric systems. This phenomenon has been reported for semi-crystalline n-PU ($n=12$)¹⁶

and n,m-PU (n=12 and m=4 or 6) ¹⁷. Lligadas and coll. ¹⁸ and Meier and coll. ¹⁹ have also reported similar thermal behavior for respectively telechelic fatty macrodiols and fatty-based polyesters both containing sulfur atom. Other sulfur-containing polymers were also studied and comparable thermal performances were observed. ²⁰⁻²³ More recently, Narine and coll. observed similar thermal behavior for thermoplastic poly(ester amide)s derived from fatty acid-based telechelic diols. Indeed, this behavior was largely observed in polyesters and poly(ester amide)s. ²⁴ The flexibility of the polymer chains seems to be one of the key point. Indeed, this kind of behavior is observed for long methylene polymer chains, which are even more flexible with incorporated sulfur atom. Moreover, as expected hydrogen bonds between amide functions increase the possibility to obtain semi-crystalline PUs as observed with PU-dA-1 and PU-mA-2, in contrast to PU-dE-1 and PU-mE-2. According to the literature and the DSC analyses, two solid phases with different crystal structures were involved in PU-dE-2. Whereof one was first in metastable form and, as the temperature was increasing, folded polymer chains melt and recrystallized into a more stable form with fully extended chains. This reorganization was interpreted in the literature by the presence of two populations of crystallites differing in size, i.e. thin and thick lamellar crystals. The lower endothermic peaks were associated to a population of less perfect crystals, that is, with a smaller crystallite thickness. Subsequently this crystal phase melted with the second semi-crystalline phase that has crystallized upon the cooling stage. ^{24, 25}

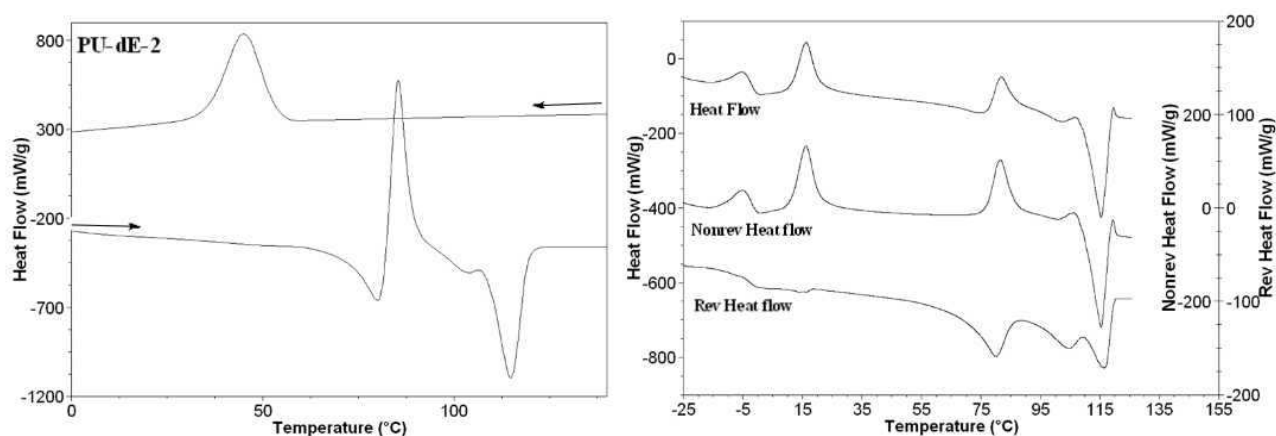


Figure I-2-10- DSC second cycle thermograms at 10°C/min of PU-dE-2 (left) and Mod DSC thermograms at 2°C/min with a modulation amplitude of 0.64 °C and a modulation period of 60 s of PU-dE-2 cooled from the melt with liquid nitrogen (right).

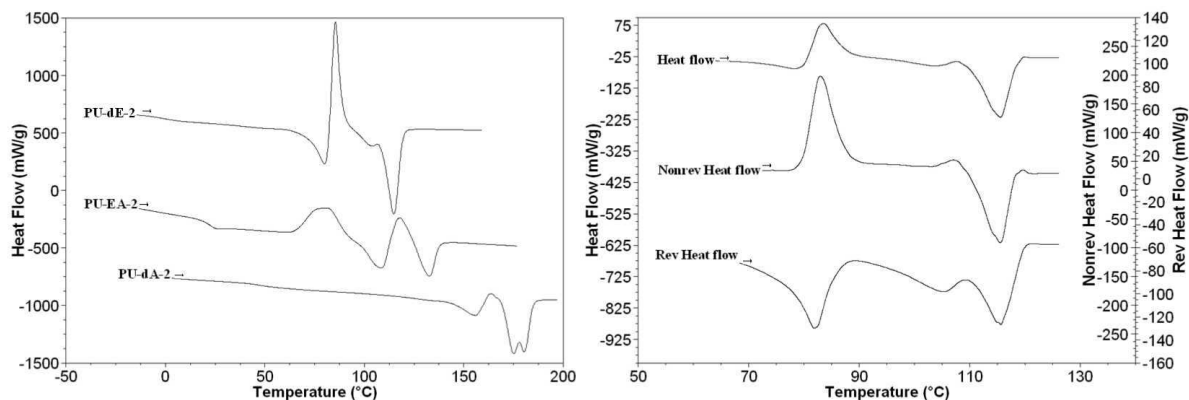


Figure I-2-11- DSC thermograms after second heating of semi-crystalline PUs: PU-dE-2 : UndPdE-diol + MDI ; PU-EA-2 : UndPEA-diol + MDI and PU-dA-2 : UndBdA-diol + MDI (left), as well as ModDSC of PU-dE-2 (right).

The dynamic mechanical behavior was further investigated as a function of temperature. DMA results were correlated with the data from the DSC analyses. The curves of $\tan \delta$ versus temperature, for amorphous PUs, are shown in Figure I-2-12. The glass transition temperatures, obtained with DMA at the maximum of $\tan \delta$, are in good agreement with the DSC values (Table I-2-2). The observed small differences are explainable by the way of measurement. Indeed, DSC and DMA measure changes of the heat capacity and the mechanical response of the polymer chains during the transition, respectively. As shown with the maxima of $\tan \delta$, the evidence of the influence of the amide functions was clearly visible. All amide-containing amorphous PUs exhibited lower maximum $\tan \delta$ than the ester-based PUs, indicating that most of the energy required to deform the sample is elastically recovered (storage modulus E') instead of being dissipated as heat (loss modulus E''). Thus, the amorphous PUs containing amide linkages were more elastic than the PUs containing ester functions. PUs with a lower content of fatty segments (PU-mE-1 and PU-mE-2) exhibit lower $\tan \delta$ maxima than PUs with more fatty segments, due to the higher urethane density. PU from OIPdE-diol and IPDI (PU-dE-5) that bears pendant chains presents a lower maximum $\tan \delta$ than PU-dE-1 (UndPdE-diol + IPDI), which is in agreement with DSC data: ΔC_p (PU-dE-5)= $0.38 \text{ J.g}^{-1}.\text{K}^{-1}$ lower than ΔC_p (PU-dE-1)= $0.73 \text{ J.g}^{-1}.\text{K}^{-1}$.

The $\tan \delta$ and storage modulus versus temperature curves for semi-crystalline PUs (PU-dE-2, PU-EA-2 and PU-dA-2) are given in Figure I-2-13. These data revealed that ester functions generate higher semi-crystallinity in the PUs in comparison to amide ones. Indeed, PU-dE-2 was more crystalline than PU-EA-2, which was even more crystalline than PU-dA-2, as can be seen with the values of the maximum $\tan \delta$. However, the storage modulus of PU-dE-2 was lower than the one of PU-EA-2, feature that could be explained by the lower glass transition temperature of PU-dE-2, related to a higher chain mobility in the amorphous state. Moreover, the melt crystallization can be highlighted by an important increase of the

storage modulus at the melt crystallization temperature. The melt crystallization behavior was more intense with ester-containing structures as can be seen with the decrease of the second $\tan \delta$ maxima from PU-dE-2 in comparison to PU-dA-2. In order to have a further understanding of the mechanical properties of the semi-crystalline PUs, tensile tests experiments were performed (See the “Mechanical properties” part).

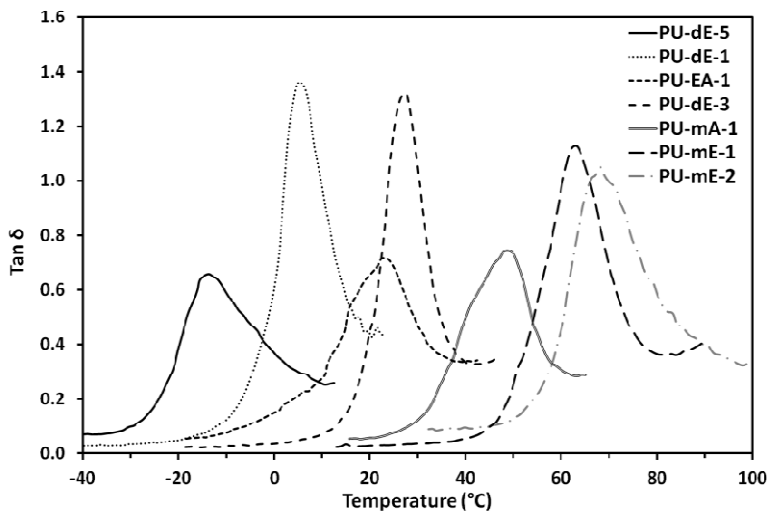


Figure I-2-12- Tan δ versus temperature curves for amorphous PUs. PU-dE-1 : UndPdE-diol + IPDI ; PU-dE-3 : UndIdE-diol + IPDI ; PU-dE-5 : OIPdE-diol + IPDI ; PU-mE-1 : UndPmE-diol + IPDI ; PU-mE-2 : UndPmE-diol + MDI ; PU-EA-1 : UndPEA-diol + IPDI and PU-mA-1 : UndPmA-diol + IPDI.

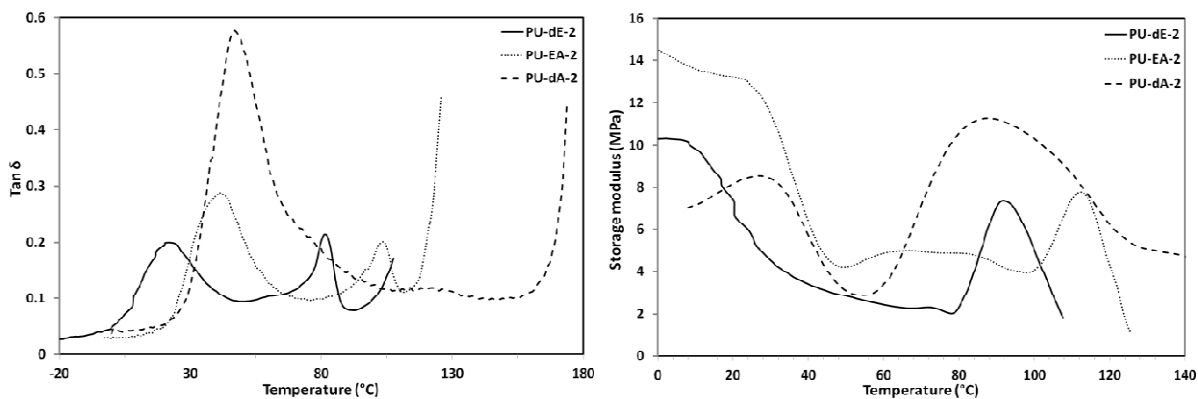


Figure I-2-13-Tan δ and storage modulus as a function of temperature for semi-crystalline PUs: PU-dE-2 : UndPdE-diol + MDI ; PU-EA-2 : UndPEA-diol + MDI and PU-dA-2 : UndBdA-diol + MDI.

The DSC analyses were supported by AFM images with temperature for PU-dE-2. The Figure I-2-14 illustrates the AFM microscopies of PU-dE-2 at different temperatures (from 20°C to 110°C). The globular structure disappeared between 70°C and 75°C and then after 85°C, a recrystallization was visible on the corresponding phase image, which confirm the melt crystallization.

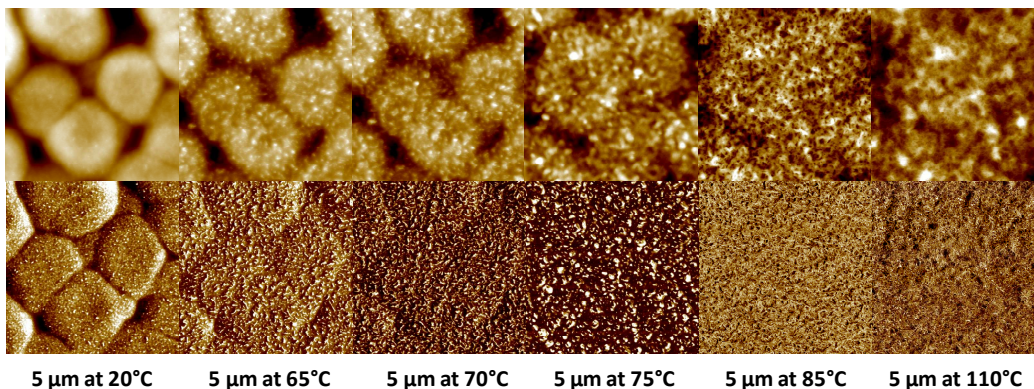


Figure I-2-14- AFM analyses of PU-dE-2 while a thermal increase from 20°C to 110°C, height on top and phase at the bottom.

While performing an isotherm of PU-dE-2 at 85°C in an oven, the crystallization that occurs at this temperature was favored. Spherulites were obtained as can be seen from the polarized optical and AFM microscopies. (See Figure I-2-15) The birefringence pattern observed by optical microscopy confirmed predominantly radial orientation of the lamellae. Moreover, AFM images revealed some banded spherulites, which are commonly attributed to the lamellae cooperative twisting or bending along the radius. This phenomenon has already been observed for other polymers and copolymers such as in poly(butylene succinate)²⁶ and in poly(ester urethane) multiblock copolymer²⁷.

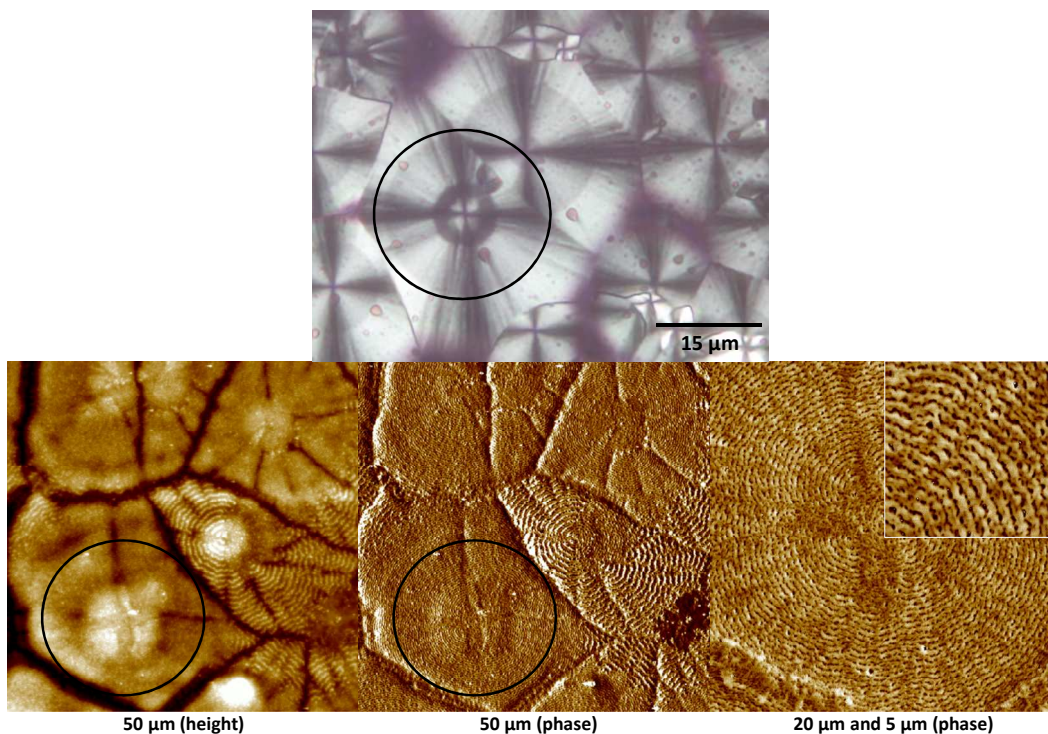


Figure I-2-15- Polarized optical and AFM microscopies of PU-dE-2 after an isotherm of 2 hours at 85°C. On top: Maltese crosses observed with the polarized optical microscope and at the bottom: AFM images and evidence of some banded spherulites.

3.3- Crystalline structure

In order to gain some more insight into the crystallinity of the so-formed semi-crystalline PUs, wide-angle X-ray diffraction measurements (WAXS) were carried out as a function of the temperature for PU-dE-2, PU-EA-2 and PU-dA-2 (See Figure I-2-16 for PU-dE-2). These results confirm the semi-crystalline character of the PUs, since a large amorphous halo is apparent, on which two groups of diffraction peaks are superimposed (at two q ranges). For PU-dE-2, at 122°C the diffraction peaks are lost and the amorphous halo appears to be more intense, which suggests that semi-crystallinity is lost above this temperature.

Several studies have shown that PUs have a similar crystal structure as their corresponding PAs.^{16, 17, 28, 29} The crystalline structure of PAs has been well studied in the literature. Several crystal phases have been observed and the most important ones are the α phase, which is composed of zig-zag chains and H bonds between anti-parallel chains, and the γ phase, which is made of helical chains and H bonds between parallel chains.^{30, 31} Compared to the present study, similar WAXS patterns were obtained with fatty acid poly(ester amide)s reported on the literature.^{6, 24} However, precise assignment of all diffraction peaks is considered to be risky. The group of peaks that are apparent at the high q range suggests that complex polymorphic structures exist in PU-dE-2. Besides, some of the characteristic distances of the PU-dE-2 unit cell, that are estimated from the diffraction peak position, are close to the distances reported for both the α and γ phases of polyamides. These peaks could be reasonably attributed to hydrogen bonds and Van der Waals interactions.

As far as the first three peaks (low q range) are concerned, they can be assigned to a part of the unit cell repetition along the polymer backbone. The distances calculated for the 2nd and 3rd peak can be consistent with the length of two parts of the diol (peak 2: mercaptoethanol + methyl undecenoate + 1,3-propanediol / 1,3-aminopropanol or 1,4-diaminobutane and peak 3: mercaptoethanol + methyl undecenoate). Besides, the distance that corresponds to the first peak (or part of the peak for the PU-dE-2) is almost equal to the sum of the distances calculated from the second and third peak, which suggest that this peak can be assigned to the diol part of the repeated unit. (See Table I-2-3)

Table I-2-3- Characteristic positions and periodicities derived for the first 3 peaks in the WAXS patterns of synthesized semi-crystalline PUs.

PUs	Peak 1		Peak 2		Peak 3	
	q(Å ⁻¹)	d(Å)	q(Å ⁻¹)	d(Å)	q(Å ⁻¹)	d(Å)
PU-dE-2	0.152*	41.3*	0.256	24.5	0.413	15.2
PU-dA-2	0.170	37.0	0.268	23.4	0.406	15.5
PU-EA-2	0.160	39.3	0.257	24.4	0.408	15.4

Where q is the scattering vector which is calculated from the equation: $q = \frac{4\pi \sin(\theta)}{\lambda}$, with θ and λ , the Bragg angle and the x-ray wavelength respectively ($\lambda=1.5418 \text{ \AA}$). The equation: $d = \frac{2\pi}{q}$ allows the calculation of the distance d . The q and d are calculated at 30°C (for PU-dA-2 and PU-EA-2) and 110°C (for PU-dE-2), due to the appearance of the second peak with temperature for the latter semi-crystalline PU. * Only part of the peak is visible.

Moreover, the intensity of the diffraction peaks as well as their position is a function of temperature. This observation can confirm the phase reorganization during the melt crystallization process, as displayed on the DSC heating profiles.

It is interesting to note that in PU-dE-2, the second peak appears only at high temperatures, while in case of PU-EA-2 and PU-dA-2 all peaks are present at room temperature. The explanation can be that they are more rigid and thus manage to pack easily whereas, extra energy should be provided for the full alignment of the diol part in case of PU-dE-2.

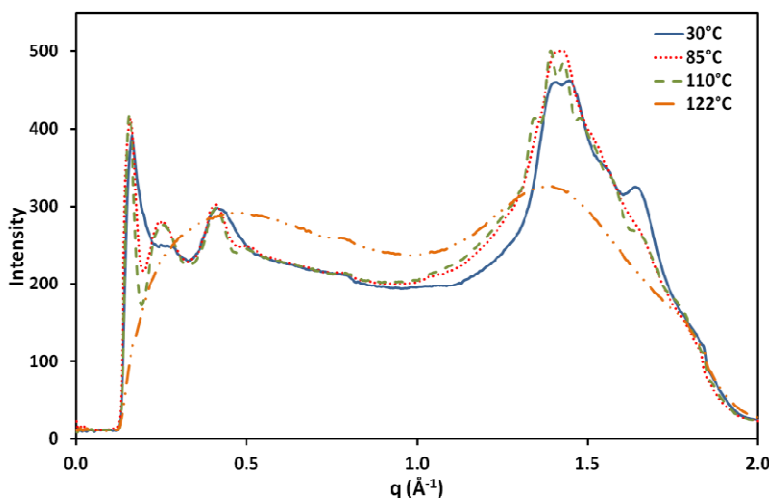


Figure I-2-16- WAXS patterns at 30 °C, 85 °C, 110 °C and 122 °C for PU-dE-2.

3.4- Mechanical properties

Tensile tests were performed on semi-crystalline PUs after annealing; the Young's modulus, ultimate tensile strength and maximum strain are given in Table I-2-4. The stress-strain curves are depicted in Figure I-2-17. Tensile tests on PU-mA-2 were not performed due to the difficulty to obtain a homogeneous film after annealing. Different mechanical properties were achieved by varying the diol structure. Yield points were visible for all the semi-

crystalline samples as a result of the presence of crystalline domains and as a typical behavior for semi-crystalline polymers. Highest Young's modulus were observed for amide-containing PUs while comparing PU-dE-2 (287 MPa) to PU-EA-2 (314 MPa) and to PU-dA-2 Young's modulus (770 MPa). The presence of amide linkages increased the value of Young's modulus by 37%. In addition, the elongation at break was similar for PU-dE-2 and PU-EA-2 and higher than for PU-dA-2. These results can be explained by intermolecular hydrogen bonds which increases the cohesion of the material. PUs from diamide diol with either IPDI or MDI presented analogous mechanical behavior. The mechanical properties of these bio-based poly(ester urethane)s, poly(ester/amide urethane)s, and poly(amide urethane)s, (E modulus from 287 MPa to 775 MPa and ϵ at break from 41 % to 269 %) make them suitable materials for a large range of applications.

Table I-2-4- Mechanical properties of semi-crystalline poly(ester urethane) (PU-dE-2), poly(ester/amide urethane) (PU-EA-2) and poly(amide urethane)s (PU-dA-1 and PU-dA-2).

Sample	Traction		
	Young's modulus (MPa)	Ultimate strength (MPa)	Maximum strain (%)
PU-dE-2	287 ± 35	17.4 ± 2.4	266 ± 24
PU-EA-2	314 ± 33	23.2 ± 1.4	269 ± 26
PU-dA-1	770 ± 68	58.1 ± 3	41 ± 2
PU-dA-2	775 ± 51	48.3 ± 3	44 ± 13

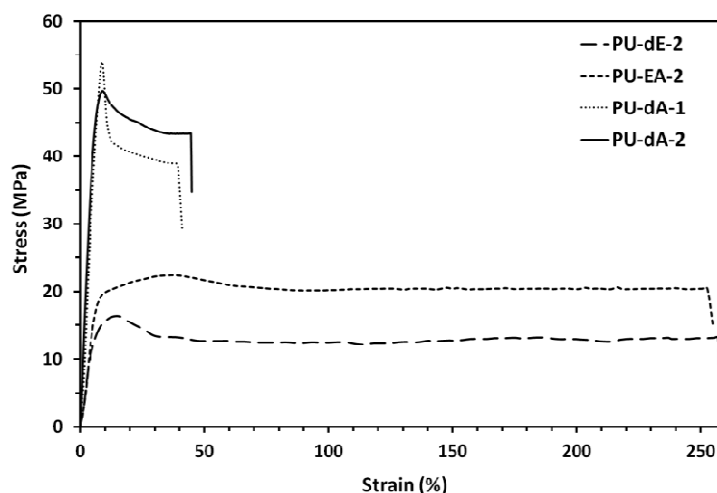
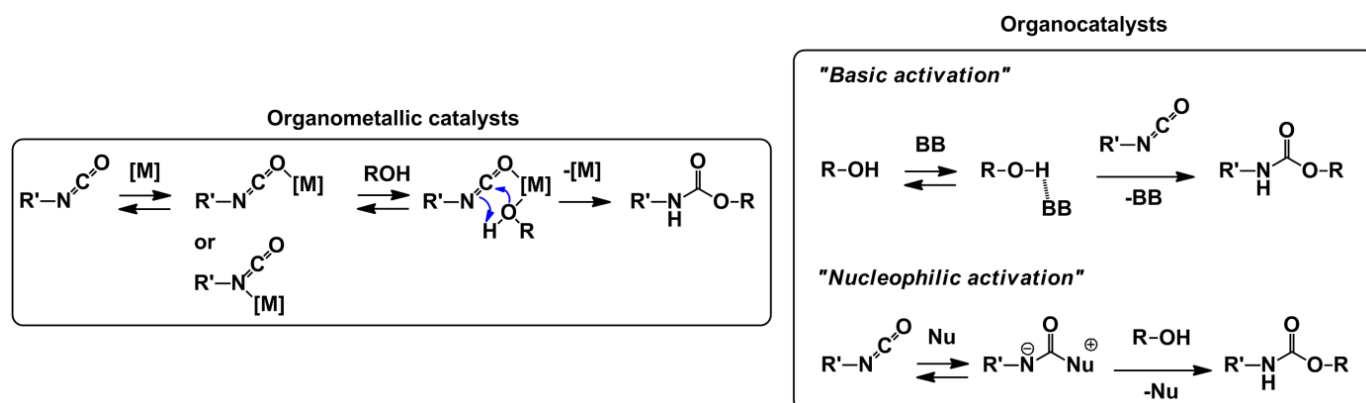


Figure I-2-17- Tensile stress versus strain curves of poly(ester urethane) (PU-dE-2), poly(ester/amide urethane) (PU-EA-2) and poly(amide urethane)s (PU-dA-1 and PU-dA-2).

4- Organocatalysis for fatty acid-based diol and diisocyanate polyaddition

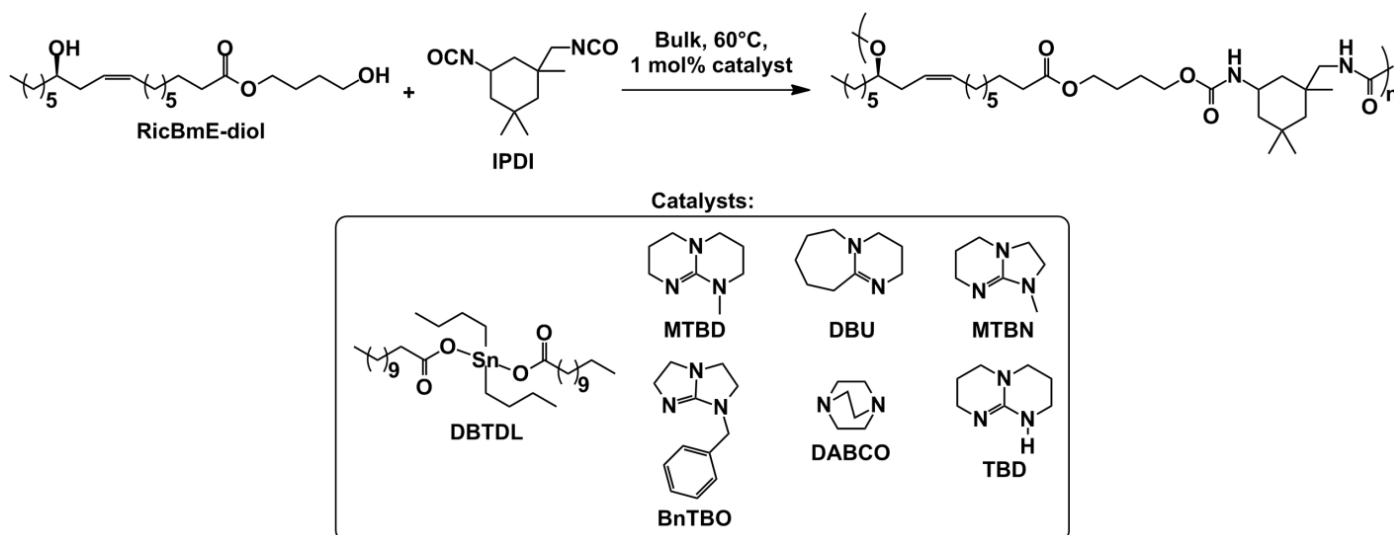
The reactivity of the isocyanate group toward nucleophilic reagent is due to the positive character of the carbon caused by the electronegativity of its oxygen and nitrogen vicinal atoms. Thus the reaction with alcohol is exothermic and, to increase the reaction rates and lower the polymerization temperatures, catalysts can be used.³² Various reviews have reported the literature on the catalysis of polyurethane synthesis.^{14, 32, 33} The polyaddition between poly- or di-ols and poly- or di-isocyanates are mainly catalyzed by organometallic compounds and tertiary amines. It has been demonstrated that tin compounds represented by the general formula Bu_2SnX_2 (X is an anion), as for instance the DBTDL (dibutyltin dilaurate) exhibit remarkable catalytic activity. Besides, organocatalysts and among them guanidines, have gained more and more interests.³⁴⁻³⁷ Recently, the groups of Taton and coll. and Destarac and coll. published a communication on the catalysis and synthesis of soluble linear PUs using the N-heterocyclic carbene 1,3-bis-(di-tert-butyl)imidazol-2-ylidene as organocatalyst.³⁸ The Scheme I-2-3 illustrates possible mechanisms with the use of organometallic and organocatalysts. Tin-based catalysts usually act as Lewis acids toward isocyanates to initiate the reaction. For this proposed mechanism, the isocyanate compound is first activated by coordination to the tin via the oxygen or nitrogen atom, followed by the nucleophilic attack of the hydroxyl group from the alcohol.³³ In the case of organocatalysts, two mechanisms are suggested: the “nucleophilic mechanism” and the “basic mechanism”.^{39, 40}



Scheme I-2-3- Proposed mechanisms of organometallic and organo-catalyses of isocyanate/alcohol reactions. [M] an organometallic catalyst; BB a Brønsted base and Nu a nucleophile.

Based on the work performed by ANR partners at the *Institut des Sciences Moléculaires (ISM)* in the group of Landais,⁴¹ organocatalysts have been evaluated in the catalysis of a fatty acid-based diol / diisocyanate polyaddition.

Various organocatalysts have been examined, on the synthesis of PUs between RicBmE-diol and IPDI, in comparison with the metallic catalyst of reference DBTDL (dibutyltin dilaurate). (See Scheme I-2-4) The polymerizations were performed in bulk at 60 °C with 1 mol% of catalyst (otherwise mentioned).



Scheme I-2-4- Polyaddition of RicBmE-diol with the diisocyanate IPDI using various catalysts.

Two commercially available guanidines, MTBD (7-methyl-1,5,7-triazabicyclo-[4.4.0]dec-5-ene - pKa=25.4) and TBD (1,5,7-triazabicyclo-[4.4.0]dec-5-ene - pKa=26.0) were investigated. Two standard catalysts for PU synthesis; the amidine base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene - pKa=24.3) and the tertiary amine DABCO (diazabicyclooctane) were also tested. Two guanidines synthesized at the ISM by Landais and coll.⁴¹ : MTBN and BnTBO were evaluated as well for the catalysis of the polymerization between RicBmE-diol and IPDI.

The progress of the reaction was monitored by analyzing at different polymerization times aliquots in FTIR-ATR. The disappearance of the NCO and OH vibrations at 2252 cm⁻¹ and around 3406 cm⁻¹ respectively was observed, together with the formation of two intense peaks corresponding to the urethane carbonyl and C-NH vibrations at 1698 cm⁻¹ and 1526 cm⁻¹ respectively. (See Figure I-2-18)

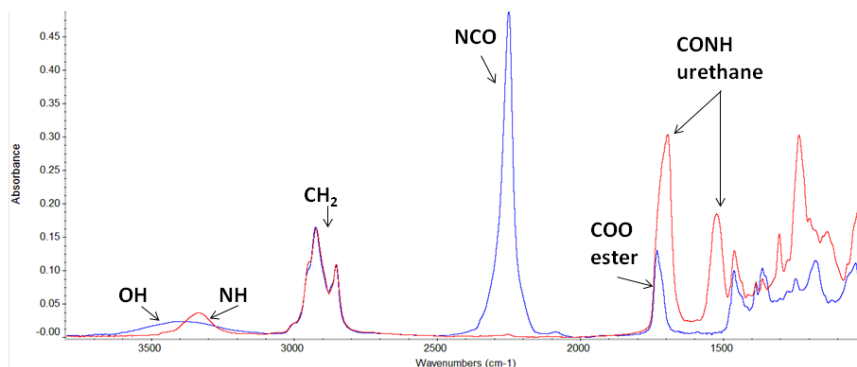


Figure I-2-18- FTIR-ATR spectra of the RicBmE-diol and IPDI polyaddition with MTBD at $t=0$ (blue) and after 20h (red).

The Figure I-2-19-(1) depicts the evolution of the isocyanate conversion with time for the polymerization between RicBmE-diol and IPDI using various catalysts. The curve for the DBTDL catalyst was plotted as a reference. The conversion was calculated by FTIR-ATR using the equation: $\text{Conversion} = 100 - \frac{(H_{\text{NCO}}/H_{\text{CH}_2})_t}{(H_{\text{NCO}}/H_{\text{CH}_2})_{t=0}} * 100$, where x , t , H_{NCO} and H_{CH_2} are the conversion, the time, the height of the peaks corresponding to the isocyanate and the unmodified CH_2 respectively.

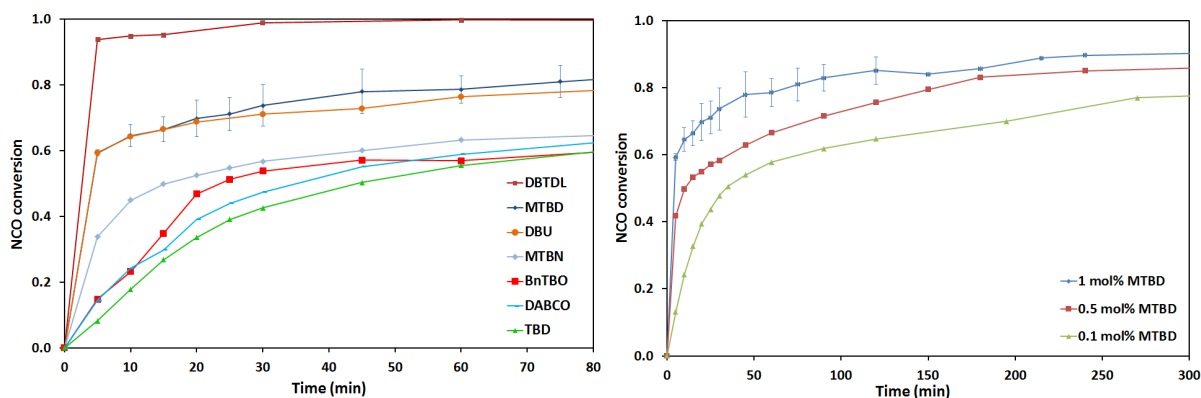


Figure I-2-19- (1) Evolution of the NCO conversion on the polymerization of RicBmE-diol and IPDI using various catalysts. (2) Increasing of the MTBD quantity lead to faster polyaddition between RicBmE-diol and IPDI.

The reproductibility has been confirmed for the polymerization using MTBD as catalyst. Besides, no allophanate and isocyanurate were observed on the FTIR-ATR spectra of the reaction mixtures. Those side products can be generated at high temperature or with the addition of catalysts.³² Thus, the tested organocatalysts were highly selective toward the reaction between alcohol and isocyanate as already reported for PEG 600 and PTMO 650 diols.⁴¹ Besides, no urea was obtained due to the inert atmosphere used. Indeed, urea can be formed by the reaction between isocyanate and amine, which is generated by the decomposition of unstable carbamic acid, product of the reaction between water and isocyanate.⁴² The kinetic curves obtained do not fit with an overall second or third order reaction. In the literature, the overall order of the polyaddition between diol and diisocyanate is usually 2. However deviations can occur with the auto-catalyzed effect of -OH

and -NH-COO- or from the solvent. Another possibility, that can explain the obtained kinetics, is the increase of the viscosity of the reaction medium with the conversion. Indeed, the bulk conditions could induce a drop of the reaction rate due to poor diffusion of the active sites.

Comparing the different organocatalysts, one can notice the higher reactivity of MTBD compared to TBD, whereas the latter is more basic and more efficient toward ring opening polymerization of lactide and lactones.³⁵ Besides, although DBU is less basic than MTBD, a similar efficiency was demonstrated. These conclusions are in accordance with an activation through a “nucleophilic” mechanism as developed by Landais and coll.⁴¹ Nevertheless, DABCO which is a nucleophile and a poor base, demonstrated poor efficiency. So the “basic” mechanism still needs to be taken into account. The polymerization rates were affected by the ring size of the different guanidines. The guanidine MTBN led to a lower reactivity than the larger analogues MTBD. Similar conclusions are observed while comparing BnTBO and MTBN.

The tested organocatalysts have not permitted to reach the reaction rates attained with DBTDL on the fatty acid-based substrates. However, molar masses up to 34 000 g.mol⁻¹ with a dispersity of 2.4 were achieved using MTBD as catalyst. Molar masses and dispersity of the synthesized PUs are given in Table I-2-5 after full conversion of the isocyanate as detected by FTIR-ATR. Similar molar masses were obtained by our partners on PEG 600 and PTMO 650 diols.⁴¹ Similar thermal degradation were observed by TGA analysis between PUs catalyzed with DBTDL and MTBD, for which the temperature at 5 wt% loss were 259°C and 267°C respectively.

Table I-2-5- Characteristics of the PUs synthesized between RicBmE-diol and IPDI using various organocatalysts.

Catalyst	Time to full conversion (h)	\bar{M}_n (g.mol ⁻¹)	\bar{M}_w (g.mol ⁻¹)	Dispersity	Tg (°C)
DBTDL	27	32 900	107 600	3.27	3
MTBD	72	34 400	82 800	2.4	8
DBU	91	27 600	72 800	2.63	7
MTBN	312	25 500	92 300	3.62	-1
BnTBO	312*	21 300	56 400	2.65	1
DABCO	336*	27 400	67 600	2.47	7
TBD	288*	27 800	55 900	2.01	7

\bar{M}_n , \bar{M}_w and dispersities are given for PUs after full NCO conversion with respect to FTIR-ATR analysis, except for * for which the conversion was 99.0% after 312 h for BnTBO, 99.2% after 336 h for DABCO and 99.8% after 288 h for TBD. (SEC in DMF with 1 wt% LiBr - Calibration with PS standards)

Polyadditions with MTBD at 0.1, 0.5 and 1 mol% were carried out and it is important to mention that the higher the catalyst concentration was, the faster the polymerizations occurred. (See Figure I-2-19-(2)) In the case of the PU catalyzed with 0.1 mol% of MTBD, an overall 3rd order can be noticed from the first 60 minutes, which is consistent with the fact that the reaction mixture can be maintained a longer time under stirring. The higher molar masses obtained with 0.1 and 0.5 mol% of MTBD compared to 1 mol% can be the result of the same experimental observation. (See Table I-2-6)

Table I-2-6- Characteristics of the PUs synthesized with different amounts of MTBD after full NCO conversion.

mol% MTBD	\bar{M}_n (g.mol ⁻¹)	\bar{M}_w (g.mol ⁻¹)	Dispersity	Tg (°C)
1	34 400	82 800	2.4	8
0.5	39 500	144 600	3.7	9
0.1	37 500	107 300	2.9	nd

Conclusion

In summary, a series of well-defined telechelic diols containing ester and/or amide linkages were synthesized from methyl undecenoate and methyl oleate. These bifunctional monomers were fully characterized and effectively used as building blocks to thermoplastic PUs in combination with IPDI and MDI. The thermo-mechanical properties of the so-formed PUs were investigated both by DSC and DMA. Amorphous PUs displayed distinct Tg in the range -27 °C to 51°C depending on the diol structure. Higher Tg were observed in the case of linear structure monomers without dangling chains, isosorbide as a central block, presence of amide functions and higher urethane function densities. Lower tan δ values were observed for amide-containing PUs than for ester-based ones, proof of their higher elastic behavior. The semi-crystalline PUs exhibited melt crystallization transitions from 83 °C to 158 °C upon heating and melting points from 116 °C to 183 °C as noticed from DSC, ModDSC and DMA. In all cases, the thermo-mechanical properties were correlated to the diol and diisocyanate structures. Amide moieties, due to high hydrogen bonds, lead to PUs with higher glass transition temperatures, higher melting points and higher Young's modulus and ultimate tensile strength. Regarding the organocatalysts, the MTBD guanidine and the DBU amidine were shown to be relatively effective catalysts for the PUs formation on fatty acid-based substrates, not reaching the same reaction rates than the DBTDL, but achieving comparable molar masses after full conversion of the isocyanate groups.

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Experimental and supporting information

Experimental methods

Monomers synthesis

1. Undecenoate diester diols (UndPdE-diol and UndIdE-diol)

Transesterification step. Methyl undecenoate, diol and TBD (1: 0.5: 0.05) were stirred under nitrogen flow at 120 °C (4 h), at 160 °C (2 h) then under vacuum at 160 °C (30 min). The reaction mixture was dissolved in ethyl acetate and washed with water (3 times). The organic layer was dried over anhydrous sodium sulfate, filtered and the solvent was evaporated under reduced pressure.

UndPdE: Methyl undecenoate (20 g, 101 mmol), 1,3-propanediol (3.8 g, 50 mmol) and TBD (702 mg, 5 mmol). UndPdE was obtained as a yellow viscous liquid. Yield = 73%. ¹H NMR (CDCl₃, 25 °C, 400 MHz) δ (ppm): 5.75 (m, 2H), 4.92 (m, 4H), 4.11 (t, 4H), 2.25 (t, 4H), 1.9 (m, 4H), 1.91 (m, 2H), 1.57 (m, 4H), 1.33 (m, 4H), 1.25 (m, 16H).

UndIdE: Methyl undecenoate (20 g, 101 mmol), isosorbide (7.4 g, 50 mmol) and TBD (702 mg, 5 mmol). UndIdE was purified by column chromatography (eluent: cyclohexane / ethyl acetate (70/30)) and obtained as a yellow viscous liquid. Yield = 50%. ¹H NMR (CDCl₃, 25 °C, 400 MHz) δ (ppm): 5.78 (m, 2H), 5.17 (d, 1H), 5.13 (m, 1H), 4.93 (m, 4H), 4.80 (t, 1H), 4.45 (d, 1H), 3.93 (m, 3H), 3.77 (m, 1H), 2.33 (t, 2H), 2.29 (t, 2H), 2.03 (m, 4H), 1.62 (m, 4H), 1.35 (m, 4H), 1.27 (m, 16H).

Thiol-ene reaction. Undecenoate diesters and mercaptoethanol (3 eq. / double bond) were stirred at room temperature under UV irradiation (254 nm). After the disappearance of double bond protons (monitored by ¹H NMR spectroscopy), the reaction mixture was taken into dichloromethane (DCM) and thoroughly washed with water (4 times). The DCM solution was dried over anhydrous sodium sulfate, filtered and solvent was removed on rotary evaporator to obtain UndPdE-diol and UndIdE-diol as white powders.

UndPdE-diol: UndPdE (17 g, 39 mmol) and mercaptoethanol (18 g, 232 mmol). The purity of UndPdE-diol (92.3%) was determined by GC-FID. Yield = 82%. ¹H NMR (CDCl₃, 25 °C, 400 MHz) δ (ppm): 4.14 (t, 4H), 3.71 (t, 4H), 2.72 (t, 4H), 2.51 (t, 4H), 2.29 (t, 4H), 2.08 (s, 2OH), 1.96 (m, 2H), 1.59 (m, 8H), 1.37 (m, 4H), 1.27 (m, 20H). ¹³C NMR (CDCl₃, 25 °C, 100 MHz) δ (ppm): 173.94 (C=O), 60.94 (COO-CH₂), 60.33 (CH₂-OH), 35.48 (S-CH₂-CH₂-OH), 34.37

(CH₂-COO), 31.77 (S-CH₂), 29.88 (S-CH₂-CH₂), 29.53 - 29.24 (CH₂), 28.94 (S-CH₂-CH₂-CH₂), 28.14 (COO-CH₂-CH₂), 25.05 (CH₂-CH₂-COO). IR (cm⁻¹): 3360, 2917, 2849, 1721, 719.

UndIdE-diol: UndIdE (13.5 g, 28 mmol) and mercaptoethanol (13 g, 169 mmol). The purity of UndIdE-diol (93.0%) was determined by GC-FID. Yield = 74%. ¹H NMR (CDCl₃, 25 °C, 400 MHz) δ (ppm) : 5.19 (d, 1H), 5.14 (m, 1H), 4.82 (t, 1H), 4.46 (d, 1H), 3.94 (m, 3H), 3.78 (m, 1H), 3.71 (t, 4H), 2.73 (t, 4H), 2.51 (t, 4H), 2.37 (t, 2H), 2.31 (t, 2H), 1.91 (s, OH), 1.58 (m, 8H), 1.37 (m, 4H), 1.27 (m, 20H). ¹³C NMR (CDCl₃, 25 °C, 100 MHz) δ (ppm): 172.96 (C=OO), 173.27 (C=OO), 86.02 (CH-O), 80.80 (CH-O), 77.95 - 77.84 (COO-CH), 73.79 - 73.53 (COO-CH), 73.79 - 73.53 (CH₂-O), 70.43 (CH₂-O), 60.37 (CH₂-OH), 35.52 (S-CH₂-CH₂-OH), 34.29 - 34.13 (CH₂-COO), 31.78 (S-CH₂), 29.90 (S-CH₂-CH₂), 29.55 - 29.19 (CH₂), 28.94 (S-CH₂-CH₂-CH₂), 24.97 (CH₂-CH₂-COO). IR (cm⁻¹): 3328, 2917, 2849, 1728, 721.

2. Oleate propyl diester diol (OIPdE-diol)

Transesterification step. The experimental procedure for the preparation of OIPdE was similar to the one of undecenoate diesters; methyl oleate (20 g, 67 mmol), 1,3-propanediol (2.6 g, 34 mmol) and TBD (469 mg, 3 mmol). The reaction mixture was dissolved in ethyl acetate (200 mL) and washed with water (3 x 50 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and solvent was removed on rotary evaporator. OIPdE was purified by column chromatography (eluent: cyclohexane / ethyl acetate (95/5 followed by 80/20)) and obtained as a yellow viscous liquid. Yield = 61%. **OIPdE:** ¹H NMR (CDCl₃, 25 °C, 400 MHz) δ (ppm): 5.35 (m, 4H), 4.14 (t, 4H), 2.27 (t, 4H), 2.02 (m, 10H), 1.61 (m, 4H), 1.30 (m, 40H), 0.89 (t, 6H).

Thiol-ene reaction. The experimental procedure for the synthesis of OIPdE-diol was similar to the preparation of UndPdE-diol, except for the use of DMPA and UV wavelength (365 nm). OIPdE (13.5 g, 22 mmol), mercaptoethanol (10 eq. / double bond - 35 g, 446 mmol) and DMPA (0.05 eq. / double bond - 572 mg, 2 mmol). OIPdE-diol was purified by column chromatography (eluent: cyclohexane / ethyl acetate (80/20)) and obtained as a yellow viscous liquid. The purity of OIPdE-diol (87.1%) was determined by GC-FID. Yield = 66%. **OIPdE-diol:** ¹H NMR (CDCl₃, 25 °C, 400 MHz) δ (ppm): 4.15 (t, 4H), 3.68 (m, 4H), 2.71 (t, 4H), 2.57 (m, 2H), 2.29 (t, 4H), 2.28 (t, OH), 1.96 (m, 2H), 1.61 (m, 4H), 1.52 (m, 8H), 1.40 (m, 8H), 1.27 (m, 36H), 0.88 (t, 6H). ¹³C NMR (CDCl₃, 25 °C, 100 MHz) δ (ppm): 173.91-173.89 (C=OO), 60.95 (COO-CH₂), 60.86 (CH₂-OH), 46.96 (S-CH), 35.17 - 35.04 (CH-CH₂), 34.35 (CH₂-COO), 33.98 (S-CH₂-CH₂-OH), 32.00 - 29.26 (CH₂), 28.14 (COO-CH₂-CH₂), 26.92 (CH₂-CH₂-CH-S), 25.01 (CH₂-CH₂-CO-O), 22.78 (CH₂), 14.22 (CH₃). IR (cm⁻¹): 3435, 2922, 2852, 1736, 722.

3. Undecenoate propyl monoester diol (*UndPmE-diol*).

Transesterification step. Methyl undecenoate (10 g, 50 mmol) with 1,3-propanediol (384 g, 5 mol) and TBD (351 mg, 2.5 mmol) (1: 100: 0.05) were stirred under nitrogen flow at 120 °C for 1 h. The reaction mixture was then dissolved in ethyl acetate (200 mL) and washed with water (3 x 50 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and solvent was removed on rotary evaporator. A column chromatography (eluent: heptane / ethyl acetate (70/30 then 50/50)) was performed to purify *UndPmE* compound obtained as a yellow liquid. Yield = 55%. ***UndPmE***: ¹H NMR (CDCl₃, 25 °C, 400 MHz) δ (ppm): 5.78 (m, 1H), 4.89 (m, 2H), 4.23 (t, 2H), 3.69 (t, 2H), 2.28 (t, 2H), 2.00 (m, 2H), 1.86 (m, 2H), 1.83 (t, OH), 1.59 (m, 2H), 1.34 (m, 2H), 1.27 (m, 8H).

Thiol-ene reaction. The experimental procedure carried out was similar to the preparation of undecenoate diester diols. *UndPmE* (5.4 g, 12 mmol) and mercaptoethanol (6 eq. / double bond - 5.8 g, 74 mmol). *UndPmE-diol* was obtained as a white powder, and the purity of *UndPmE-diol* (97.1%) was determined by GC-FID. Yield = 76%. ***UndPmE-diol***: ¹H NMR (CDCl₃, 25 °C, 400 MHz) δ (ppm): 4.23 (t, 2H), 3.69 (m, 4H), 2.72 (t, 2H), 2.51 (t, 2H), 2.30 (t, 2H), 2.17 (t, OH), 1.86 (m, 2H), 1.83 (t, OH), 1.59 (m, 4H), 1.37 (m, 2H), 1.27 (m, 10H). ¹³C NMR (CDCl₃, 25 °C, 100 MHz) δ (ppm): 174.47 (C=OO), 61.31 (COO-CH₂), 60.33 (CH₂-OH), 59.38 (CH₂-OH), 35.46 (S-CH₂-CH₂-OH), 32.42 (CH₂-COO), 31.93 (COO-CH₂-CH₂-CH₂-OH), 31.77 (S-CH₂), 29.86 (S-CH₂-CH₂), 29.50 - 29.22 (CH₂), 28.91 (S-CH₂-CH₂-CH₂), 25.08 (CH₂-CH₂-COO). IR (cm⁻¹): 3388, 2918, 2849, 1729, 719.

4. Undecenoic propyl esteramide diol (*UndPEA-diol*)

Amidation-transesterification step. Methyl undecenoate (30 g, 151 mmol), 1,3-aminopropanol (5.7 g, 76 mmol) and TBD (1 g, 7.6 mmol) (1: 0.5: 0.05) were stirred under nitrogen flow at 120 °C (4 h) then at 160 °C (2 h). The reaction mixture was dissolved in ethyl acetate (200 mL) and washed with water (3 x 50 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and solvent was removed on rotary evaporator. *UndPEA* compound was purified by column chromatography (eluent: DCM / MeOH (95/5)) and obtained as a white powder. Yield = 58%. ***UndPEA***: ¹H NMR (CDCl₃, 25 °C, 400 MHz) δ (ppm): 5.81 (m, 2H), 5.79 (s, NH), 4.94 (m, 4H), 4.16 (t, 2H), 3.30 (m, 2H), 2.31 (t, 2H), 2.18 (t, 2H), 2.03 (m, 4H), 1.84 (m, 2H), 1.62 (m, 4H), 1.31 (m, 4H), 1.29 (m, 16H).

Thiol-ene reaction. The experimental procedure for the synthesis of *UndPEA-diol* was similar to the preparation of *UndPdE-diol*, except that DCM (5 mL / g) was used as a solvent. *UndPEA* (14 g, 34 mmol) and mercaptoethanol (18 eq. / double bond - 97 g, 1.2 mol).

UndPEA-diol was obtained as pink / off white powder and the purity of UndPEA-diol (94.5%) was determined by GC-FID. Yield = 70%. **UndPEA-diol:** ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 5.96 (s, NH), 4.09 (t, 2H), 3.67 (m, 4H), 3.24 (m, 2H), 2.67 (t, 4H, OH), 2.47 (t, 4H), 2.26 (t, 2H), 2.11 (t, 2H), 1.79 (m, 2H), 1.55 (m, 8H), 1.32 (m, 4H), 1.23 (m, 20H). ^{13}C NMR (CDCl_3 , 25 °C, 100 MHz) δ (ppm): 174.26 (C=ONH), 173.39 (C=OO), 61.79 (COO-CH₂), 60.41 (CH₂-OH), 36.94 (CH₂-CONH), 36.27 (CONH-CH₂), 35.36 (S-CH₂-CH₂-OH), 34.41 (CH₂-COO), 31.77 (S-CH₂), 29.83 (S-CH₂-CH₂), 29.49 - 29.22 (CH₂), 28.88 (COO-CH₂-CH₂-CH₂-NHCO), 25.83 (CH₂-CH₂-CONH), 25.05 (CH₂-CH₂-COO). IR (cm^{-1}): 3291, 2917, 2848, 1724, 1632, 1541, 720.

5. Undecenoic butyl diamide diol (UndBdA-diol)

Amidation step. Methyl undecenoate (20 g, 101 mmol), butane-1,4-diamine (4.4 g, 50 mmol) and TBD (702 mg, 5 mmol) (1: 0.5: 0.05) were stirred under nitrogen flow at 120 °C (4 h) then at 160 °C (2 h). The reaction flask was cooled down at 90 °C and NMP (60 mL) was added to obtain a homogeneous phase. The required UndBdA was slowly precipitated while reaching room temperature. The precipitated solid was filtered and washed with methanol to obtain UndBdA as a white powder. Yield = 83%. **UndBdA:** ^1H NMR (CDCl_3 , 50 °C, 400 MHz) δ (ppm): 5.79 (m, 2H), 4.98 (m, 4H), 3.26 (m, 4H), 2.15 (t, 4H), 1.99 (m, 4H), 1.65 (m, 4H), 1.53 (m, 4H), 1.40 (m, 4H), 1.32 (m, 16H).

Thiol-ene reaction. UndBdA (16 g, 38 mmol), mercaptoethanol (12 eq. / double bond – 71 g, 913 mmol) and AIBN (5% molar / UndBdA – 312 mg, 1.9 mmol) were stirred in NMP (5 mL / g), under static vacuum into a bath preheated at 80 °C. After two hours, the reaction mixture was cooled to room temperature. The UndBdA–diol got precipitated and was filtered. The white solid obtained was washed thoroughly with water and dried. It was not possible to determine its purity by GC due to its poor solubility. Yield = 92%. **UndBdA-diol:** ^1H NMR (DMSO-d_6 , 50 °C, 400 MHz) δ (ppm): 4.59 (t, OH), 3.52 (m, 4H), 3.02 (m, 4H), 2.55 (t, 4H), 2.50 (t, 4H), 2.03 (t, 4H), 1.49 (m, 8H), 1.37 (m, 8H), 1.25 (m, 20H). ^{13}C NMR (DMSO-d_6 , 50 °C, 100 MHz) δ (ppm): 171.58 (C=ONH), 60.69 (CH₂-OH), 37.94 (CONH-CH₂), 35.28 (CH₂-CONH), 33.91 (S-CH₂-CH₂-OH), 31.32 (S-CH₂), 29.16 (S-CH₂-CH₂), 28.65 - 28.34 (CH₂), 27.93 (CONH-CH₂-CH₂), 26.51 (S-CH₂-CH₂-CH₂), 25.07 (CH₂-CH₂-CONH). IR (cm^{-1}): 3292, 2917, 2848, 1631, 1537, 713.

6. Undecenoic propyl monoamide diol (UndPmA-diol)

Amidation step. Methyl undecenoate (20 g, 101 mmol) and 1,3 aminopropanol (15 g, 202 mol) (1: 2) were stirred under nitrogen flow at 150 °C (2 h) then at 160 °C (2 h). After

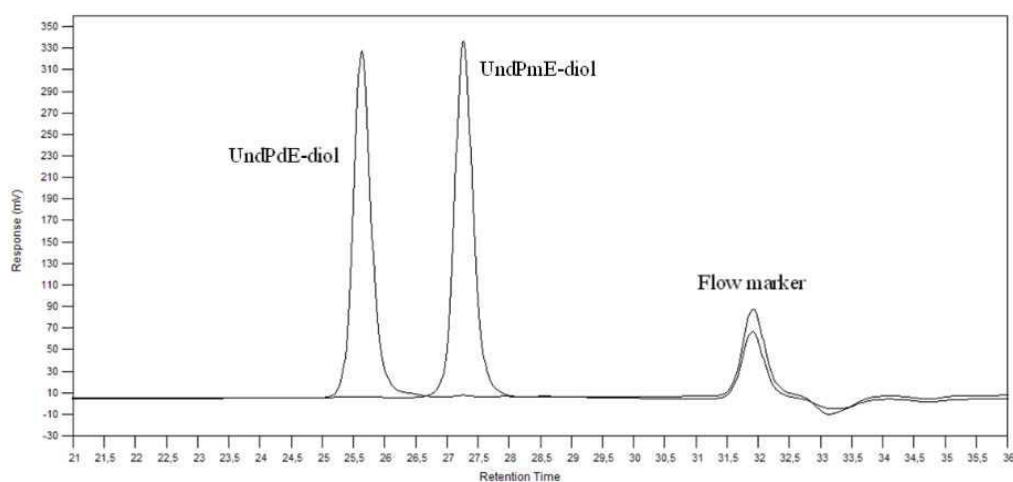
completion of the reaction, the reaction mixture was dissolved in THF (70 mL) and reprecipitated in water. The solid obtained was filtered and washed with water. UndPmA compound was purified by column chromatography (eluent: cyclohexane / ethyl acetate (70/30 then 30/70)) and obtained as a yellow / brown product. The purity of the compound (99.9%) was determined by GC-FID. Yield = 53%. **UndPmA:** ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 5.78 (m, 1H), 5.76 (s, NH), 4.97 (m, 2H), 3.62 (m, 2H), 3.42 (m, 2H), 3.20 (t, OH), 2.19 (t, 2H), 2.03 (m, 2H), 1.67 (m, 4H), 1.37 (m, 2H), 1.29 (m, 8H).

Thiol-ene reaction. The experimental procedure for the synthesis of UndPmA-diol was similar to the preparation of UndPEA-diol. UndPmA (5 g, 12 mmol) and mercaptoethanol (6 eq. / double bond – 5.7 g, 73 mmol). UndPmA-diol was obtained as a white powder with a purity of 99.9% as determined by GC-FID. Yield = 72%. **UndPmA-diol:** ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm) : 5.86 (s, NH), 3.70 (m, 2H), 3.62 (m, 2H), 3.42 (m, 2H), 3.28 (t, OH), 2.73 (t, 2H), 2.51 (t, 2H), 2.31 (t, OH), 2.19 (t, 2H), 1.66-1.57 (m, 6H), 1.37 (m, 2H), 1.27 (m, 10H). ^{13}C NMR (CDCl_3 , 25 °C, 100 MHz) δ (ppm): 174.70 (C=ONH), 60.35 ($\text{CH}_2\text{-OH}$), 59.28 ($\text{CH}_2\text{-OH}$), 36.89 ($\text{CH}_2\text{-CONH}$), 36.21 (CONH- CH_2), 35.48 (S- $\text{CH}_2\text{-CH}_2\text{-OH}$), 32.60 (CONH- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$), 31.78 (S- CH_2), 29.84 (S- $\text{CH}_2\text{-CH}_2$), 29.47 - 29.22 (CH_2), 28.88 (S- $\text{CH}_2\text{-CH}_2\text{-CH}_2$), 25.89 ($\text{CH}_2\text{-CH}_2\text{-CONH}$). IR (cm^{-1}): 3289, 2920, 2849, 1633, 1549, 727.

General procedure for polyurethane synthesis

Two diisocyanates, viz IPDI (isophorone diisocyanate) and MDI (methylene diphenyl diisocyanate) were used as comonomers for the PU syntheses. Except for UndPEA-diol, UndBdA-diol and UndPmA-diol, PU syntheses with IPDI were performed in bulk, at 80 °C with 0.1 wt% of DBTDL as catalyst. All PUs synthesized by bulk polymerization were purified by dissolution in minimum amount of DMF and precipitation in large excess of water, followed by washing the precipitated polymer. The following three monomers: UndPEA-diol, UndBdA-diol and UndPmA-diol were reacted with IPDI in neat anhydrous DMF (UndPEA-diol and UndPmA-diol) or in anhydrous DMF containing 4 wt% LiCl (UndBdA-diol). PUs with MDI as comonomer were synthesized in anhydrous DMF at 80 °C without catalyst. Additional 4 wt% LiCl was also used particularly in case of UndBdA-diol as monomer with MDI. The polymers synthesized by solution polymerization were purified by precipitation in methanol. Water was used as a non-solvent specifically in case of PU-mA-1.

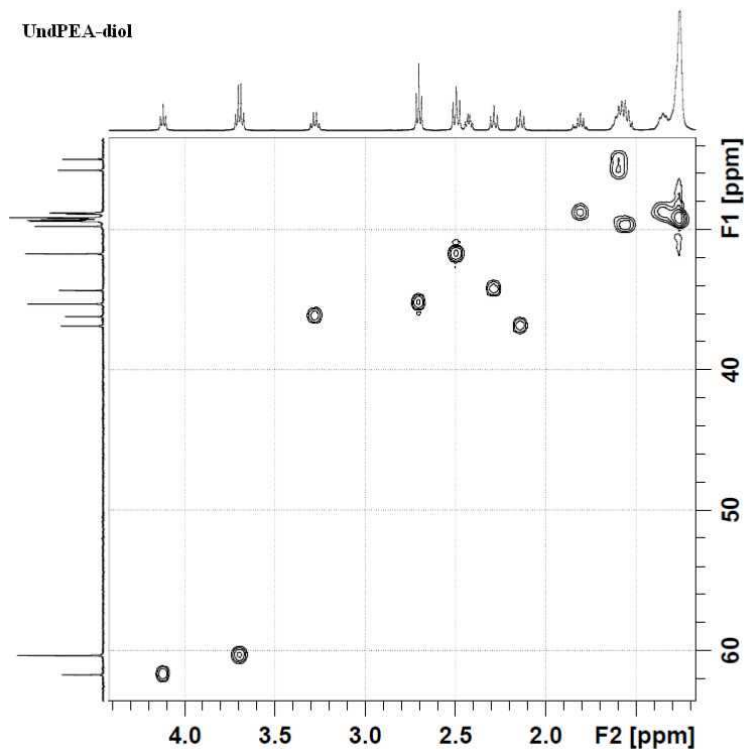
Supporting information



SI Figure I-2-1- SEC trace of UndPdE-diol.

SI Table I-2-1- Characterizations of the diols containing ester, ester-amide and amide linkages. (1) Determined by Kofler bench. (2) Determined by DSC, 10°C/min. (3) Soluble only in DMSO with temperature.

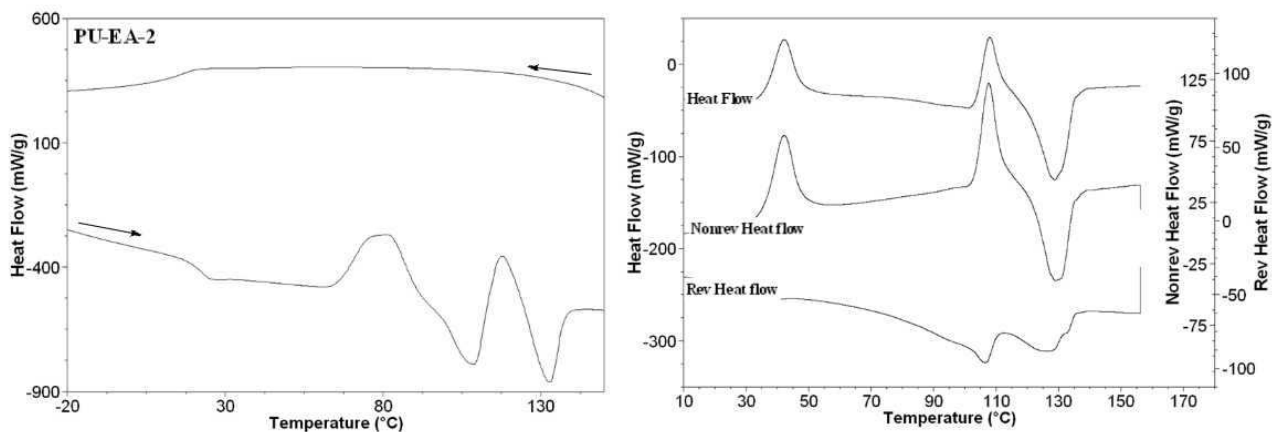
Synthesized diol	wt% Yield (Step 1 - 2)	%purity GC	T _m (°C) ¹
Esters			
UndPdE-diol	73 - 82	92.3	70
UndIdE-diol	50 - 74	94.9	64
OIPdE-diol	61 - 66	87.1	-43 ²
UndPmE-diol	55 - 76	97.1	57
Amides			
UndPEA-diol	58 - 70	94.5	92
UndBdA-diol	83 - 92	nd ³	145
UndPmA-diol	45 - 72	99.9	86



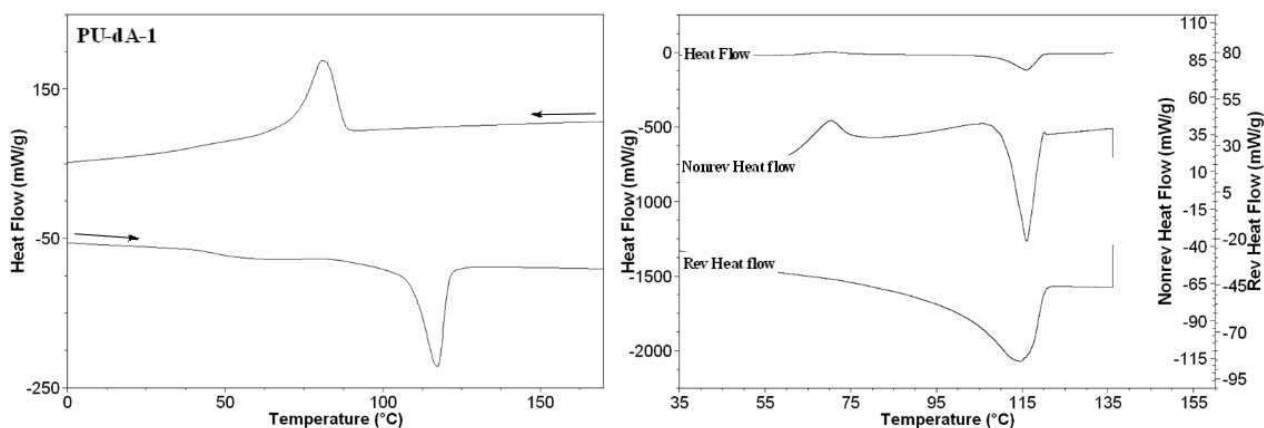
SI Figure I-2-2- ^1H - ^{13}C HSQC-NMR of UndPEA-diol. (Analysis in CDCl_3)

SI Table I-2-2- Solubility of PUs in THF, chloroform and DMF.

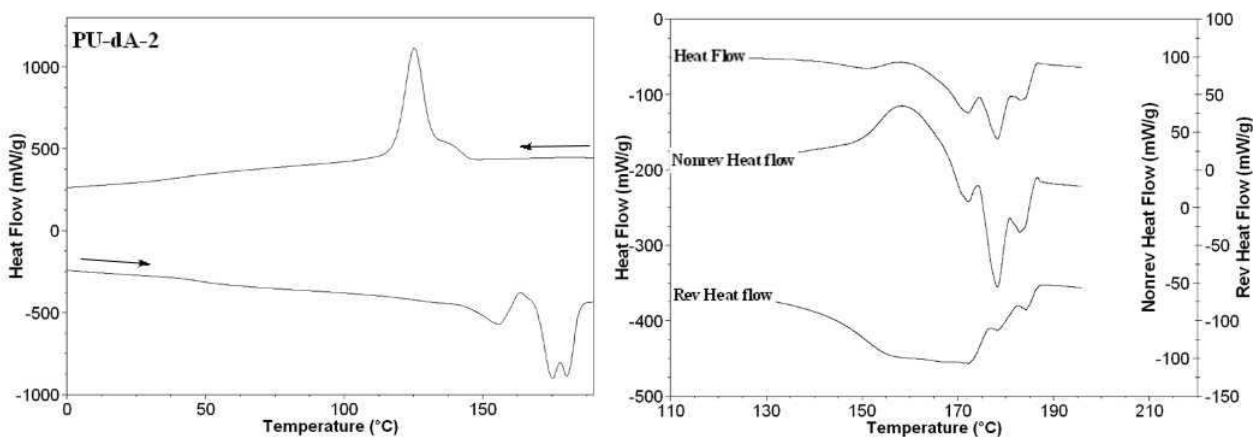
Sample	THF	Chloroform	DMF
Poly(ester urethane)s			
PU-dE-1	+	+	+
PU-dE-2	+	+	+/-
PU-dE-3	+	+	+
PU-dE-4	+	+	+
PU-dE-5	+	+	+
PU-dE-6	+	+	+
PU-mE-1	+	+	+
PU-mE-2	+/-	+/-	+/-
Poly(esteramide urethane)s and Poly(amide urethane)s			
PU-EA-1	+	+	+
PU-EA-2	+ heat	+ heat	+
PU-dA-1	+/- heat	+ heat	-
PU-dA-2	-	-	-
PU-mA-1	+ heat	+	+
PU-mA-2	-	-	+ heat



SI Figure I-2-3- DSC second cycle thermograms at 10°C/min (left) and Mod DSC thermograms at 2°C/min with a modulation amplitude of 0.64 °C and a modulation period of 60 s of PU-EA-2 (right).

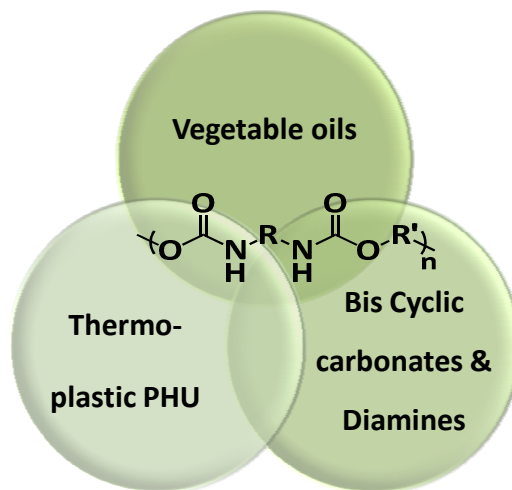


SI Figure I-2-4- DSC second cycle thermograms at 10°C/min (left) and Mod DSC thermograms at 2°C/min with a modulation amplitude of 0.64 °C and a modulation period of 60 s of PU-dA-1 (right).



SI Figure I-2-5- DSC second cycle thermograms at 10°C/min (left) and Mod DSC thermograms at 2°C/min with a modulation amplitude of 0.64 °C and a modulation period of 60 s of PU-dA-2 (right).

PART II



Mots clés : polyuréthanes thermoplastiques, poly(hydroxyuréthane)s, bio-sourcé, huiles végétales, acide gras, sans isocyanate, sans phosgène, (bis) carbonate cyclique, (di)amine, catalyse.

Keywords : thermoplastic polyurethanes (TPUs), poly(hydroxyurethane)s (PHU), bio-based, vegetable oils, fatty acid, isocyanate free, phosgene free, (bis) cyclic carbonate, (di)amine, catalysis.

PART II - Chapter 1: Literature

Toward non-phosgene and non-isocyanates polyurethanes from vegetable oils

Table of contents

Introduction	87
1- Non-phosgene or non-isocyanate routes to PU	88
1.1- Non-phosgene isocyanate syntheses to PU	88
1.1.1- Reductive carbonylation of nitro compounds	88
1.1.2- Curtius, Hofmann and Lossen rearrangements	89
1.2- Phosgene non-isocyanate routes to PU	90
1.2.1- ROP of cyclic urethanes	90
1.2.2- From bis-(dialkyl carbonate)s	91
2- Non-phosgene and non-isocyanate routes to PUs	92
2.1- Transurethanization with non-phosgene-based bis-(dialkyl carbamate)s	92
2.1.1- Bis-(Dialkyl Carbamate)s from dimethylcarbonate	92
2.1.2- Bis-(Dialkyl Carbamate)s from ethylene carbonate	93
2.2- Thermoplastic polyhydroxyurethanes (PHUs)	94
2.2.1- Synthesis of cyclic carbonates	96
2.2.1.1- Synthesis of 5-membered cyclic carbonates (5CC)	96
2.2.1.2- Synthesis of 6- and 7-membered cyclic carbonates (6CC and 7CC)	99
2.2.1.3- Synthesis of bis-cyclic carbonates (bCC)	101
2.2.1.4- Reactivity of cyclic carbonates	102
2.2.2- Synthesis of amines	104
2.2.3- Studies on the model cyclic carbonate / amine reaction	106
2.2.3.1- Mechanism	107
2.2.3.2- Kinetic and reaction conditions	108
2.2.3.3- Effect of the chemical structure of the amine	111
2.2.3.4- Effect of the substituents and size of the cyclic carbonate	112
2.2.3.5- Selectivity of the reaction and by-products	114
2.2.4- Thermoplastic poly(hydroxyurethane)s (PHUs)	116
2.2.4.1- Reaction conditions, yield and kinetic	117
2.2.4.2- Molar masses	119
2.2.4.3- Selectivity and side reactions	120
2.2.4.4- Different reactivity for specific monomers	121
2.2.4.5- Thermo-mechanical properties and thermal stability	124
2.2.5- Additives and catalysts for the cyclic carbonate/amine reaction	125
2.2.6- Conclusion	128

3- Vegetable oils transformations to non-isocyanate and non-phosgene PUs	129
3.1- Transurethanization approach	129
3.1.1- Carbamate synthesis via Curtius rearrangement	129
3.1.2- Carbamate synthesis from ethylene carbonate	130
3.1.3- Carbamate synthesis via Lossen rearrangement	131
3.2- Vegetable oils-based 5-membered cyclic carbonates to poly(hydroxyurethane)s	131
3.2.1- Synthesis of poly(5-membered cyclic carbonates) from vegetable oil derivatives	131
3.2.2- Non-isocyanate PHU networks from vegetable oil derivatives	133
3.2.3- Fatty acid-based thermoplastic PHUs	136
3.3- Toward vegetable oils-based diamines	137
Conclusion	140
References	141

Introduction

Classically, PUs are prepared from a poly- or di-ol and a poly- or di-isocyanate as presented in the first part. In order to find alternatives to phosgene and isocyanate, non-phosgene isocyanates as well as phosgene non-isocyanate routes have been developed. Moreover, non-phosgene and non-isocyanates pathways have been studied notably using the reaction between cyclic carbonates and amines. Figure II-1-1 presents an overview of the main synthetic routes to polyurethanes according to their dependence in phosgene and isocyanate. Recently, Meier and coll. reviewed sustainable routes to PUs precursors.¹ Other reviews also reported different pathways to PUs.²⁻⁶

In the current context of sustainable chemistry development and new regulations, research groups have an increasing interest of replacing of isocyanates in the synthesis of polyurethanes. This chapter (Part II - Chapter 1) first briefly exposes separately main non-phosgene isocyanate syntheses as well as phosgene non-isocyanate routes to PUs. As the phosgene has to be avoided at any stage of the PU production, all the reaction steps are considered before classifying them. *In situ* generated isocyanates (or masked isocyanates) from phosgene, are not described.⁷

PHOSGENE

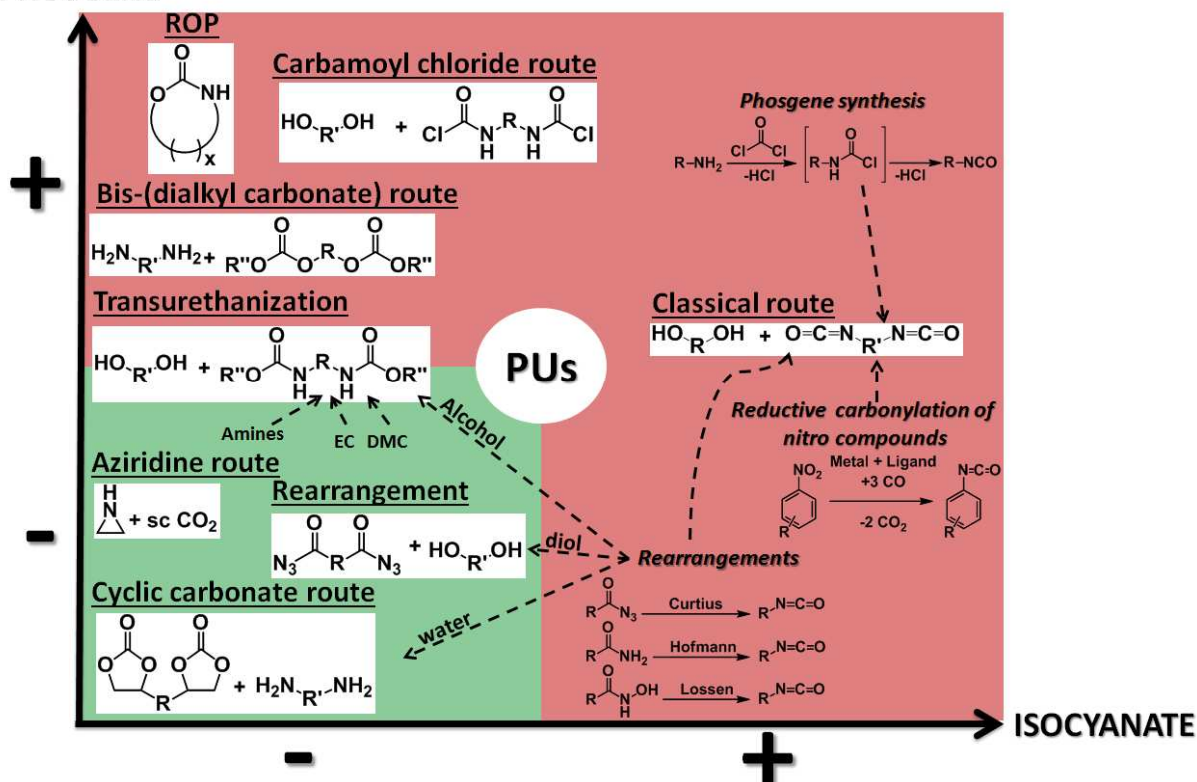


Figure II-1-1- Overview of synthetic routes to polyurethanes.

Then a detailed description is made of thermoplastic poly(hydroxyurethane)s regarding the synthesis of cyclic carbonates and amines, the corresponding model reactions, mechanisms, catalysts and polymerizations. The functionalization of the generated hydroxyl groups and petroleum-based cross-linked poly(hydroxyurethane)s are out of the scope of this literature study. Finally, in the third part, the specificity of the use of vegetable oil derivatives to synthesize non-phosgene and non-isocyanate polyurethanes or potential precursors is detailed.

1- Non-phosgene or non-isocyanate routes to PU

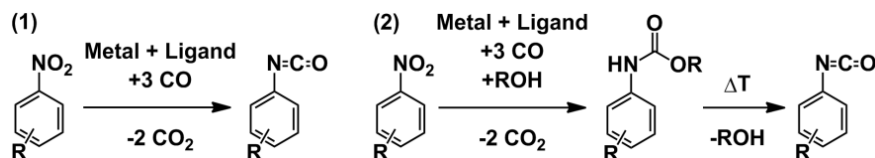
1.1- Non-phosgene isocyanate syntheses to PU

Isocyanates are industrially synthesized using the traditional phosgene route from the corresponding amines with the release of two equivalents of hydrogen chloride. Some alternatives to phosgene issued isocyanates are briefly developed herein including reductive carbonylation of nitro compounds and Curtius, Hofmann and Lossen rearrangements.

1.1.1- Reductive carbonylation of nitro compounds

A promising sustainable route to isocyanates is the reductive carbonylation of nitro compounds.^{1, 8-10} This pathway is preferred for aromatic nitro precursors as the reactivity of aliphatic nitro compounds is different and moreover aliphatic nitro compounds are not the most easily available starting materials.⁸ There are two related routes in which the reductive carbonylation of nitro compounds can lead to isocyanates. (See Scheme II-1-1) In the direct method, the catalyst (non-toxic transition metals of group 8-10, but also sulfur, selenium and tellurium catalysts) activates the nitro group and the carbon monoxide to generate the isocyanate with the release of carbon dioxide. A drawback of this pathway is the generation of highly-toxic catalyst residues in the final products.

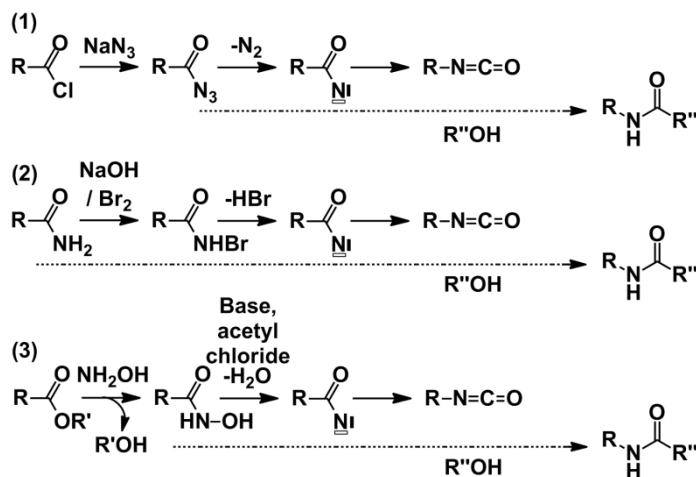
In the two-step carbonylation process, the isocyanate is first trapped with an additional alcohol forming the N-phenyl carbamate. Then the subsequent thermal cracking of the carbamate leads to the isocyanate. A large range of catalysts have been evaluated from palladium, platinum, ruthenium or rhodium complex to cheaper iron catalysts, and high selectivity has been reported.⁹



Scheme II-1-1- (1) Direct and (2) indirect reductive carbonylation methods of nitro compounds to isocyanates.

1.1.2- Curtius, Hofmann and Lossen rearrangements

Three known rearrangements namely Curtius (Scheme II-1-2-(1)), Hofmann (Scheme II-1-2-(2)) and Lossen (Scheme II-1-2-(3)) rearrangements can lead to isocyanates without the use of phosgene. In the presence of monofunctional alcohol or diol, carbamate precursors or PUs respectively can also be obtained with an *in situ* generation of isocyanates. The Scheme II-1-2 illustrates these rearrangements.



Scheme II-1-2- Synthesis of NCO and subsequent carbamates via (1) Curtius, (2) Hofmann and (3) Lossen rearrangements.

The Curtius rearrangement involves the thermal decomposition of acyl azides with the release of N_2 . Following the Curtius rearrangement, acyl azides have to be synthesized. They can be prepared using dangerous sodium azide or safer hydrazine hydrate. Inert and dried conditions are requested to obtain isocyanates in high yields. This strategy to isocyanates is only used at a laboratory scale due to the high toxicity and explosive properties of the needed azides and acyl azide intermediates. In the presence of water, carbamic acids are formed which are unstable and lead to the formation of amines with the release of carbon dioxide.¹

The Hofmann rearrangement corresponds to the oxidation of primary amides with bromine or chlorine. This method is known to prepare amines but modified procedures allow the synthesis of isocyanates. The Lossen rearrangement is based on the generation of an isocyanate via thermal or base-mediated rearrangement of an activated hydroxamate.¹¹⁻¹³

The latter is generated from the corresponding hydroxamic acid and this activation as well as the rearrangement can occur in one pot. Such hydroxamic acids are synthesized from their corresponding esters or acids using hydroxylamine, however, only few references in the literature concern this transformation. The amine formation is also usually observed with the Lossen rearrangement in the presence of water due to the direct degradation of isocyanates to primary amines. The disadvantages of the latter two procedures are the use of stoichiometric amounts of toxic and corrosive reagents (Br_2 in the case of the Hofmann rearrangement and acetic anhydride or acetyl chloride with base in the case of the Lossen rearrangement). Moreover, those rearrangements are not atom efficient procedures to isocyanates.

1.2- Phosgene non-isocyanate routes to PU

Non-isocyanate routes have been developed, however, some of them still require the use of phosgene as precursor. Among them, the use of carbamoyl chlorides, the ring opening polymerization (ROP) of cyclic urethanes and the use of bis-(dialkyl carbonates) can be named. (See Figure II-1-1) The latter two are described below.

1.2.1- ROP of cyclic urethanes

Most studies on the synthesis of cyclic urethanes and their successive ROP to PUs have been done by the research group of Höcker.¹⁴⁻²⁰

The cyclic urethanes can be synthesized from the corresponding aminoalcohol using toxic phosgene, dialkyl carbonates such as ethylene carbonate^{21, 22}, carbonyl chloride/ O_2 via oxidative carbonylation²³, carbonyl chloride²⁴ or urea²⁵. A particular non-phosgene-based cyclic urethane, synthesized from aziridines, has been recently reported.²⁶

Concerning the cationic ROP, different reactivities have been demonstrated as function of the cyclic urethane size, probably due to the strain energies of the rings and the corresponding stabilities. The polymerizations of 7-membered cyclic urethanes are performed at temperature only slightly above the monomer melting point. The 6-membered cyclic urethanes polymerize at 100 °C, while the 5-membered structures do not polymerize at all.^{15, 16, 19, 27, 28} Besides, substituted 6-membered cyclic urethanes are less reactive due to hindrance effects.¹⁵ Höcker and coll. have reported mechanistic studies. They demonstrated

that the propagation step involves a nucleophilic attack of the active species at the monomer followed by a double isomerization process and regeneration of the active species.¹⁸ Possible initiators are methyl trifluoromethanesulfonate¹⁴ and boron trifluoride etherate²². The drawback of this approach is certainly that not all of the cyclic urethanes are easily synthesized. Moreover, those that are easily prepared are thermodynamically stable and thus less reactive toward ROP.

Following another strategy, some research groups have synthesized polyurethanes from tetramethylene urea and a cyclic carbonate such as ethylene carbonate^{29, 30} or 2,2-dimethyltrimethylene carbonate³¹.

1.2.2- From bis-(dialkyl carbonate)s

Non-isocyanate polyurethanes have also been synthesized using bis-(dialkyl carbonate)s precursors and diamines. This process requires the removal of a volatile alcohol to shift the reaction toward the formation of the polymer. Phenol was found to be a good leaving group while following this strategy. Diphenyl carbonate is prepared from phosgene (or direct derivatives) and phenol but research is going on for more sustainable routes such as the transesterification of dimethyl carbonate (DMC) and phenol, the direct oxidative carbonylation of phenol, and transesterification of dialkyl oxalates and phenol.³² Fidalgo *et al.* prepared bis-(phenylcarbonate)s from phenyl chloroformate and D-mannitol. After polymerization with the corresponding amine and N,N-diisopropylethylamine, PUs with molar masses up to 17 000 g.mol⁻¹ were reached.³³

Following the same strategy, Arce *et al.* reported the synthesis of ω -amino- α -phenylcarbonate alkanes (AB monomer) for the synthesis of [n]-PUs.³⁴ The procedure involves the N-Boc protection of the amino group, followed by activation of the alcohol with phenyl chloroformate. Removal of the N-Boc affords the corresponding ω -amino- α -phenylcarbonate alkane hydrochlorides. A base (triethylamine or N,N-diisopropylethylamine) is then required for the polymerization (in DMF, 100°C, 24-48h) and molar masses up to 13 000 g.mol⁻¹ were obtained.

Recently, the group of Hedrick reported the synthesis of different PUs in aqueous media from activated 1,6-hexanediol and poly(ethylene glycol) with bis-(pentafluorophenyl) carbonate. The polycondensation of the latter mentioned precursors with Jeffamine and the subsequent release of pentafluorophenol, led to PUs with molar masses in the range 15 000-16 000 g.mol⁻¹.³⁵

Various research groups have taken the advantage of urethane synthesis from alkyl carbonates to prepare AA* monomers with both “open” and cyclic carbonates.^{2, 36-39} The latter have been used to prepare PUs as well as polyfunctional polymers.

2- Non-phosgene and non-isocyanate routes to PUs

In this part, non-phosgene and non-isocyanates routes to PUs are developed. Main routes are the poly(transurethanization) and the polyaddition of cyclic carbonates and amines. Recently, Ihata *et al.* induced a promising non-phosgene and non-isocyanate route to PUs. They copolymerized 2-methylaziridine and supercritical carbon dioxide to prepare thermoresponsive PUs.⁴⁰

2.1- Transurethanization with non-phosgene-based bis-(dialkyl carbamate)s

The non-isocyanate transurethanization process has been developed to synthesize PUs from bis-(dialkyl carbamate)s and diols by polycondensation. The carbamate precursors can be prepared by non-phosgene routes for instance from carboxylic acids via Curtius, Hofmann or Lossen rearrangements (See Scheme II-1-2), from amines via the oxidative carbonylation⁸, from dimethylcarbonate or from ethylene carbonate. Dimethylcarbonate can potentially be derived from phosgene free resources such as for instance carbon dioxide, monoxide or urea.^{1, 41, 42} Only PUs from non-phosgene bis-(dimethyl carbamate)s will be reported here.

2.1.1- Bis-(Dialkyl Carbamate)s from dimethylcarbonate

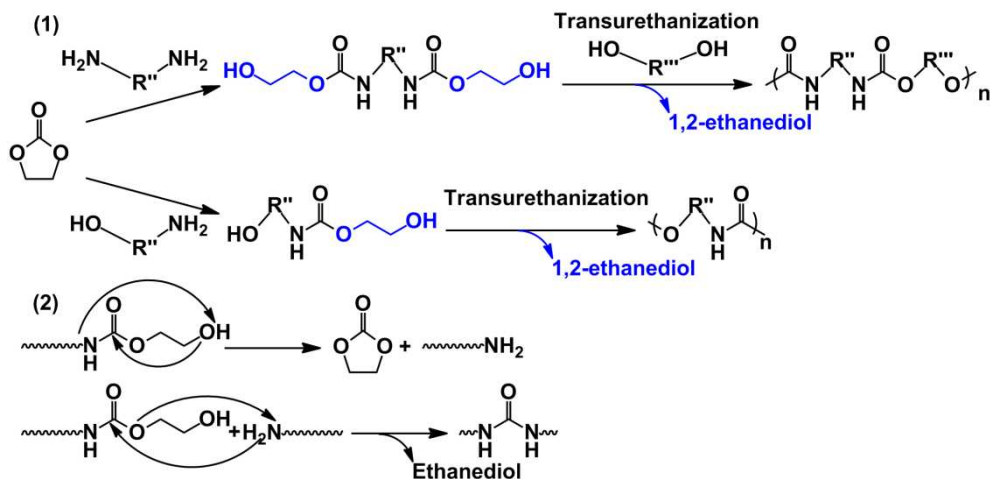
Following the transurethanization strategy, Deepa *et al.* reported the preparation of bis-(methyl carbamate)s from dimethylcarbonate and the corresponding amines using NaOMe as catalyst.⁴³ Then, they prepared under solvent-free conditions PUs of 10 000-20 000 g.mol⁻¹ from aliphatic to cycloaliphatic substrates. This approach requires the removal of methanol to shift the equilibrium of the reaction toward the polymer, as well as the presence of a catalyst such as titanium butoxide and high temperatures (150°C). Yields were comprised between 80% and 89%. The same group used this method to prepare PUs from

oligo(phenylenevinylene).⁴⁴ Recently, Firdaus *et al.* synthesized diamines and the corresponding bis-(methyl carbamate)s from limonene.⁴⁵ PUs are obtained by polycondensation of the latter and limonene-based diols, 1,6-hexanediol or a C20 fatty acid-based diol with molar mass up to 13 000 g.mol⁻¹ are reached. The higher molar masses are obtained with the long flexible C20 fatty acid-based diol. Long polymerization times (16h), high temperatures (120°C) and transesterification catalyst (TBD) are required.

2.1.2- Bis-(Dialkyl Carbamate)s from ethylene carbonate

Different research groups have followed the strategy to synthesize bis-(dialkyl carbamate)s from ethylene carbonate, to then polycondensate them with diols while removing the volatile ethylene glycol. The Scheme II-1-3-(1) illustrates this method to obtain PU without using neither phosgene nor isocyanate.

In 1957, Dyer *et al.* reported the use of ethylene carbonate for the preparation of PUs.²¹ They first prepared bis(2-hydroxyethyl carbamate)s from ethylene carbonate and a diamine. PU was then achieved while vacuum distillation with an alcohol at 150°C in the presence of barium oxide or zinc borate as catalysts. Moreover, they managed to synthesize N-substituted polyurethanes from amino alcohols. Following the same method, Rokicki *et al.* also used this transurethanization strategy and synthesized bis(2-hydroxyethyl carbamate)s from ethylene carbonate and 1,4-diaminobutane or 1,6-diaminohexane.²² Then they performed a polycondensation with 1,6-hexanediol or 1,10-decanediol at 150°C in the presence of tin catalyst, Bu₂Sn(CH₃)₂ or Bu₂SnO. The authors used an azeotropic solvent (xylene) that enable continuous removal of the by product and attained molar masses up to 5 500 g.mol⁻¹. While characterizing the formed PU, they found urea evidences both with the formation of the urethane groups. They suggested that the urea was generated by back-biting side reactions. (Scheme II-1-3-(2))



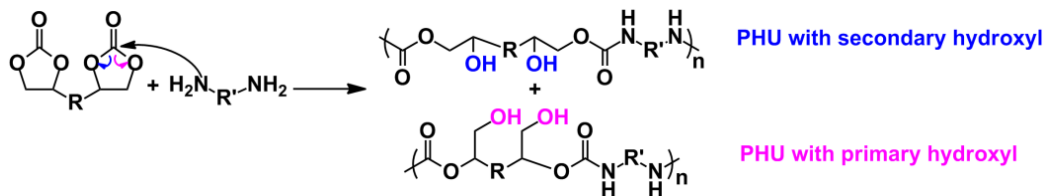
Scheme II-1-3- (1) Hydroxyurethanes formation from ethylene carbonate to subsequent PU synthesis. (2) Urea back-biting side reaction.

Recently, Ochiai *et al.* also studied this poly(transurethanization) route to PUs and observed the formation of urea (Scheme II-1-3-(2)) at high temperature (180°C) as well.⁴⁶ However, this side reaction was relatively suppressed at 150°C. The authors found that at similar molar masses, the PU obtained with the classical isocyanate-alcohol route, presented similar glass transition, melting and degradation temperatures (at 5 wt% loss).

Blank *et al.* patented the preparation of urethane diols and their condensation products with other diols.⁴⁷ In another way, McCabe *et al.* and Yanagishita *et al.* from the same group used urethane diols, synthesized from ethylene carbonate, along with 1,4-butanediol and adipic acid to yield poly(esterurethane)s under enzymatic catalysis (lipase B).⁴⁸⁻⁵⁰

2.2- Thermoplastic polyhydroxyurethanes (PHUs)

Among non-isocyanate and non-phosgene routes to PUs, the approach involving the reaction of cyclic carbonate and amine functions is one of the most studied. The polyaddition of bis-5-membered cyclic carbonates and diamines leads to the formation of linear PHUs with primary or secondary alcohols, as illustrated in Scheme II-1-4. One of the pioneers in the hydroxyurethane field are Groszos *et al.*, they patented in 1957 the preparation of oligo hydroxyl-urethanes by the reaction between cyclic carbonate, amine compound and urea.⁵¹ The studies on cyclic carbonates⁵²⁻⁵⁴ and PHUs^{2, 4-6, 55, 56} have been reviewed by different research groups.



Scheme II-1-4 - Synthesis of polyhydroxyurethanes from bis 5-membered cyclic carbonates and diamines.

The PHUs obtained by this route exhibit various advantages such as the circumvent of isocyanate and phosgene making the process safer, and the capture of CO₂ (if using cyclic carbonates issued from CO₂). The non-moisture sensitivity is also an important point. Indeed, no particular caution during the storage processes is required and no formation of irreversible side products (urea and CO₂) like in the classical isocyanate/alcohol route is observed.⁵ Besides, the possibility to prepare materials with no volatile organic compound releases promotes the use of this route for coatings applications.³ The presence of the hydroxyl groups in the polymer, and so of the inherent resulting hydrogen bonds, gives specific properties to the material. The hydroxyl groups formed at the β-carbon atom of the urethane moiety can participate into intramolecular and intermolecular hydrogen bonds, as illustrated in Figure II-1-2. Those hydrogen bonds combined with non-porous materials and the absence of thermally labile biuret and allophanate groups allow improved thermal stability and chemical resistance to non-polar solvents.^{5, 57} The authors didn't agree on the water absorption effect of PHUs compared to classical PUs. Some claimed lower water absorption thanks to the hydrogen bonds⁵⁶, but others presented higher water absorption due to the hydrophilicity of the polymer formed⁵⁸. Moreover, the reactive pendant hydroxyl groups enable further post-functionalizations of the PHUs with chemical and biological functionalities.² Numerous types of cross-linkers can also be used to design the properties of the obtained PHUs. The final properties will depend on the nature of the material (thermoplastic or cross-linked), the carbonate to amine ratio and on the structures of the cyclic carbonates and amines used.

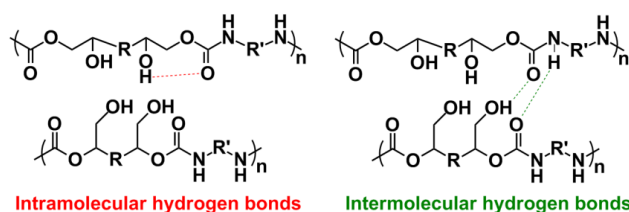


Figure II-1-2- Possible intramolecular and intermolecular hydrogen bonds in poly(hydroxyurethane)s.

These various properties endow PHUs with numerous potential applications from chemical-resistant coatings and sealants to adhesives.⁴ Among the various companies which already started to sell PHUs; Eurotech Ltd., Nanotech Industries Inc. and Go Green World Products LLC. can be quoted.⁵⁹⁻⁶¹

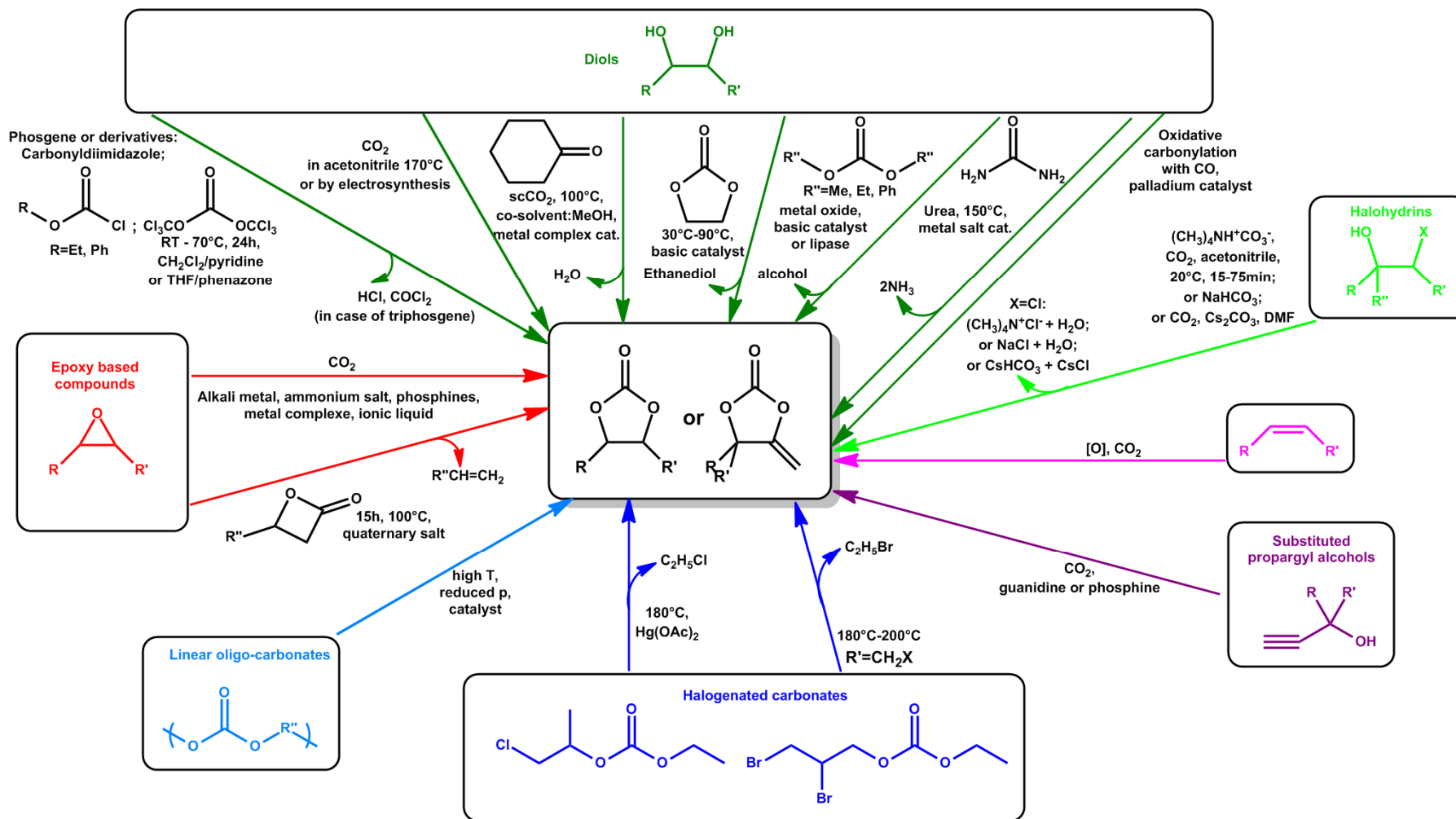
2.2.1- Synthesis of cyclic carbonates

2.2.1.1- Synthesis of 5-membered cyclic carbonates (5CC)

The synthesis of 5-membered cyclic carbonates (or 1,3-dioxolan-2-one)-based compounds has been extensively studied along the years and can be prepared by various methods. Two of them, ethylene carbonate and propylene carbonate, have been commercially available since over 45 years. The 5-membered cyclic carbonates can be achieved from linear oligo-carbonate, diols, halohydrins, olefins, substituted propargyl alcohols, halogenated carbonates and in a larger proportion from epoxy compounds and CO₂.^{53, 62, 63} The main approaches are summarized in the Scheme II-1-5.

The group of Carothers was the first to report the synthesis of various size cyclic carbonates in the early 1930s.⁶⁴⁻⁶⁷ They obtained cyclic carbonates by depolymerization of the respective linear oligo-carbonates using high temperatures and reduced pressure as well as various catalysts. The most effective catalysts for this depolymerization were Sn(II), Mn(II), Fe(II), and Mg(II) chlorides, carbonates, and oxides. A mixture of volatile cyclic carbonates, mainly monomeric and dimeric ones was distilled off with yields in the range 40% - 80%.

Diols and polyols are one of the main precursors, with epoxy compounds, for the synthesis of 5-membered cyclic carbonates. The first route from diols is the phosgenation approach using phosgene or its derivatives such as the triphosgene. For the first time in 1883, Nemirovsky synthesized ethylene carbonate directly by using phosgene and ethylene glycol.⁶⁸ As another example, Burk and Roof⁶⁹ synthesized 5-membered cyclic carbonates from 1,2-diols and triphosgene using pyridine in CH₂Cl₂ at 50°C with yields in the range 87% to 99%. Endo and coll. also used triphosgene for the synthesis of cyclic carbonates.^{58, 70} The high toxicity and hazards of phosgene make this way not suitable even if high yields of cyclic carbonates could be reached.



Scheme II-1-5- Main routes for the synthesis of 5-membered cyclic carbonates. ^{3-5, 71}

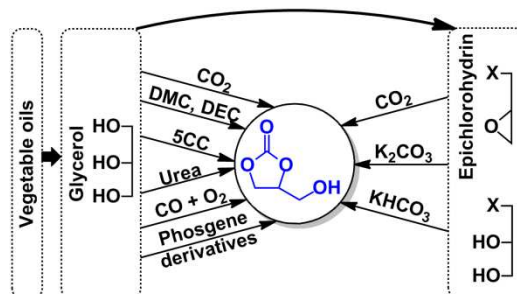
Other methods are the reaction of 1,2-diols with carbon dioxide using metallic acetates in acetonitrile⁷² or by electrosynthesis^{73, 74}, and the oxidative carbonylation with carbon monoxide using for instance palladium-based catalysts.^{75, 76} The approach involving the formation of a ketal from ethylene glycol and cyclohexanone, which then cyclized in the presence of supercritical CO₂ is also a route to cyclic carbonates.⁷⁷ In another way, the carbonate interchange reaction between 1,2-diols and ethylene carbonate⁷⁸ or dialkyl carbonates (dimethyl carbonate, diethyl carbonate or diphenyl carbonate), leads to cyclic carbonates with good yields (40-80%) in presence of catalyst such as for instance basic, metal oxide (MgO, CaO) catalysts, hydrotalcite or lipases.^{6, 62, 79-81} The reaction with urea in the presence of catalysts is another possibility for the synthesis of cyclic carbonates from 1,2-diol.^{82, 83}

Cyclic carbonates can also be prepared from halohydrins using sodium bicarbonate⁸⁴ or cesium carbonate in DMF⁸⁵ under mild conditions, or directly from olefin by oxidative carboxylation^{86, 87}. Furthermore, the reaction of substituted propargyl alcohols with CO₂ in the presence of guanidine catalyst could produce cyclic carbonates with yields up to 82%.⁸⁸ The phosphine catalyzed transformation of propargyl alcohol gives also access to cyclic carbonates.⁸⁹ Taking another example, halogenated carbonates can be converted into cyclic carbonates at a temperature between 180°C and 200°C.^{90, 91}

In addition, epoxy compounds can be converted into cyclic carbonates by the reaction with β -butyrolactone⁹² or in a much more common approach by the chemical insertion of CO₂. The later strategy has been extensively studied throughout different reaction conditions and catalysts optimizations. This method presents various advantages compared to the previous presented routes. Indeed, first the recapture of the CO₂ is a benefit regarding both the economical and environmental points of view.⁹³ Second, even if this reaction is usually performed at high pressure, in presence of a suitable catalyst, very high yields can be reached and it is 100% atom economical reaction. The carbon dioxide acts both as an aprotic solvent and as a reagent.⁹⁴ A plethora of catalysts has been investigated including; homogeneous or heterogeneous ionic liquids, ammonium or phosphonium salts, amines, metal oxide, metal halide and metal complexes. The most commonly used catalysts are the tetraalkylammonium halide. As a comparison study, Foltran *et al.* investigated a series of ionic salts to catalyze the coupling reaction between epoxide and carbon dioxide, and more particularly on tetrabutylammonium, imidazolium and guanidinium salts.⁹⁵ For a given reaction time, the best yields were obtained with 1,5,7-triaza-bicyclo[4.4.0]dec-5-enium bromide (TBD.HBr) and 1-methyl-3-methylimidazolium iodide (MMII). Various reviews have

been devoted to the catalysis of the reaction of carbon dioxide with epoxides. Among them, some focused more on mechanisms⁹⁶, heterogeneous catalysis⁹⁷, or ionic liquid catalysts⁹⁸. In the review of North and coll., the various catalytic system activities, obtained in earlier literature, are compared.⁹⁹ The authors then conclude that the most effective catalysts combine a Lewis-acid to activate the epoxide with a nucleophile to ring open the epoxide and subsequently act as a leaving group and a Lewis- or Brønsted-base to activate the CO₂. As previously said, the high temperature and pressure required are a limiting aspect for this process, both in terms of energy consumption and economy. Commercially viable catalysts, efficient at atmospheric pressure and room temperature still need to be discovered in order to synthesize cyclic carbonates from epoxides in a more sustainable way.

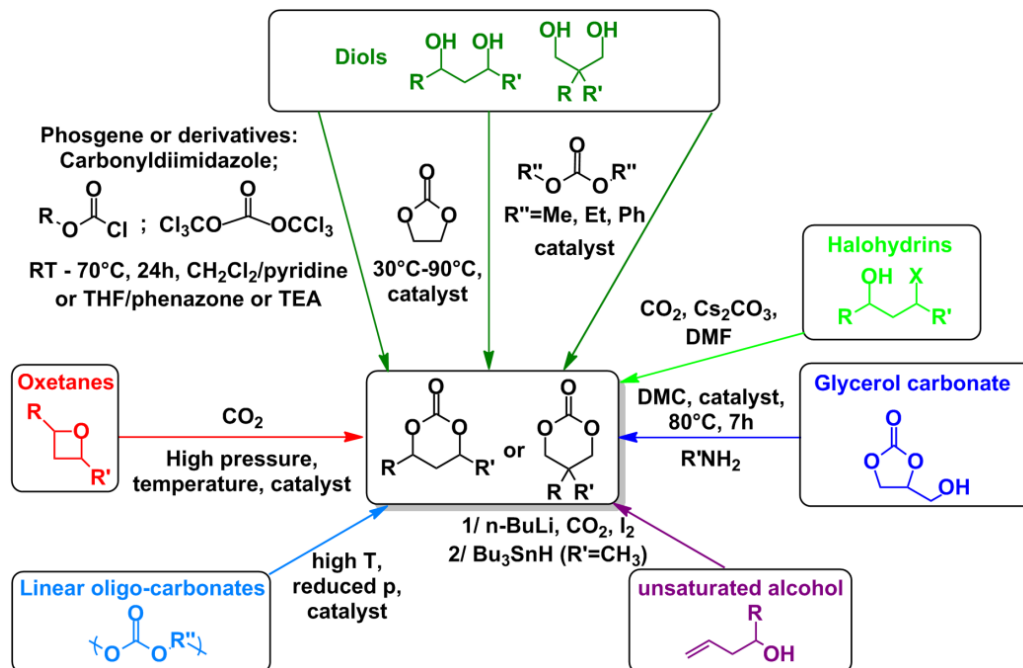
A particular case of 5-membered cyclic carbonate, which is already commercially available and bio-based, is the glycerol carbonate.^{100, 101} The latter can be synthesized either from glycerol (obtained from vegetable oils by saponification or methanolysis) following the methods developed above, or from activated glycerol (3-chloro-1,2-propanediol) or epichlorohydrin using CO₂ or alkaline (hydrogen) carbonate as sketched in Scheme II-1-6. From glycerol, the most interesting route would be the use of CO₂ due to the atom efficiency; however this route suffers from low conversions and yields. The more suitable processes thus are the use of ethylene carbonate or dialkyl carbonates.



Scheme II-1-6- Synthesis of glycerol carbonate. (DMC=dimethyl carbonate, DEC=diethyl carbonate, 5CC=ethylene carbonate).

2.2.1.2- Synthesis of 6- and 7-membered cyclic carbonates (6CC and 7CC)

The 6-membered cyclic carbonates can be prepared by similar methods as the ones used for the synthesis of 5-membered cyclic carbonates.⁵ They can be achieved in a large proportion from 1,3-diols (also indirectly from glycerol carbonate), and in a lower extent from 3,4-unsaturated alcohols, oxetanes using CO₂, or halohydrins. The main approaches are summarized in the Scheme II-1-7.



Scheme II-1-7- Main synthetic methods for the synthesis of 6-membered cyclic carbonates.

The depolymerization process of linear oligo-carbonate presented in the previous part is still applied in the synthesis of 6- and 7-membered and of larger size aliphatic cyclic carbonates. In another method, the 1,3-diols or 1,4-diols can be transformed into 6- and 7-membered cyclic carbonates respectively using phosgene derivatives such as triphosgene^{70, 102} or ethyl chloroformate. The reaction conditions while using ethyl chloroformate are the use of stoichiometric amount of triethylamine (TEA) in THF at room temperature for 2-12h.^{103, 104} A closed method to afford 6-membered cyclic carbonates from 1,3-diols is the use of dialkyl carbonates. The presence of a catalyst is essential for this carbonate interchange.⁶³ Possible catalysts are alkaline metals,^{105, 106} amines, basic ion-exchange resins,⁵⁶ oxide, alkoxide, or carboxylate salt of zinc, titanium, or tin,¹⁰⁷⁻¹⁰⁹ enzymatic catalyst,¹¹⁰... Pyo *et al.* recently reported that six-membered cyclic carbonates with functional groups could be synthesized in the presence of lipase (Novozym 435), in a solvent-free medium.^{110, 111} The possibility of synthesizing 5- and 6-membered cyclic carbonates with an α -urethane group from glycerol carbonate and dimethyl carbonate has been investigated in the presence of various catalysts, without solvents.¹¹² These carbonate interchange reactions are preferable to certain other methods because their reactants and by-products are not noxious. The reaction of oxetane with CO₂ can also be used to prepare 6-membered cyclic carbonates. The addition of CO₂ is less efficient in the case of oxetane than for epoxides. Moreover, the efficiency of this reaction dramatically decreases with the number and the size of the substituents.^{113, 114} The 6-membered cyclic carbonates have also been synthesized from halohydrins with CO₂ using cesium carbonate in DMF.⁸⁵

To summarize, the 7-membered cyclic carbonates can be prepared by the same carbonation reaction pathways as those leading to 5- and 6-membered cyclic carbonates, or by the reaction of an appropriate diol with phosgene (or its derivatives) in the presence of phenazone. Moreover, according to the depolymerization method, the corresponding cyclic dimers are formed almost exclusively when the expected monomer cycle size is from 7 to 12.⁵³

2.2.1.3- Synthesis of bis-cyclic carbonates (bCC)

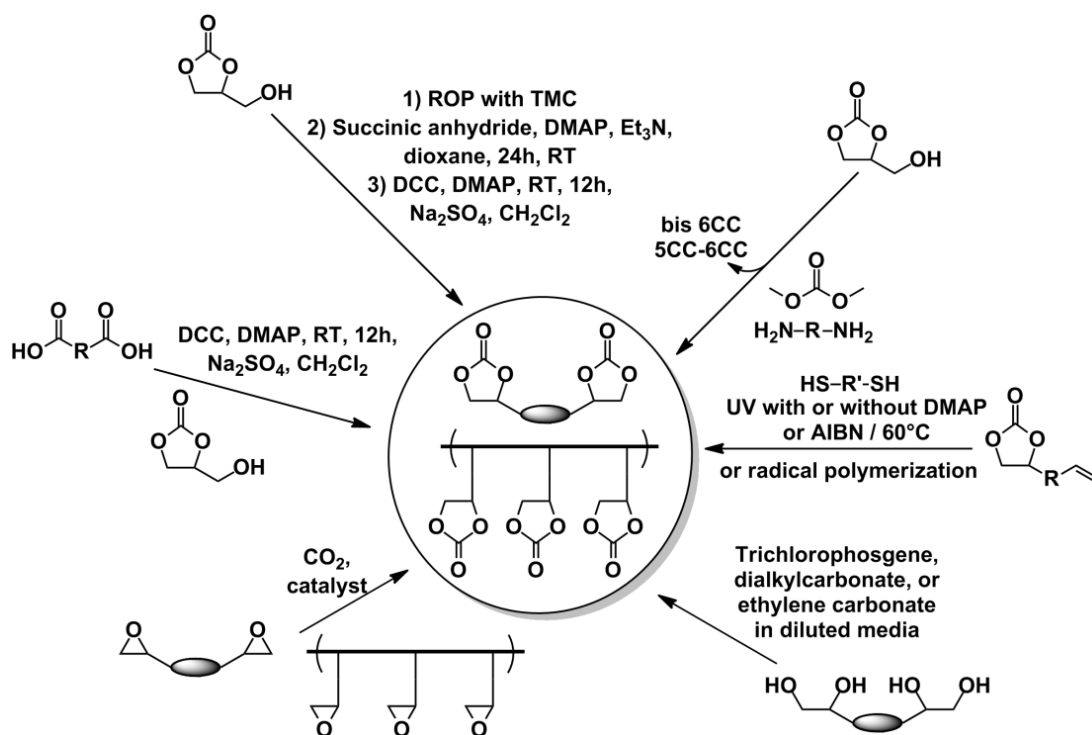
In order to obtain polymers by polyaddition, various techniques have been developed to synthesize bis cyclic carbonates. For the first presented methods, the bis 5-membered cyclic carbonates are derived from already formed 5-membered cyclic carbonates which present another reactive group such as in glycerol (hydroxyl) or in unsaturated-based cyclic carbonate (double bond). In order to keep the cyclic carbonate functions, mild reaction conditions are required for the coupling. From glycerol carbonate, a transesterification with a diacid using dicyclohexylcarbodiimide and dimethylaminopyridine at room temperature allows the formation of a bis cyclic carbonate.^{3, 115} Ring opening polymerization has also been carried out using the hydroxyl of the glycerol carbonate as initiator. The bis cyclic carbonate was then obtained using the same mild condition coupling.¹¹⁶ Another option is the thiol-ene reaction on unsaturated cyclic carbonates by photochemical initiation (UV at 254 nm with or without 2,2-dimethoxy-2-phenylacetophenone (DMPA) under solvent free or not conditions),^{117, 118} or via thermal means using azobisisobutyronitrile (AIBN), 60°C, 8h-24h).^{58, 117, 119}

Numerous studies deals with the synthesis of unsaturated cyclic carbonates such as vinyl ether, vinylic, allylic, styrenic, vinylene, acrylate and methacrylate cyclic carbonates. The radical polymerization or copolymerization of those cyclic carbonates bearing an unsaturation is another possibility to obtain poly(cyclic carbonate)s.^{54, 120-122}

Recently, Mouloungui and coll. prepared a mixture of 5- and 6-membered cyclic carbonates directly from glycerol carbonate, dimethyl carbonate and diamine. They optimized the conditions by playing on the solubility properties of dimethyl carbonate and methanol and by using a strong basic liquid catalyst.¹¹²

Following another strategy, other bis or poly 5-membered cyclic carbonates were synthesized either from bis¹²³⁻¹²⁵ or polyepoxides¹²⁶ by the insertion of CO₂, or from tetraols or polyols using phosgene derivatives¹²⁷, diethyl carbonate¹²⁸, imidazole carboxylic esters

¹²⁹ or ethylene carbonate ⁷⁸ (as describe above) in particular conditions. The Scheme II-1-8 illustrates the various routes to synthesize bis 5-membered cyclic carbonates. Similar methods have been employed for the coupling to obtain bis 6-membered cyclic carbonates. 58, 119



Scheme II-1-8- Synthesis of 5-membered bis-cyclic carbonates.

2.2.1.4- Reactivity of cyclic carbonates

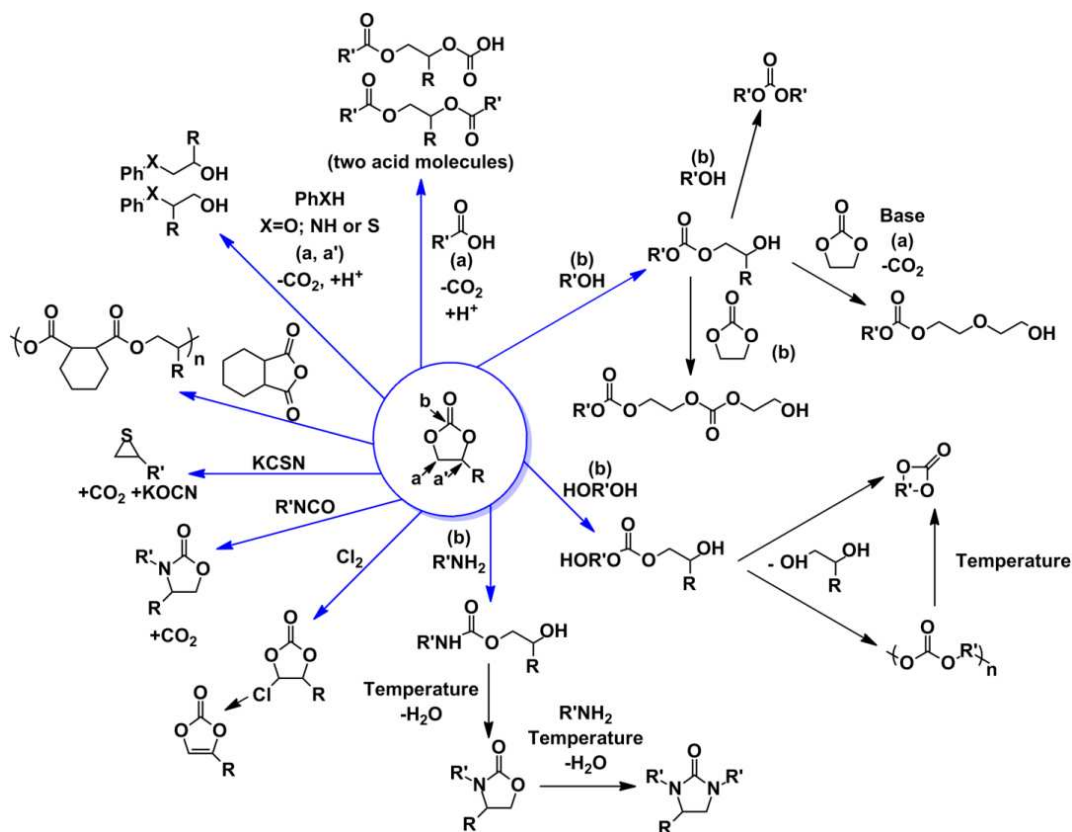
The formed cyclic carbonates can undergo several unwanted side reactions either during the coupling reaction, work-up or during the polymerization itself. Indeed, 5-membered cyclic carbonates react in two ways with nucleophilic reactants, depending on the nucleophilicity of the reactants, the cyclic carbonate structure and the reaction temperature. The two pathways involve either the attack of the carbon atom neighboring an oxygen atom or the attack of the carbonyl group. ⁶³ Cyclic carbonates can react with active-hydrogen-containing aromatics, carboxylic acids, aliphatic alcohols and amines as alkylation or alkoxycarbonylation agent as illustrated in Scheme II-1-9. ^{63, 109}

Cyclic carbonates, particularly 5-membered ones, can be used to alkylate active-hydrogen-containing aromatics such as phenol, thiophenol and aniline ¹³⁰ in the presence of catalysts such as alkali ones or phosphonium-based ionic liquid under relatively high temperatures ($T > 140^\circ\text{C}$). The general hydroxyalkylation is characterized by a nucleophilic attack at the alkylene carbon and the subsequent loss of carbon dioxide.

The 5-membered cyclic carbonate reacts with carboxylic acid in the same way with similar catalysts and reaction temperatures. With aliphatic alcohols, thiols and amines, the 5-membered cyclic carbonate reacts differently via the generalized transcarbonation route. The use of monofunctional alcohols lead to dialkylcarbonates, while the use of diols can give other cyclic carbonates or polycarbonates via alkoxy carbonylation. Catalysts and high temperatures are required. In a similar mechanism, aliphatic amines undergo attack at the carbonyl carbon atom followed by the ring-opening to give a urethane product. Unlike reactions that occur in the presence of aliphatic alcohols, the hydroxyalkylurethane species produced does not usually react with a second amine to produce an imidazolidinone or urea, except at temperatures around 150 °C.

The synthesized cyclic carbonates can thus be used to prepare polycarbonates by ROP⁶, but also PHUs as described in the following parts.

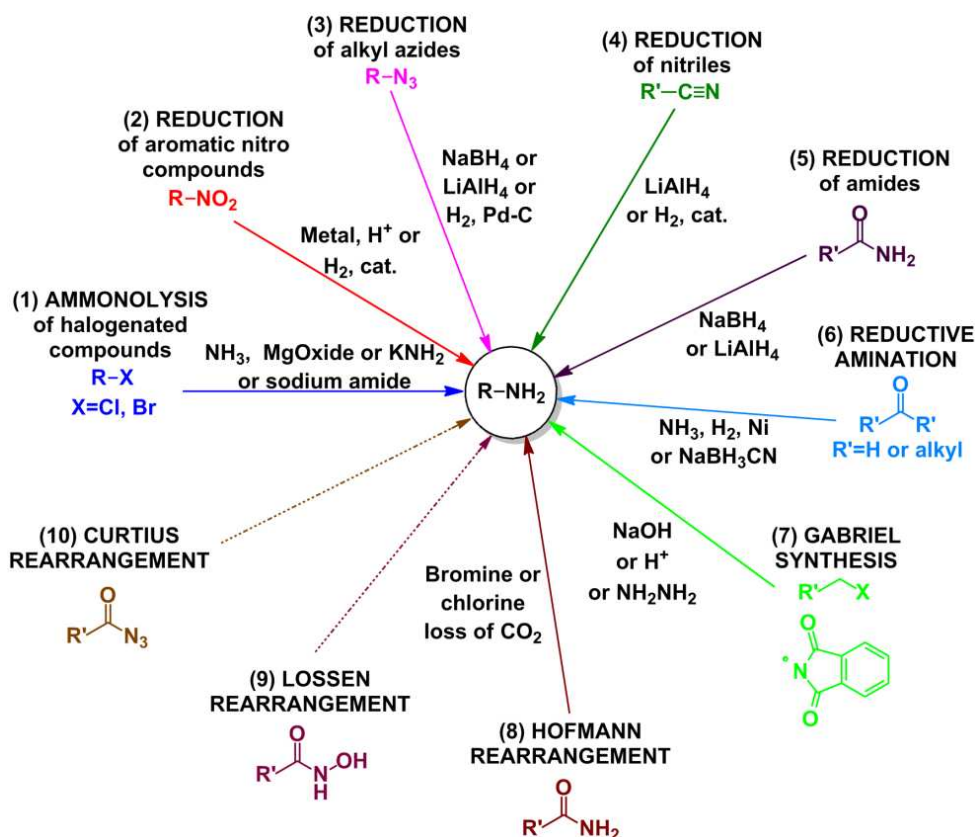
The ROP of 5-membered cyclic carbonates is complicated. However, polymerization has been reported to proceed in the presence of metal alkoxides, metal acetylacetonates as well as metal alkyls as catalysts. Nevertheless, the polymerization involved partial decarboxylation and the loss of carbon dioxide, leading to poly(alkylene ethercarbonate), instead of thermodynamically disfavored poly(alkylene carbonate). (contents of carbonate units < 50 mol%)⁶³



Scheme II-1-9- Reactivity of 5-membered cyclic carbonate towards aromatics, carboxylic acids, aliphatic alcohols and amines as alkylation or alkoxy carbonylation agent.^{63, 109}

2.2.2- Synthesis of amines

Amines have been synthesized for a long time, however harmful or multi-steps reactions are usually involved. In organic chemistry, amines are synthesized following different main routes (See Scheme II-1-10). The ammonolysis of halogenated compounds (Scheme II-1-10-(1)), or the reduction of nitro (Scheme II-1-10-(2)), alkyl azide (Scheme II-1-10-(3)), nitrile (Scheme II-1-10-(4)) or amide (Scheme II-1-10-(5)) compounds result in the synthesis of amines. Besides, amines can be prepared by the reductive amination of ketones or aldehydes (Scheme II-1-10-(6)), by the Gabriel synthesis (Scheme II-1-10-(7)) or by the Hofmann rearrangement (Scheme II-1-10-(8)). Indirectly, the Lossen (Scheme II-1-10-(9)) and Curtius (Scheme II-1-10-(10)) rearrangements can also lead to amine compounds in the presence of water.



Scheme II-1-10- Main strategies for the synthesis of amine compounds.

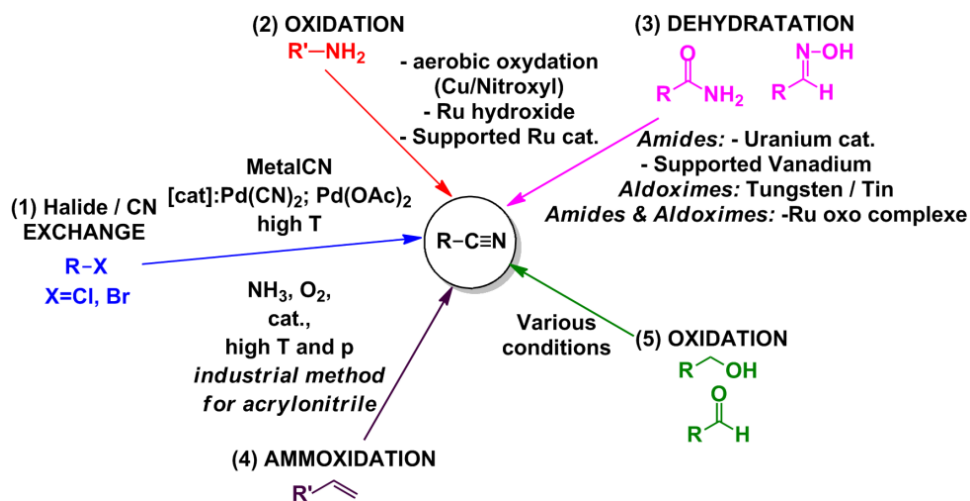
Various remarks can be pointed out from these reaction methods. The ammonolysis of halogenated compounds is mainly limited to the synthesis of aliphatic amines, due to the generally low reactivity of aryl halides toward nucleophilic substitution. Another disadvantage of this method is the inherent generation of a mixture of different classes of amines due to successive alkylation reactions. Moreover, the use of gaseous ammonia is not safe and hard conditions are usually requested. The reduction of aromatic nitro compounds

is by far the most practical method for primary aromatic amines since it uses available starting materials. Among the other methods, the reduction of alkyl azide intermediates involves a large number of steps and also a nucleophilic attack with azide-based intermediates, such as sodium azide, which are explosive and toxic substances. The reduction of nitriles and amides lead to an increase in the length of the carbon chain. The reductive amination from aldehyde and ketones in the presence of ammonia or amines can lead to the preparation of any class of amines. In this case, the formation of multiple classes of amines is more controlled than in ammonolysis of halogenated compounds. Following the Gabriel procedure, the atom efficiency is not acceptable due to the generation of phthalimide ion derivative wastes. Finally, Hofmann degradation of primary amides induces a decrease in the length of the carbon chain by carbon dioxide removal. (See rearrangement section in part 1) Industrially, the most important of all amines is the aniline and it is prepared either by reduction of nitrobenzene (using iron and dilute hydrochloride, or by catalytic hydrogenation) or by ammonia treatment of chlorobenzene at high temperature and high pressure in the presence of a catalyst. Methylamine, dimethylamine and trimethylamine are prepared from methanol and ammonia with Al_2O_3 at high temperature (450°C). Halogenated compounds are also used to prepare longer alkyamines.

Nitriles and amides represent attractive platforms to prepare, after reduction, amine-based monomers.

Amides are mainly synthesized from acyl chloride derivatives which are prepared using thionyl chloride or oxalyl chloride. They can also be obtained from esters and amines by the removal of a low boiling point alcohol using transesterification catalysts. Concerning nitrile derivatives, they represent vital synthetic intermediates for pharmaceuticals, agricultural products and fine chemicals. The most common synthetic strategies to nitriles are illustrated in Scheme II-1-11 and include halide / CN exchange^{131, 132} (Scheme II-1-11-(1)), the oxidation of amines¹³³⁻¹³⁵ (Scheme II-1-11-(2)), the dehydration of amides and aldoximes¹³⁶⁻¹³⁹ (Scheme II-1-11-(3)), the ammoxidation¹⁴⁰⁻¹⁴² (Scheme II-1-11-(4)) or the oxidation of alcohols and aldehydes (Scheme II-1-11-(5)). However, to promote efficient nitrile formation, usually toxic reagents and solvents as well as expensive reagents are required. Moreover, high temperature and high pressure, inorganic wastes and tedious work up are involved. Concerning the oxidation of aldehydes and alcohols to nitriles, usually stoichiometric amount of oxidants are requested.¹⁴³⁻¹⁴⁷ Recently, catalytic aerobic reactions have emerged as one of the preferred green oxidation methods.¹⁴⁸⁻¹⁵⁰ The use of abundant and low costs

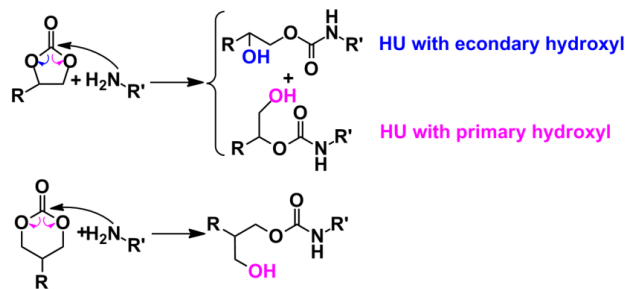
O₂ as oxidant is an advantage. The tandem Cu / TEMPO has been extensively used for the aerobic oxidation of alcohols to aldehydes¹⁵¹⁻¹⁵⁵, but copper-based catalysts have also been employed for the aerobic oxidation of amines to nitriles^{156, 157} and aldehydes to nitriles^{158, 159}. The direct preparation of nitriles from alcohols using oxygen and ammonia has been reported but the use of heterogeneous catalysts, high pressure and temperature were requested.¹⁶⁰⁻¹⁶² Very recently different research groups synthesized nitriles under mild conditions directly from alcohols with O₂ or air using copper-based complexes.¹⁶³⁻¹⁶⁶ This method is highly desirable due to the cheap commercially available starting materials such as alcohols, aqueous ammonia and copper. Besides, not only high conversions can be reached under mild conditions with high atom efficiency, but also only a benign by-product (H₂O) is generated.



Scheme II-1-11- Major strategies toward the synthesis of nitriles.

2.2.3- Studies on the model cyclic carbonate / amine reaction

Before performing the synthesis of PHUs, authors have studied the reactivity of cyclic carbonates with amines on model reactions to have a better understanding of the nucleophilic addition reaction between cyclic carbonates and amines. Model reactions were performed on a least one monofunctional compound, between a cyclic carbonate and an amine to obtain hydroxyurethane as illustrated in the Scheme II-1-12. In the appendix, the Table A-2 presents an inventory of the model reactions reported in the literature.

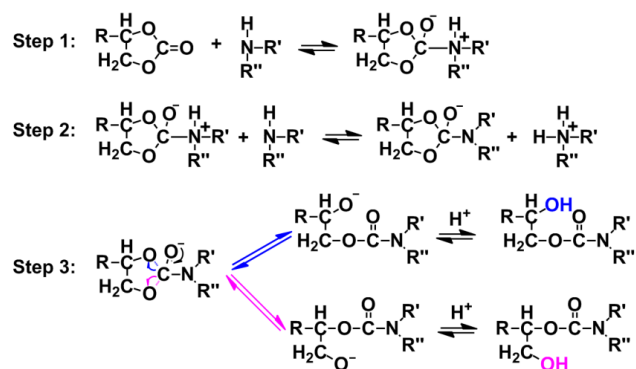


Scheme II-1-12- Model reaction on 5- and 6-membered cyclic carbonates leading to hydroxyurethanes.

2.2.3.1- Mechanism

Two reaction mechanisms have been proposed. First, Tomita *et al.* proposed a mechanism through an amphoteric tetrahedral intermediate.¹⁶⁷ During the reaction, a nucleophilic attack of the amine on the carbonyl group of the cyclic carbonate takes place resulting in the formation of a tetrahedral intermediate. Then, a deprotonation reaction occurs thanks to another molecule of amine. The carbon-oxygen bond is finally cleaved, favored by the high electron density of the nitrogen atom. At the same time, the generated alkoxide ion combines with a proton, resulting in the product formation.

Garipov *et al.* proposed a similar mechanism proceeding in three steps.^{168, 169} The first step is the nucleophilic attack of the amine, which results in the formation of a tetrahedral intermediate. The second step is the removal of hydrogen ion by the subsequent attack of another amine, and in the final step the carbon-oxygen bond is broken leading to the formation of hydroxyurethane isomers. In the case of the addition reaction of 5-membered cyclic carbonates with amines, two isomers can be formed. The selectivity toward primary or secondary alcohol is discussed later. The Scheme II-1-13 illustrates this first presented mechanism.



Scheme II-1-13- Mechanism through the formation of a tetrahedral intermediate for the reaction between 5-membered cyclic carbonates and amines.

In another way, the mechanism of hydroxyurethane formation has been studied in terms of DFT calculations by Zabalov *et al.*¹⁷⁰ They reported both one-stage and multistage pathways, including the formation of numerous solvated intermediates and their transformation into products (See Figure II-1-3). Based on the model reaction of ethylene carbonate or propylene carbonate with methylamine, they established that the hydroxyurethane formation may progress notably throughout a six centers ring intermediate based on the 5-membered cyclic carbonate and two amines molecules. In both single step and multistep mechanisms, the activation energies of the transition states were reduced (by around three in the case of the single step mechanism) while involving two amine molecules in the mechanism. The authors concluded that the second amine molecule plays a catalytic role. One can wonder if in protic solvent, the second amine in the six centers ring intermediate could be replaced by a solvent molecule.

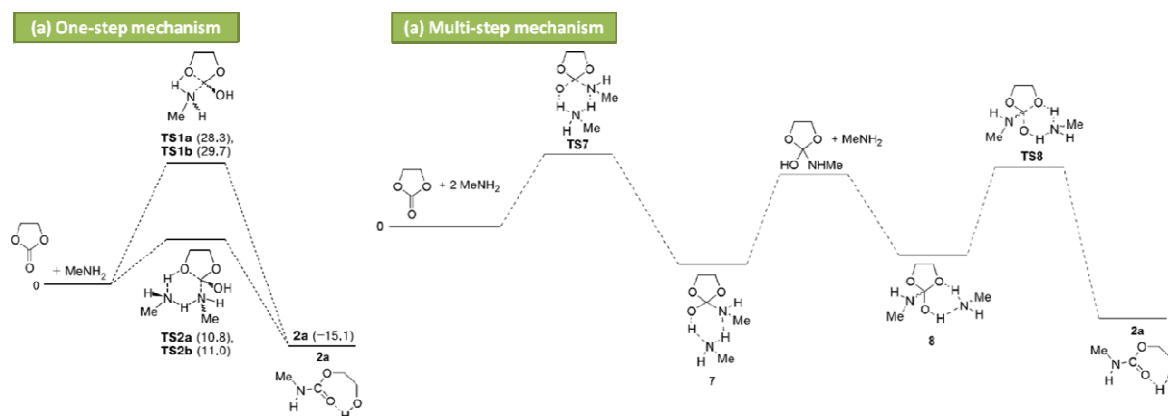


Figure II-1-3- Relative energies to the sum of energies of the starting reactants (=0) for the intermediates and stable compounds following (a) the one-stage and (b) the multi-step mechanisms of the reaction of ethylene carbonate with methylamine involving one and/or two methylamine molecules. (The activation energies for the transition states are in brackets)¹⁷⁰

Finally, regarding the different mechanisms proposed in this part, the authors agree that the participation of a second amine molecule is necessary and substantially accelerates the process.

2.2.3.2- Kinetic and reaction conditions

The kinetic of the reaction has been studied by different research groups. Moreover, various reaction conditions have been tested in the literature for the addition of amines on cyclic carbonates. Some authors pointed out the effect of the temperature, the initial concentration of the reactants and the solvent.

The increase of the reaction temperature leads to higher reaction rate. However, Burgel *et al.* proved that using a temperature higher than 100°C resulted in the formation of side products as discussed later in the selectivity and side reactions part.^{171, 172}

Besides, depending on the selected solvent, the reaction rates are variable. Most of the reactions are performed in DMSO or DMF. Tomita *et al.* demonstrated a very slight increase of conversion and yields for reaction in toluene compared to DMSO.^{167, 173}

Concerning the effect on the reaction of the presence of solvent and the initial concentration of the reactants, it has been shown in various studies that the reaction of cyclic carbonates and amines occurs faster in bulk than in solvent.¹²¹ As an example, the reaction rates for the reaction between glycerol carbonate and butylamine are equivalent in DCM at 60°C and in bulk at 25°C; $k_{\text{glycerol carbonate/butylamine}}=1.67 \text{ L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ in DCM at 60°C and $k_{\text{glycerol carbonate/butylamine}}=1.17 \text{ L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ without solvent at 25°C. A decrease of the initial concentration of the reactants also affects the reaction rate as it has been shown by Tabushi *et al.* (review by Webster *et al.*)⁵², Nemirovsky *et al.*¹⁷⁴ and Burgel *et al.*¹⁷⁵

The majority of the authors who studied the kinetic of the reaction of cyclic carbonates with amines in aprotic solvents agree on a kinetic of an overall second order.^{39, 70, 121, 167, 174, 176} However, few reports relate higher order with respect to the amine,¹⁶⁸ as well as the auto-catalytic effect of the hydroxyurethane formed.⁵²

Higher order with respect to the amine was firstly reported by Burgel *et al.*¹⁷⁵ who described a reaction rate containing both an uncatalyzed and catalyzed part. Based on the 3 steps mechanism they proposed, Garipov *et al.* exposed the difference in the reaction rate between protic solvents and aprotic ones.¹⁶⁸ In protic solvents, the first stage (See Scheme II-1-13) occurs relatively rapidly due to the formation of hydrogen bonds between solvent molecules and the oxygen atoms of the cyclic carbonate (See Figure II-1-4), which induces an increase of its electrophilicity. In protic solvent, the limiting step which will determine the reaction order, is thus the deprotonation step. The authors reported that the reaction is of 3rd order overall and of 2nd order with respect to the amine. Regarding the three steps mechanism and the explanation proposed, this result involves necessarily the approximation that the limiting step is not reversible. However, this observation can be explained with the concerted mechanism with the six centers ring intermediate defined by calculation by Zabalov *et al.*¹⁷⁰ Besides, they demonstrated that in protic solvent the reaction rates decrease with the permittivity of the solvent.

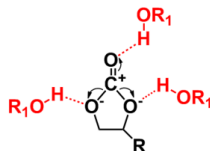


Figure II-1-4- Effect of protic solvents on cyclic carbonate. ¹⁶⁸

In aprotic solvent, no hydrogen bonds are possible with the solvent. The first step, which consists of the nucleophilic attack of the amine on the carbonyl carbon, is thus considered by the authors as the rate-controlling stage. The reaction is then of an overall 2nd order. To correlate with the three steps mechanism they proposed, one has to consider that the limiting step is not reversible. While regarding the concerted mechanism with the six centers ring intermediate, this result could be explained by the fact that the limiting stage is another elementary step than the nucleophilic attack of the amine on the carbonyl carbon. In contrary to protic solvent, the reaction rates increase with the permittivity of the aprotic solvent.

Mikheev *et al.* found that the reaction rates were higher in protic solvents than in aprotic solvents, although the reaction rates increased as the permittivity of the aprotic solvent increased as reviewed by Webster *et al.*⁵²

For Zabalov *et al.*, the second amine molecule plays the role of the catalyst of the process, resulting in a substantial decrease in the activation energy of the reaction.¹⁷⁰

Concerning the auto-catalytic effect, Tabushi *et al.*⁵², Nemirovsky *et al.*¹⁷⁴ and Burgel *et al.*¹⁷⁵ demonstrated on model reaction that the hydroxyurethane formed enhanced the reaction rate.

As presented, the effect of protic and aprotic solvents has been studied. Another research group studied the particular case of using water as solvent. In aqueous media, the nucleophilic addition of the amine onto the cyclic carbonate competes with the chemical instability of the latter in the presence of water. While performing the reaction in water at 70°C during 24h, Ochiai *et al.* observed different hydrolysis rates from 16% to 100% for the 5-membered cyclic carbonate depending on the hydrophobicity of the cyclic carbonate used with hexylamine.¹⁷⁷ In a study on the reaction of aliphatic amines on glycerol carbonate, the decarboxylation of glycerol carbonate to glycerol was favored with short-chain amines, because water then could easily reach the cyclic carbonate, which is not the case when longer hydrophobic amines were used due to solubility counterparts.¹⁷⁸ Malkemus *et al.* also performed the opening of cyclic carbonates in the presence of ammonium hydroxide solution; however, they did not mention the formation of by-product.¹⁷⁹ As discussed in the

part concerning the effect of the chemical structure of the cyclic carbonate, the 5- and 6-membered cyclic carbonates present different hydrolysis behaviors.

2.2.3.3- Effect of the chemical structure of the amine

The chemical structure of the amine influences the reaction rate as proved by numerous studies. All authors agree that secondary amines are less reactive, even non-reactive, toward cyclic carbonate compared to primary ones. The nucleophilicity of the amine seems to govern its reactivity.^{52, 70, 168, 172, 175, 180} The model reaction with diethylenetriamine and monofunctional 5-membered cyclic carbonates with two ratio of 1/2eq or 1/3eq proved the difference in reactivity between primary and secondary amines. At a temperature below 100°C and a ratio 1/3eq., Ochiai *et al.* observed only 66% cyclic carbonate conversion, whereas the reaction with 1/2eq. demonstrated 100% conversion for the same reaction time. However, while increasing the temperature at 170°C and performing the reaction in bulk, they observed that the secondary amines are only partially converted.¹⁸¹

Tomita *et al.* have calculated the reaction rate constant for hexylamine and benzylamine with 5-membered cyclic carbonate at 50°C in DMAC, and found that hexylamine is more reactive than benzylamine probably due to the lower basicity and steric hindrance of the phenyl group: $k_{\text{SCC/hexylamine}}=0.04 \text{ L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ and $k_{\text{SCC/benzylamine}}=0.01 \text{ L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$.⁷⁰

Webster *et al.* studied the reaction rate of propylene carbonate with a wide variety of mono-, di-, tri-amines either aliphatic, cyclic or with other functional groups using real-time FTIR¹⁸². Primary amines as well as cyclic secondary amines are the most reactive. No reaction could be detected with propylene carbonate under relatively mild conditions (80°C) with dibutylamine, 4-sec-butylaniline and tert-octylamine, representative of an acyclic secondary amine, an aromatic amine, and a primary amine on a tertiary carbon, respectively. The authors concluded that the reaction rate depends on the nucleophilicity and the steric hindrance of the amine.

The reactivity of amine toward cyclic carbonate was also studied by Diakoumakos *et al.* by reaction with an aliphatic tricyclic carbonate (Laprolate-803)¹⁸³ They demonstrated that amines with strong electron withdrawing groups in the α or β position with respect to the reactive amino group are more reactive. Besides, their research indicates that the molar mass of amines has a certain influence on their reactivity. Higher molar mass amines are less reactive than shorter ones. The authors illustrated the scale of reactivity of the tested

amines (See Figure II-1-5). Demonstrating a same trend, Nohra *et al.*¹⁷⁸ found that as the alkyl chain of the amine increases, the yield slightly decreases.

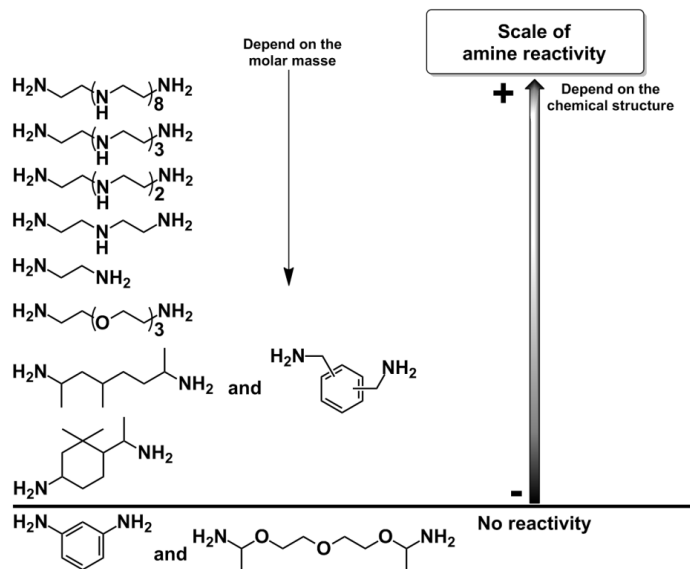


Figure II-1-5- Scale of reactivity of various amines toward a model cyclic carbonate.¹⁸³

The chemical structure of the amine also influences the isomer ratio as developed in the selectivity section.

2.2.3.4- Effect of the substituents and size of the cyclic carbonate

Several studies relate the effect of the cyclic carbonate substituent on the reaction rate and the final isomer product. First papers reported either that electron withdrawing groups on the cyclic carbonate retarded the reaction rate (Mikheev *et al.* reviewed by Webster *et al.*⁵²), or that the cyclic carbonate substituent has a limited influence on the reaction rate (Couvret *et al.*¹²¹). Those conclusions are not in accordance with more recently published literature.

Tomita *et al.* studied a large series of mono-substituted 5-membered cyclic carbonates and found that the reaction rate with amine increased as the electron withdrawing character of the substituent increased.¹⁶⁷ They calculated the reaction rate constant (k_{CC}) for various cyclic carbonate substituents (CC) and found the following scale of reactivity with hexylamine in DMSO at 70°C and 1 mol.L⁻¹: $k_{CF_3}=64 \text{ L.mol}^{-1}.\text{h}^{-1} > k_{CH_2OPh}=0.42 \text{ L.mol}^{-1}.\text{h}^{-1} > k_{Ph}=0.38 \text{ L.mol}^{-1}.\text{h}^{-1} > k_H=0.23 \text{ L.mol}^{-1}.\text{h}^{-1} > k_{CH_3}=0.05 \text{ L.mol}^{-1}.\text{h}^{-1}$. For the less reactive substituent R=CH₃, the conversion was 75% after 50 days.

Garipov *et al.* also found differences in reactivity while considering the substituent of the cyclic carbonate.¹⁶⁸ They proved that the presence of an electron releasing substituent (+I) in the cyclic carbonates results in a decrease of the partial positive charge on the carbonyl

carbon. This results in a decrease in the reactivity of the cyclic carbonate. On the contrary, electron withdrawing substituents (-) increase the electrophilicity of the carbonyl carbon and thus favor higher reaction rate with amines. (See Figure II-1-6)

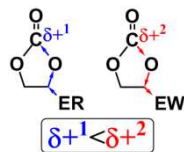


Figure II-1-6- Effect of the electron releasing (ER) and electron withdrawing (EW) substituents.

He *et al.* examined the reactivity of various 5-membered cyclic carbonates bearing either urethane with the oxygen atom near the cyclic carbonate in α (-OCONHR α) and β (-OCONHR β) position, or urethane with the nitrogen atom near the cyclic carbonate in α position (NHCOOR α) or ether group (-OR).³⁹ The most reactive was the cyclic carbonate bearing urethane with the nitrogen atom nearby in α position (-NHCOOR α). The authors also concluded that the more distant the electron withdrawing group is from the cyclic carbonate, (OCONHR β compared to OCONHR α), the less reactive it is. They measured a scale of reactivity (k_s) of the cyclic carbonates bearing the different substituents (S) with hexylamine in DMSO (0.5 mol.L⁻¹) at room temperature: $k_{\text{NHCOOR}\alpha}=0.204 \text{ L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1} > k_{\text{OCONHR}\alpha}=0.124 \text{ L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1} > k_{\text{OCONHR}\beta}=0.057 \text{ L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1} > k_{\text{OR}}=0.018 \text{ L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$.

In another study, Ochiai *et al.* exposed the difference in reactivity of non-spiro bicyclic carbonates, which consist of a 5-membered cyclic carbonate and a 5- or 6-membered cycloalkane group.¹⁷⁶ The cyclic carbonate bearing the 6-membered alicyclic group ([4,3,0] 5CC-6) was more reactive than the one containing the 5-membered alicyclic group ([3,3,0] 5CC-5). In comparison, the ethylene carbonate presented an even higher reactivity. Besides, the obtained yields were higher with 5CC-6 (82%) than with 5CC-5 (54%). The authors determined the activation energies of the two bicyclic carbonates: $E_{a5\text{CC-5}}=29.9 \text{ kcal}\cdot\text{mol}^{-1}$ and $E_{a5\text{CC-6}}=22.4 \text{ kcal}\cdot\text{mol}^{-1}$. They supposed that this difference in reactivity comes from the different ring-strain of the carbonate groups due to the restriction from the alicyclic rings.

Only few papers related the reactivity variation of different sized cyclic carbonates towards amines on model reaction. Tomita *et al.* reacted 5- and 6-membered cyclic carbonates with hexylamine and benzylamine in DMAC (1 mol.L⁻¹) at 30, 50 and 70°C.⁷⁰ They clearly found that 6-membered cyclic carbonates were more reactive than the 5-membered homologues, with reaction rate constants 29 to 62 times higher (30-70°C). The authors also estimated the activation energies with hexylamine of 6CC// and 5CC// and found that

$E_{a_{5CC}}=5.88 \text{ kcal.mol}^{-1}$ is higher than $E_{a_{6CC}}=2.42 \text{ kcal.mol}^{-1}$. To explain this difference in reactivity, they demonstrated a $2.86 \text{ kcal.mol}^{-1}$ larger ring-strain energy for trimethylene carbonate (6CC) compared to ethylene carbonate (5CC) by molecular modeling: $\Delta H_{f_{5CC}}=-1.14 \text{ Kcal.mol}^{-1}$ and $\Delta H_{f_{6CC}}=-4.00 \text{ Kcal.mol}^{-1}$. (See Figure II-1-7)

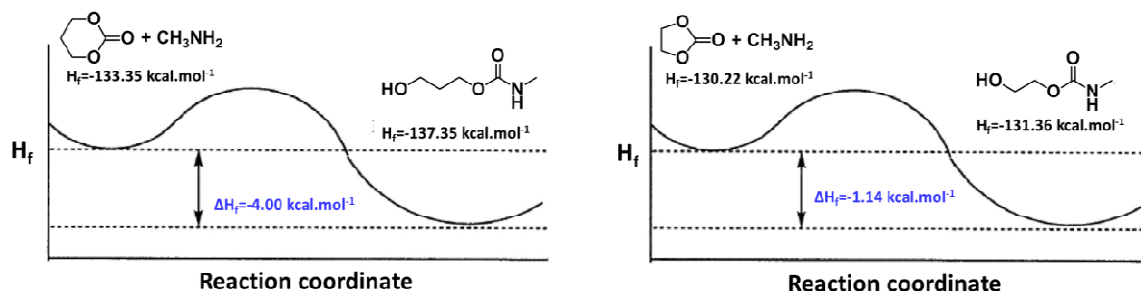


Figure II-1-7- Energy profiles of the reactions of 6CC and 5CC with methylamine calculated by PM3 MO method.⁷⁰

Clements *et al.* also took advantage of the increase ring strain in 6-membered cyclic carbonates as compared with their 5-membered counterparts and patented a way to better purified hydroxyurethanes from 6-membered cyclic carbonates.^{184, 185}

In a study of bifunctional couplers bearing 5- and 6-membered cyclic carbonates, He *et al.* also demonstrated the difference in reactivity of the two different size rings. Although only 6-membered cyclic carbonates reacted in THF ($2.6\text{-}3.3 \text{ mol.L}^{-1}$) at room temperature after 18h, both cyclic carbonates reacted in ethyl acetate (2 mol.L^{-1}) at 60°C after 18h.¹⁰⁴ Moreover in the same study, the authors compared the hydrolysis of the two different size rings. At room temperature (20 days), at 60°C (7 days) or 90°C (7 days), the authors do not observe hydrolysis of the 5-membered cyclic carbonate, which is not the case with 6-membered ones. The latter undergo hydrolysis at different rate depending on the conditions: from 15% to 100%.¹⁰⁴

Tomita *et al.* demonstrated as well that 7-membered cyclic carbonates were even more reactive than 6-membered ones.¹⁰² Due to the too high reactivity of the 7-membered cyclic carbonates, they were not able to calculate its reaction rate constant in DMSO at 50°C .

2.2.3.5- Selectivity of the reaction and by-products

As previously presented, two isomers can be formed while reacting 5-membered cyclic carbonates with amines: one with primary hydroxyl groups and one with secondary ones. In the case of the reaction between 6-membered cyclic carbonates, only primary hydroxyl groups are obtained if the carbonate is substituted in β of the oxygen. (See Scheme II-1-12)

In a general trend, it was found that substituted 5-membered cyclic carbonates react with amines to give preferentially secondary hydroxyl groups. Steblyanko *et al.* reacted glycerine carbonate benzoate with benzyl amine at room temperature.¹²⁴ The secondary hydroxyl group product was predominant in a ratio of OH I:OH II of 18/82%. They carried out theoretical calculations and confirmed that the secondary hydroxyl product was enthalpically more stable than the primary hydroxyl group product by about 1.67 kcal.mol⁻¹: $\Delta H_{f_{OH\ I}} = -8.10$ Kcal.mol⁻¹ and $\Delta H_{f_{OH\ II}} = -9.77$ Kcal.mol⁻¹. (See Figure II-1-8)

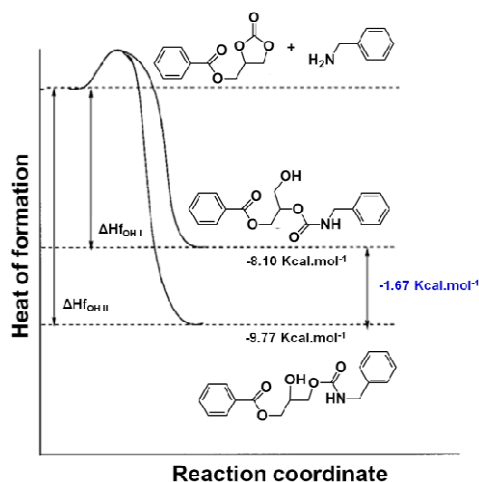


Figure II-1-8- Energy profile of ring-opening addition of 5-membered cyclic carbonate with benzylamine.¹²⁴

Tomita *et al.* also proved this tendency. According to the bond orders in substituted 5-membered cyclic carbonate calculated by the ab initio method, there should be more of the hydroxyurethane containing the secondary hydroxyl moiety than of that containing the primary hydroxyl group. (See Figure II-1-9)^{167, 173}

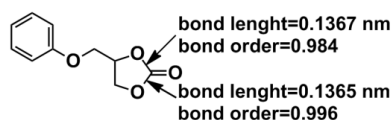
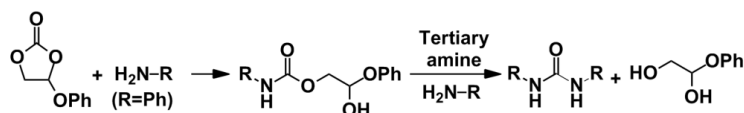


Figure II-1-9- Bond lengths and order calculated by the ab initio method using the STO-3G basis set.¹⁷³

Authors found an influence of the solvent and the chemical structure of amines and cyclic carbonates on the isomers ratio, although the selectivity of hydroxyurethane seems independent of the reaction temperature. Tomita *et al.* conducted a study of the effect of reaction conditions on the structure of the urethane formed¹⁷³. Their analysis indicated an isomer ratio slightly dependent on the solvent polarity and the amine structure. For instance the isomer with secondary hydroxyl is less formed in DMSO than in toluene.^{167, 173} The influence of the amine¹ chemical structure was reported by different research groups and in first attempt by Stout *et al.* and Doane *et al.*^{186, 187} Tomita *et al.* observed lower amount of hydroxyurethanes containing secondary hydroxyl while using benzylamine compared to hexylamine.¹⁷³ Nohra *et al.* concluded that as the alkyl chain of the amine increases, the

yield increases and the ratio OH I:OH II increases.¹⁷⁸ With secondary amines, they even found an equivalent proportion of OH I and OH II. In addition, the effect of the cyclic carbonate substituents was clearly demonstrated and explained by the mechanism. (See Scheme II-1-13)^{121, 167, 168} The selectivity of the reaction favored the secondary hydroxyl-based hydroxyurethane as the electron withdrawing character of the substituent increased.¹⁶⁷ Indeed, the inductive effect increases the acidity of the negatively charged oxygen and stabilizes the transition state. The reaction thus favors the formation of structures with secondary hydroxyl groups. Iwasaki *et al.* also observed this trend with phenyl substituents having para-groups of different electron withdrawing effect.¹⁸⁸ As an extreme result, Ochiai *et al.* obtained only secondary hydroxyl group performing the reaction between diethyltriamine and carbonated epichlorohydrin.¹⁸⁹

Very few papers related the formation of by-products during the reaction of cyclic carbonates with amines. On one hand, Burgel *et al.* reported in the early 1990's the formation of urea as side product. They studied the model reaction of benzylamine and cyclic carbonates. At low temperature, the reaction results in hydroxyurethanes, whereas at elevated temperatures (>100°C), they found that another amine molecule is able to attack the hydroxyurethane formed yielding to a substituted urea, as illustrated in Scheme II-1-14.^{172, 175, 190} The second step may be especially accelerated by tertiary amines.



Scheme II-1-14- Side reaction during the reaction of cyclic carbonate with phenylamine as observed by Burgel *et al.*¹⁷⁵

On the other hand, Endo and coll.^{124, 173} studied a model reaction between monofunctional ester-containing cyclic carbonate and benzylamine. After 20 h, no amidation product (N-benzylbenzamide) was observed.

Finally, as previously exposed, Nohra *et al.* observed in a larger amount the formation of glycerol during the reaction of glycerol carbonate with amine while using water, primary amines and shorter amines.¹⁷⁸

2.2.4- Thermoplastic poly(hydroxyurethane)s (PHUs)

The reaction of cyclic carbonates and amines lead to hydroxyurethanes, so the authors then prepared PUs with pendant hydroxyl groups from bis- or poly-cyclic carbonates and di- or

poly-amines or from AB or AB_x monomers with a cyclic carbonate and an amino group (See Table A-3 in appendix). In the case of PHUs networks, the authors usually used partially carbonated polyepoxides, which then lead to hybrid PHUs network due to the reaction of amines both towards epoxides and cyclic carbonates.

To prepare cross-linked PHUs, at least a cyclic carbonate or amine compound with a functionality higher than 2 (poly(cyclic carbonate) and / or polyamines) has to be used. Following another strategy, the hydroxyl groups of linear PHUs can be modified either by monofunctional molecules (functionalization with improved properties) or by di- / polyfunctional couplers (network formation).

Three pathways have been followed by the different research groups to prepare poly(cyclic carbonate)s. First, the poly(cyclic carbonate)s can be obtained from the radical polymerization of unsaturated monomers bearing a cyclic carbonate.^{54, 182} Besides, the poly(cyclic carbonate)s used can be also issued from the carbonation of polyepoxides, thus remaining unreacted epoxy groups can take part as well in the network formation of the hybrid PHUs.¹⁹¹ In another route, authors have made the reaction of well-defined multifunctional cyclic carbonate or amine compounds respectively with amines or 5-membered cyclic carbonates with well-defined functionality.^{115, 118, 192, 193} The cross-linked structure allows the improvement of the mechanical properties and the chemical resistance to aqueous solutions of acids and alkali.

Due to the scope of this manuscript, only thermoplastic poly(hydroxyurethane)s will be discussed in this part.

2.2.4.1- Reaction conditions, yield and kinetic

The polyaddition of bis 5-membered cyclic carbonates and diamines are mostly carried out in a solvent medium of high polarity such as DMSO, DMAc, and DMF at a reactant concentration from 0.5 to 1 mol.L⁻¹ and from room temperature (longer reaction times in days) to 100 °C. Proempers *et al.* are one of the research groups who used different solvents. They demonstrated that higher yield can be obtained with less polar solvents such as dioxane and THF compared to DMAC and diglyme.¹⁹⁴ Ochiai *et al.* tried to use water and ionic liquids as solvents. In water, they tested the polymerization of two bis 5-membered cyclic carbonates with hexane-1,6-diamine or 4,4'-diamino-dicyclohexylmethane at 0.5 mol.L⁻¹ without surfactants and at a temperature between 50°C and 100°C.¹⁷⁷ They

found that the polymerization was possible in case of quite hydrophobic bis 5-membered cyclic carbonate and hexane-1,6-diamine. In this case the reaction mixture stays heterogeneous along the reaction, and thus the cyclic carbonate is somewhat slightly protected from the hydrolysis. However, hydrolysis was observed for both bis 5-membered cyclic carbonates (See model reaction section), which can explain the low molar masses obtained even in the best case ($\bar{M}_n=4\ 200\ \text{g}\cdot\text{mol}^{-1}$ and $\bar{D}=1.86$ -in DMF/LiBr, PS standards-).¹⁷⁷ The same group studied the same polymerization in ionic liquid and in a mixture of water and ionic liquid (0.5:1).¹⁹⁵ In the case of purely ionic liquids, comparable results with the ones obtained in DMSO are achieved. However, while using a proportion of water, hydrolysis of the cyclic carbonate is observed and lower molar masses are obtained compared to the ones in DMSO. The authors did not detect the alkyl-exchange reaction between the diamines and the imidazolium ionic liquids. They observed the formation of ionic composites; originated from the interactions between hydroxyl groups of the side chains of the polymer and the ionic liquids.¹⁹⁵

While considering the results presented above, one can wonder why the authors use especially polar aprotic solvents, the reason being the solubility of the PHUs. Indeed, the solubility, a critical parameter, of the PHUs was reported by various studies. It depends on the chemical structures of the monomers used but there were found to be less soluble in organic solvents than the corresponding model PUs.¹²³ Due to the hydrophilicity given by the hydroxyl groups along the polymer backbone, the PHUs were in majority only soluble in aprotic solvents with high polarity such as DMSO, DMF and DMAC.^{124, 125} Moreover, Steblyanko *et al.* observed that using less soluble monomers lead to lower yields.¹²⁴ Besides, as for the model reaction, it has been shown that an increase of the reactants concentration leads to an increase in yields.¹⁹⁴

The temperature of the reaction has also a certain influence on the polyaddition of bis 5-membered cyclic carbonates (b5CC) and diamines. This expected behavior has been observed and quantify by the group of Endo.^{58, 196} They observed that the yield increase with the temperature¹⁹⁶ and they calculated the effect of the temperature on the reaction rate constant : $k_{b5CC-30^\circ\text{C}}=0.03\ \text{L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$; $k_{b5CC-50^\circ\text{C}}=0.06\ \text{L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$; $k_{b5CC-70^\circ\text{C}}=0.10\ \text{L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$.⁵⁸ This deviation from the Arrhenius law at higher temperature is explained by the decrease of the viscosity of the mixture with temperature. The increase of the viscosity with the formation of the polymer is an important parameter,¹⁹² taking into account that PHU can undergoes a lot of hydrogen bonds as presented previously. In order to optimize the reaction temperature, Benyahya *et al.* performed a complete rheological study on the

polyaddition of a bis 5-membered cyclic carbonate and decane-1,10-diamine. The authors demonstrated that a temperature beyond 120°C is too excessive for the polymerization (side reactions and solvent evaporation).¹⁹⁷

2.2.4.2- Molar masses

While comparing the different molar masses and dispersities obtained, one must be sure to compare SEC analyses performed with the same solvent and the same standards for the calibration. Besides, one can notice that no indications about the quenching of the reaction mixture are given. Most of the authors used DMF with LiBr and PS standards. In those conditions, the molar masses obtained for the polyaddition of 5-membered cyclic carbonates and diamines are from 6 300 g.mol⁻¹ to 28 000 g.mol⁻¹, with dispersities in the range 1.39 to 2.16. In other SEC solvents, the molar masses were in the range 3 800-9 000 g.mol⁻¹ (Đ:1.5-3.2, DMF, PMMA standards), 5 000-76 250 g.mol⁻¹ (Đ:1.4-1.6, DMAC, LiCl, PS standards), 4 300-12 900 g.mol⁻¹ (Đ:1.18-1.99, chloroform) and 960-7 700 g.mol⁻¹ (Đ:1.6-2.35, THF, PS standards). Particularly high molar masses are not taken into account in those ranges and are exposed in the following paragraph.

Using optimized reaction conditions determined by rheology (in DMF at 90°C), Benyahya *et al.* managed to reach relatively high molar masses up to 20 000 with dispersities up to 2.5 (DMF, PMMA standards).¹⁹⁷

Various parameters can influence the molar masses notably the temperature,^{123, 194} the concentration of the monomers in the solvent,¹⁹⁴ the chemical structure of the monomers and the solvent.

Furthermore, the chemical structure of the monomers influences the molar masses. Less soluble diamines lead to lower molar masses.¹²⁴ The use of aromatic diamines, also cause a decrease in molar masses due to a lowering of the structural flexibility.¹²⁵

The chemical structure of the 5-membered cyclic carbonate also influences the molar masses. As exposed in the model reaction section, the inductive effect of the substituent of the 5-membered cyclic carbonate plays a role on its reactivity. All the polymerizations reported in the literature were performed with cyclic carbonates bearing an electron-withdrawing substituent on the α , β or γ position, except one. In the latter study, Tomita *et al.* polymerized an inactivated 5-membered cyclic carbonate with 4,9-dioxadodecane-1,12-diamine. They managed to reach only a conversion of 95% and a molar mass of 15 000 g.mol⁻¹ after 14 days. (DMF, LiBr, PS standards)⁵⁸

As discussed above, the use of water as solvent or co-solvent leads to the hydrolysis of the cyclic carbonates and thus to lower molar masses.¹⁷⁷ Proempers *et al.* also demonstrated an influence of the solvent.¹⁹⁴ They obtained higher molar masses in aprotic less polar solvents (dioxane, THF), than in high polar aprotic ones (DMAC, diglyme), which is in agreement with the corresponding difference in yield.¹⁹⁴

Another study described the direct synthesis of PUs from bis epoxide, carbone dioxide and diamine in one pot.¹⁹⁸ Lithium chloride allows a complete conversion of the epoxides into 5-membered cyclic carbonates. While all epoxides were converted, dodecane-1,12-diamine was added to the mixture and PUs with molar mass up to 12 000 g.mol⁻¹ were achieved. (DMF, LiBr and phosphoric acid, PS standards)

Because the molar masses obtained from PHUs are usually around 10 000 - 20 000 g.mol⁻¹, this reaction can be used to synthesize prepolymer or to cross-link polymers bearing cyclic carbonate or for chain extension of preformed polymers.^{52, 199}

2.2.4.3- Selectivity and side reactions

The polyaddition of bis 5-membered cyclic carbonates and diamines lead to the formation of primary and secondary alcohols along the polymer chain. The same trend as in model reaction was observed in PHUs. The various authors found that more secondary alcohols were formed with a ratio between primary and secondary alcohols from 38:62 to 6:94 (without additives).^{194, 195} These results are in accordance with the difference of stability between primary and secondary alcohols discussed in the model reaction section.

Concerning side reactions, only few studies reported the presence or the analysis of potential side products. Kihara *et al.* found lower molar masses while using ethylene and propylene diamines. Their hypothesis was that side reaction occurs with these diamines by cyclization with the neighboring urethane to afford cyclic urea. (See the section of the reactivity of cyclic carbonates). However, they were not able to confirm this supposition maybe due to the really low quantity of the formed rings.¹²³ Urea formation was also reported by Bürgel *et al.* when performing the polyaddition in bulk at high temperature.¹⁹⁰

In theory, the use of cyclic carbonates bearing ester functions could lead to amidation reaction while performing the reaction with amines, if the amine reacts with the ester function instead of the carbonyl of the cyclic carbonate. However, Endo and coll. demonstrated that no amidation of the ester function occurs during the polymer formation both by IR analyses¹²⁴ and, by obtaining totally comparable molar masses and dispersities

than those of bis 5-membered cyclic carbonates bearing no ester groups.¹²³ With fatty acid based 5-membered cyclic carbonates, different observations have been made. Finally, the use of water as solvent or co-solvent for the preparation of PHUs was accompanied with the hydrolysis of the cyclic carbonates as discussed above.¹⁷⁷

2.2.4.4- Different reactivity for specific monomers

PHUs from other monomers such as protected amines or salt of amines, bis 6- and 7-membered cyclic carbonates, bis thio-cyclic carbonates, AA* monomers with 5-membered cyclic carbonates and either an open carbonates, a thio- lactone, or a 6-membered cyclic carbonate have also been prepared. The specificity of those monomers as well as the difference in reactivity depending on the monomer chemical structure is developed in this part.

2.2.4.4.1- Protected amine and amine salt

One example of AB monomer has been reported in the literature by Tomita *et al.* in 2001.²⁰⁰ They synthesized a precursor bearing a protected amine group and at the same time a 6-membered cyclic carbonate. The polymerizations were performed at different temperature (30°C, 50°C and 70°C) in DMSO at 1 mol.L⁻¹ during 14 days. The use of 10 mol% of tertiary amines such as N,N-diisopropylethylamine, 4-(dimethylamino)pyridine or triethylamine was necessary for the in-situ deprotection of the amino group. The molar masses were in the range 3 200-11 000 g.mol⁻¹ with dispersities of 1.1/1.2. (DMF, LiBr, PS standards). Better molar masses were obtained while using N,N-diisopropylethylamine or 4-(dimethylamino)pyridine. On the contrary with the evolution of the molar masses with temperature described above, a decrease of the molar masses with temperature is observed in this case. The two latter observations can be explained by the higher stability of the 6-membered cyclic carbonates with N,N-diisopropylethylamine and 4-(dimethylamino)pyridine at lower temperature toward anionic polymerization with a tertiary amine as an initiator. The authors carried out some stability test reactions. At 50°C, for 14 days less than 1% of conversion for the 6-membered cyclic carbonate was observed, but at 70°C for 7 days already 55% conversion was reached.

However, using more nucleophilic triethylamine, a faster reaction was observed even at 30°C.²⁰⁰

Using another strategy, Kihara *et al.* synthesized optically active PHUs from a 5-membered cyclic carbonate and L-lysine hydrochloride.¹⁹⁶ They used 2 equivalents of triethylamine or 1 equivalent of DBU. The higher molar mass obtained was 24 000 g.mol⁻¹ with a dispersity of 1.58. (DMF, LiBr, PS standards)

In this part, a particular close case concerning the branched cationic PHUs prepared by Ochiai *et al.* in 2012 can be mentioned.¹⁸⁹ The polyaddition proceeded through the nucleophilic addition of the primary amino group of diethylenetriamine onto the carboxyl group of carbonated epichlorohydrin (THF, RT), followed by the quarternization of the secondary amino group with the chloromethyl group in molten salts.

2.2.4.4.2- AA* monomers with one 5CC

Various AA* with at least one 5-membered cyclic carbonate have been synthesized along the literature. The first example of AA* monomers was reported by Ubaghs *et al.*³⁶ They synthesized a precursor having both a 5-membered cyclic carbonate and an open carbonate with phenol as leaving group. The polymerizations were carried out in DMAC at 2 mol.L⁻¹ at room temperature for 20 hours using various aliphatic diamines. Molar masses in the range 6 400-8 700 g.mol⁻¹ were obtained with dispersities from 1.46 to 1.57. (DMAC, LiCl, PS standards). This polymerization involved the removal of phenol as by-product. Other leaving groups were also tested by the preparation of different bifunctional carbonate couplers from glycerol.³⁷

Recently, another AA* monomer bearing a 5-membered cyclic carbonate and a 5-membered thio-lactone has been prepared by Keul *et al.*²⁰¹ This AA* was reacted with a purely aliphatic amine or ones having urethane or ether linkages in DMF or THF at 0.35 mol.L⁻¹ at 70°C to give poly(hydroxyurethaneamide)s. In order to prevent cross-linking of the thiol groups of the resulting polymer, 1 to 5 mol% of D,L-dithiothreitol was added. Molar masses in the range 3 100-6 400 g.mol⁻¹ were reached with relatively high dispersities from 1.99-3.33. The dispersities above 2 have been explained by the presence of few disulfide bonds formed. Based on the higher reactivity of the thio-lactone group, the authors were able to prepare dimers with having two 5-membered cyclic carbonates.²⁰¹

Following a similar strategy, He *et al.* synthesized AA* monomers with one 5- and one 6-membered cyclic carbonate.¹⁰⁴ The aim of this AA*, as bifunctional coupler, is to prepare multifunctional polymers either (i) by reacting polyamines with bifunctional couplers already reacted with monofunctional amines, or (ii) by reacting polyamines already functionalized with bifunctional couplers with monofunctional amines. This is possible by the difference in reactivity of 5- and 6-membered cyclic carbonates. By reacting the bifunctional coupler with diamines, molar masses from 1 340 g.mol⁻¹ to 8 800 g.mol⁻¹ were obtained (Đ:1.45-2.11). (DMF, LiBr, PS standards)

2.2.4.4.3- Comparison between bis 5CC, 6CC and 7CC

In this part, an additional development on the difference in reactivity of bis 5- and 6-membered cyclic carbonates is presented. In 2001, Tomita *et al.* synthesized two chemically similar bis cyclic carbonates, one with two 5-membered rings (b5CC), and the second one with 6-membered rings (b6CC).⁵⁸ Following the same trend as presented in the Model reaction part, bis 5-membered cyclic carbonates are less reactive than bis 6-membered cyclic carbonates. Indeed, the bis 6-membered cyclic carbonate was converted quantitatively after 48 hours although the conversion of the bis 5-membered cyclic carbonate was only 67% during this period. Moreover, the bis 6-membered cyclic carbonate allowed the formation of PHUs with a molar mass of 26 000 g.mol⁻¹ after 48h, whereas the molar mass obtained in the case of bis 5-membered cyclic carbonate was only of 15 000 g.mol⁻¹ after 14 days. (DMF, LiBr, PS standards) The authors studied the kinetic of the reaction and found a 2nd order overall law. The reaction rate constant allows to quantify the higher reactivity of the 6-membered cyclic carbonate toward the 5-membered one: $k_{b6CC-30^{\circ}C} = 0.70 \text{ L.mol}^{-1}.\text{h}^{-1}$; $k_{b6CC-50^{\circ}C} = 0.89 \text{ L.mol}^{-1}.\text{h}^{-1}$; $k_{b6CC-70^{\circ}C} = 1.07 \text{ L.mol}^{-1}.\text{h}^{-1}$ and $k_{b5CC-30^{\circ}C} = 0.03 \text{ L.mol}^{-1}.\text{h}^{-1}$; $k_{b5CC-50^{\circ}C} = 0.06 \text{ L.mol}^{-1}.\text{h}^{-1}$; $k_{b5CC-70^{\circ}C} = 0.10 \text{ L.mol}^{-1}.\text{h}^{-1}$. The reaction rate for the bis 6-membered cyclic carbonate was lower than the one calculated for the 6-membered cyclic carbonate, probably because of the lower mobility of the reactive sites of the bifunctional monomer and polymer end. In contrast, they were almost equal in the case of bifunctional and monofunctional 5-membered cyclic carbonate, certainly because of its slow reactivity. The activation energies were also estimated ($E_{a-b6CC} = 9.2 \text{ kJ.mol}^{-1}$ and $E_{a-b5CC} = 24.9 \text{ kJ.mol}^{-1}$), confirming a clear higher reactivity of the 6-membered cyclic carbonates toward the 5-membered ones. Besse *et al.* in 2013 also observed higher molar

mass for the PHU from bis 6-membered cyclic carbonate compared to the ones from bis 5-membered cyclic carbonate.¹¹⁹ The bis 6-membered cyclic carbonate was issued from 2-ethyl-2-[(prop-2-en-1-yloxy)methyl] propane-1,3-diol.

Going even further the group of Endo prepared bis 7-membered cyclic carbonates and observed higher reactivity and molar mass than bis 5- and 6-membered cyclic carbonates.¹⁰² Molar masses up to 35 700 g.mol⁻¹ (\bar{D} =2.8) were obtained after only 6 hours of reaction. (DMF, LiBr, PS standards) Regarding, 6- and 7-membered cyclic carbonates, the authors did not mentioned any side reaction generating by the attack of the primary hydroxyl group formed onto the carbonyl of the cyclic carbonate.

Recently, Besse *et al.* studied the compared reactivity of bis thio-cyclic carbonates.¹¹⁹ Slightly lower molar mass (\bar{M}_n =7 000 g.mol⁻¹ and \bar{D} =1.9) was obtained for the poly(thiourethane) prepared with diethylenetriamine, compared with the bis 5-membered cyclic carbonates (\bar{M}_n :10 300-13 000 g.mol⁻¹ and \bar{D} =2.1-2.2). (DMF, PMMA standards) Moriguchi *et al.* also studied the polyaddition of bis 5-membered thio-cyclic carbonates with diamines and obtained molar masses from 5 000 g.mol⁻¹ to 12 000 g.mol⁻¹ (\bar{D} =1.38-1.62, THF, PS standards).²⁰²

2.2.4.5- Thermo-mechanical properties and thermal stability

Numerous studies have been reported on the thermo-mechanical properties as well as the thermal stability of the synthesized PHUs. The results clearly showed the expected influence of the chemical structure of the monomers onto the glass transition temperature, the presence or not of a melting point and the degradation temperature as expose below.

The glass transition temperatures ranged between -30°C¹¹⁷ and 100°C¹²⁵, depending on the chemical structure of reactants. Semi-crystalline PHUs were also achieved with melting points in the range 80°C¹⁹³ to 190°C¹⁹⁴. With aliphatic diamines, different studies demonstrated that the glass transition temperature decreases with longer aliphatic diamines due to lower urethane linkages, able of hydrogen bonds, along the polymer backbone.^{36, 115, 124} In the case of aromatic diamines, Kim *et al.* demonstrated higher glass transition temperatures than with aliphatic ones.¹²⁵ Moreover, Besse *et al.* observed similar glass transition temperatures with bis 5- and 6-membered cyclic carbonates.¹¹⁹

Concerning the degradation temperatures, only general trends can be given due to the disparity of the analyses: performed at $5^{\circ}\text{C}\cdot\text{min}^{-1}$ ^{119, 203}, $10^{\circ}\text{C}\cdot\text{min}^{-1}$ ^{36, 123, 125, 194} or $20^{\circ}\text{C}\cdot\text{min}^{-1}$ ¹¹⁷ with the study of either the initial decomposition temperature or after 5%, 10% or 20 wt% loss. The highest thermal degradation was reported by Kim *et al.* to be up to 388°C ($10^{\circ}\text{C}\cdot\text{min}^{-1}$), these correspond to PHUs with a large part of aromatic structures.¹²⁵ In contrary, Proempers *et al.* reported a starting thermal decomposition as low as 180°C ($10^{\circ}\text{C}\cdot\text{min}^{-1}$).¹⁹⁴ The thermal study of Kihara *et al.* can be reported here.¹²³ They proved with one example that similar initial decomposition temperatures (around 310°C) are obtained with PHUs in comparison with the corresponding conventional PU without pendant hydroxyl groups.

Moreover, only recently, Fleischer *et al.* were the first to study some mechanical properties for linear PHUs.¹⁹² They obtained Young modulus of 7 ± 1 MPa, tensile strength of 9 ± 2 MPa and elongation at break of $280\pm 50\%$ for a PHU from a 5-membered cyclic carbonate and hexane-1,6-diamine.

The presence of hydroxyl groups allows further post-functionalization on the PHUs. The functionalization or chemical modification permits to improve the properties of the initial PHU, increasing its molar mass, bringing new functions and/or cross-linking the structure.¹⁹⁶ Hydroxyl groups can be converted to other functional groups with monofunctional molecules.^{194, 198, 204} Using another approach, polyamines were used by He *et al.* with bifunctional couplers bearing 5- and 6-membered cyclic carbonates. Thanks to the difference in reactivity of the two size rings and a two steps procedure, they were able to prevent a cross-linked structure but multifunctional polymers bearing pendant hydroxyurethane functions linked to various specific entities as discussed in the AA* monomers section.^{39, 104}

2.2.5- Additives and catalysts for the cyclic carbonate/amine reaction

How can the reaction between cyclic carbonates and amines be activated? Theoretically, the ring opening reaction of cyclic carbonates by amines may be accelerated by activating the monomers, that is, either by the additions of weakly Lewis acidic and oxophilic additives to increase the electrophilicity of the cyclic carbonate group, or by the addition of basic additives to increase the nucleophilicity of amines, even to deprotonate the amines. Another possibility is to use a Lewis base to attack the carbon of the cyclic carbonate carbonyl. The

Lewis base will be then a potential good leaving group while the attack of the amine molecule.

Concerning the question of the catalysis of this reaction, almost exclusively patents have been reported. There are only few papers that deal with this specific point. They are discussed in priority after a general overview. Indeed, in patent, it is hard to take things into consideration. All tested catalysts and additives used are summarized in Figure II-1-10. The selected order can be subjected to changes because, no mechanism of activation has been exposed and the ways of activation of the various catalysts can only be envisaged. Different classes of catalysts have been tested, among them organic catalysts, organometallic catalysts and salts.

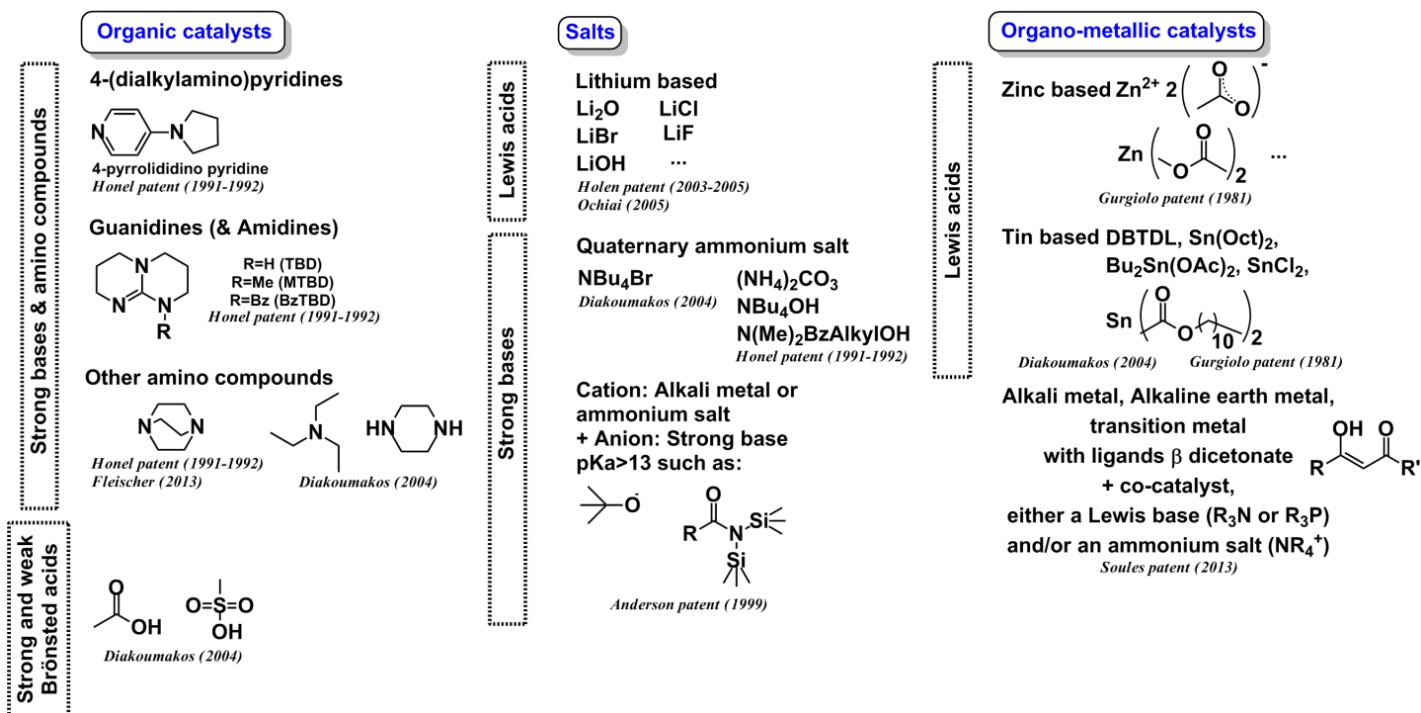


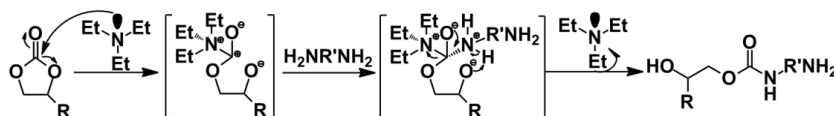
Figure II-1-10- Various tested catalysts for the cyclic carbonate / amine reaction.

Concerning organic catalysts, either strong bases (such as 4-pyrrolidino pyridine, guanidines (TBD, MTBD), 1,4-diazabicyclo[2.2.2]octane (DABCO), piperazine and triethylamine)^{183, 192, 205-207}, or strong or weak Brønsted acids (glacial acetic acid, methanesulfonic acid)¹⁸³ have been used for the catalysis of the cyclic carbonate / amine reaction. Salts combining an alkali metal or ammonium salt cation, with an anion such as OH^- , CO_3^{2-} , Br^- , Cl^- ,... or a strong base which corresponding acid has a $\text{pKa} > 13$ have also been tested.^{183, 205, 206, 208} In this category lithium based salts such as Li_2O , LiBr , LiCl , LiOH , LiF ,... were investigated.^{192, 209-211} For organometallic catalysts, zinc, tin and chrome-based compounds have been found to have some activity to catalyze the cyclic carbonate / amine

reaction.^{183, 211-213} Nanoclays have also been patented for a beneficial effect on the speed of gelling and cure time.²¹⁴

The 5-membered cyclic carbonates will react with primary and some secondary amines at room temperature. Although most reactions can be accomplished without the aid of a catalyst, alkali metal-based Lewis acid such as LiCl, LiBr or LiF can be employed to increase the reaction rate.^{118, 198} They activate the carbonyl group without the deactivation of the amine. Thus the increased electrophilicity of the activated cyclic carbonate by the appropriate Lewis acids is the most plausible factor for the enhanced of the molar masses of the poly(hydroxyurethane)s. In this study, Ochiai *et al.* observed that the higher molar masses were obtained with LiCl, LiF and Bu₄Sn, which give molar masses of 36 700 g.mol⁻¹ (Đ=1.84), 31 600 g.mol⁻¹ (Đ=1.71) and 32 700 g.mol⁻¹ (Đ=1.70) respectively, compared to 19 300 g.mol⁻¹ (Đ=1.88) without catalysis in the same conditions. (DMF, phosphoric acid, LiBr, PS standards)²¹¹

The reaction can also be effectively catalyzed by the use of triethylamine which reduces the activation energy of the reaction by up to 17.5% compared to that of the non-catalyzed system.¹⁸³ The introduction of triethylamine halved the reaction times necessary for 100% conversion at both 25°C and 60°C. The authors proposed a mechanism for the catalysis with triethylamine as depicted in Scheme II-1-15. In the same study, various other catalysts, including acid (glacial acetic acid, methanesulfonic acid), base (piperazine, TBABr, or tin-based catalysts (tin (II) octanoate, DBTDL),... were also used effectively, even if no quantitative data were reported.



Scheme II-1-15- Proposed mechanism of the activation of cyclic carbonates with triethylamine.¹⁸³

Recently, Fleischer *et al.* performed the polyaddition between a bis 5-membered cyclic carbonate and hexane-1,6-diamine in mold. They observed that 1 wt% of DABCO increases the reactivity at 25°C. Reaction without catalyst led to 60% conversion, whereas with DABCO, 90% conversion was reached within 2 minutes.¹⁹²

2.2.6- Conclusion

As mentioned in the introduction, a main issue in PU chemistry is the high toxicity of the used precursors, namely phosgene and isocyanate. Thus, both industrial and academical research is focused on environmentally benign and safer processes for the synthesis of PUs. The cyclic carbonate / amine reaction seems to be one of the best ways to solve the toxicity concerns and avoid the use of isocyanates during the preparation of PUs. While considering non-porous materials, cyclic carbonates are especially preferred over open carbonates since no volatile compounds are released during the polymer formation, and pore-free PUs are thus obtained.

However, some limitations to develop PHU commercialization can be pointed out concerning its synthesis. On one hand, the reaction rate of this reaction has been shown to be quite slow compared with the direct addition of isocyanates and alcohols. Elevated temperatures are thus requested which make the PHUs unsuitable systems for room temperature curing. Therefore methods are nowadays in development to circumvent this lack of reactivity. For instance, the reaction rate of the system may be improved by working with and designing more reactive cyclic carbonates such as 6- and 7-membered ones, or by tailoring high effective catalysts under mild conditions.

Another important remaining issue for PHUs is the mechanical properties and chemical resistance of these materials to aqueous solutions of acids and alkalis since it lacks cross-linked network structure. Besides, the elasticity of PHUs not allows elastomer applications. A way to overcome those limitations is the preparation of hybrid PHUs, based on the epoxy-amine- cyclic carbonate oligomers to build a network structure.⁴ Moreover, the thermal stability, the water absorption capacity and the molar mass stability when heating should also be particularly verified. Indeed, the reversibility of the β -hydroxyurethane bond could produce isocyanate and an excess of OH groups with further recondensation.

For those various reasons, more research and development is certainly necessary before the transition to a greener production of suitable PUs, using the cyclic carbonate /amine route.¹

3- Vegetable oils transformations to non-isocyanate and non-phosgene PUs

3.1- Transurethanization approach

The transurethanization is effectively an interesting route to non-isocyanate and non-phosgene PUs. This approach have already been described by Dyer *et al.*²¹, Rokicki *et al.*²², Blank⁴⁷ and Ochiai *et al.*⁴⁶ (See the section 2) Applying this strategy to fatty acid-based resources, the non-isocyanate and non-phosgene carbamate precursors have been synthesized via the Curtius rearrangement, from ethylene carbonate or via the Lossen rearrangement.

3.1.1- Carbamate synthesis via Curtius rearrangement

Self-polycondensation and transurethane approaches have been used to prepare TPUs using novel vegetable oil-based AB-type monomers with an *in situ* generation of isocyanates. (See Scheme I-1-6)

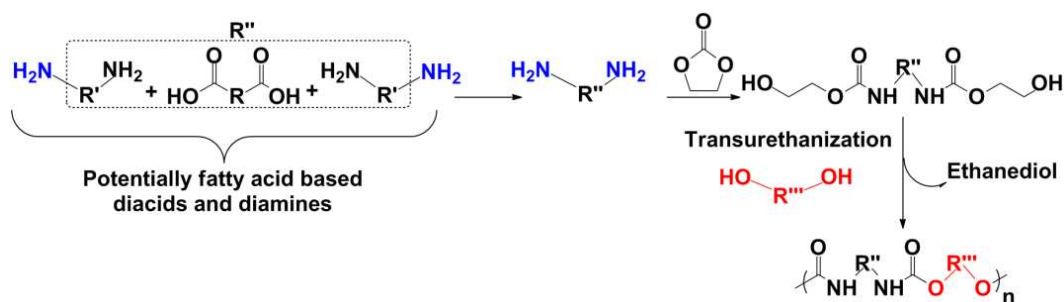
Two different kinds of monomers have been prepared from methyl oleate and ricinoleic acid. In both routes, the hydroxyl groups have been obtained either from the naturally occurring OH in ricinoleic acid, or by epoxidation of the double bond of methyl oleate and ring opening of the epoxide with methanol. In the first approach, AB-type monomers with hydroxyl and acyl azide functionalities, namely a mixture of 10-hydroxy-9-methoxyoctadecanoyl azide/9-hydroxy-10-methoxyoctadecanoyl azide (HMODAz) and 12-hydroxy-9-cis-octadecenoyl azide (HODEAz) were prepared as described previously using sodium azide.²¹⁵ The polymerizations of HMODAz and HODEAz monomers were carried out by the acyl-azido and hydroxyl AB-type self-condensation upon heating, with and without catalyst. It was demonstrated that the polymerization of the acyl azide occurred through its thermal decomposition to isocyanate in the first minutes of the reaction, known as the Curtius rearrangement. The isocyanate further condensed with the hydroxyl group to form the TPUs. In the second route, AB-type monomer with hydroxyl and methyl carbamate functionalities that is methyl-N-11-hydroxy-9-cisheptadecen carbamate (MHHDC) were obtained by reacting the above acyl azide with methanol. Transurethanization can then be conducted using a titanium catalyst to give TPUs. Self-

polycondensation of an AB-type monomer has the advantage of controlling the stoichiometry to achieve high molar masses TPUs. However, due to the formation of macrocycles, comparatively low molar masses in the range 740 to 8 890 g.mol⁻¹ with dispersity in the range 1.5 to 2.3 were observed for all TPUs formed by both processes. Two different Tg for soft segments (-53°C to -22°C) and hard segments (around 26°C) were observed in these TPUs, which indicates a phase-separated morphology. Only very small difference, in terms of thermo-mechanical properties, was noticed between the PU obtained by the two methods.

In order to obtain higher glass transition TPUs and to limit the macrocycles formation, More *et al.* used methyl undecenoate as starting material and introduced the hydroxyl functions via thiol-ene reaction. Therefore, four new AB type monomers from methyl oleate (HETOAz and MHETHC) and from methyl undecenoate (HETUAz and MHETDC) were synthesized following the same strategy. Both amorphous and semi-crystalline TPUs with reasonable high molar masses were achieved. By taking the advantage of the different thermo-mechanical properties of poly(HETOAz) and poly(MHETHC), random copolymers were also prepared to adjust the final nature of the TPUs.^{216, 217}

3.1.2- Carbamate synthesis from ethylene carbonate

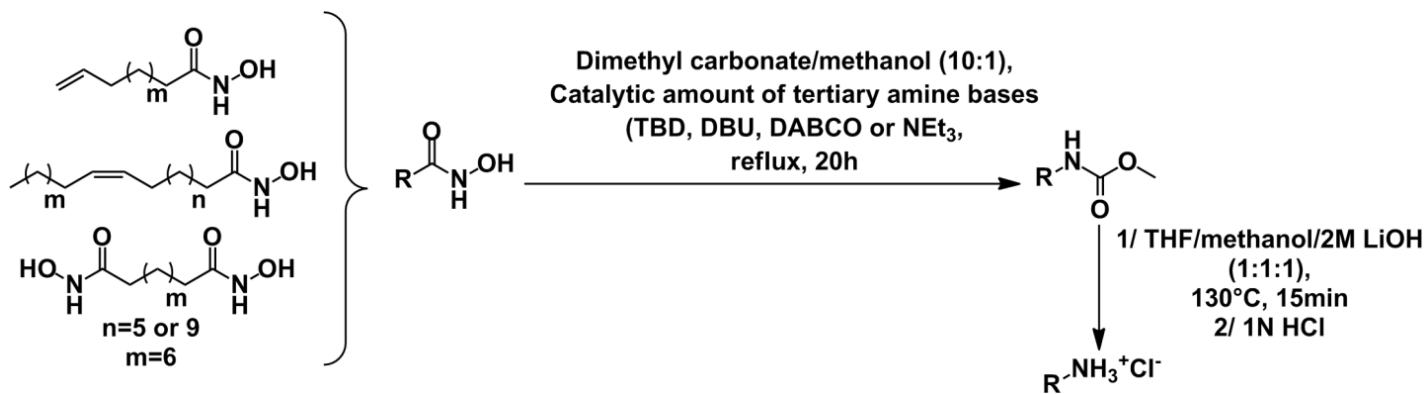
Narayan and coll have used vegetable oil derivatives to PUs via the transurethanization as presented in the 2013 AOCS meeting.²¹⁸ Following the route illustrated in Scheme II-1-16, they have synthesized poly(amideurethane)s. The carbamate precursor was obtained by first reacting a fatty acid-based diacid with an excess of diamines in order to end up with a fatty acid based diamine. Then after ring opening of ethylene carbonate, a carbamate-based diol was reached. The latter finally undergo transurethanization and poly(amideurethane)s with a number average molar mass of 8 000 g.mol⁻¹ was produced by polycondensation and removal of ethanediol. A Tg and a Tm of -10 °C and 73 °C respectively were observed.



Scheme II-1-16- Polyurethanes from ethylene carbonate by transurethanization.²¹⁸

3.1.3- Carbamate synthesis via Lossen rearrangement

A promising route can be exposed here. Recently, Meier and coll. used a variant of the Lossen rearrangement on fatty acid-based hydroxamic acids to prepare methyl carbamates using dimethyl carbonate in methanol with a catalytic amount of tertiary amine bases such as TBD, DBU, DABCO, and triethylamine (Scheme II-1-17).²¹⁹ The dimethyl carbamates from dimethyl sebacate was used in PU synthesis without the use of isocyanate, by transurethanization with 1,10-decanediol or 1,20-eicosanediol.²²⁰



3.2- Vegetable oils-based 5-membered cyclic carbonates to poly(hydroxyurethane)s

3.2.1- Synthesis of poly(5-membered cyclic carbonates) from vegetable oil derivatives

As presented in the first part, numerous studies have been developed to prepare 5-membered cyclic carbonate. From vegetable oils, the 5-membered cyclic carbonates have almost exclusively been synthesized by the epoxidation followed by the carbonation of the fatty acid chain unsaturations or by the use of glycerol carbonate precursors. In this part, only the first route will be developed. The epoxidation have been performed using various reactants as described in the previous section. As an interest for the preparation of non-isocyanate PU from vegetable oil, epoxidized soybean oil, resulting from the epoxidation of the double bonds of soybean oil using hydrogen peroxide, either in acetic acid or in formic acid, has gained attention and is now industrially available in large volumes and at reasonable costs.^{4, 5} After the epoxidation, the carbonation has been performed using carbon dioxide and various conditions. (See carbonated soybean oil in Figure II-1-11)

Different parameters have to be taken into account such as the catalyst concentration, the temperature, the carbon dioxide pressure and the reaction time in order to evaluate the difference in epoxy conversion or yield.

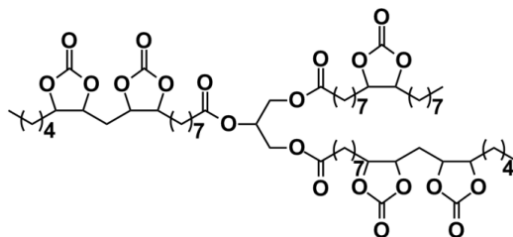


Figure II-1-11- Structure of carbonated soybean oil.

The reactions of epoxy soybean oil with carbon dioxide can generally result in high conversion, but required harsh conditions. Tetrabutylammonium bromide (TBABr) has been widely used as carbonation catalyst for vegetable oil derivatives. In 2004, Tamami *et al.*^{221, 222} obtained a yield of 94% while using 5 mol% of TBABr at 100°C with 1 Bar of CO₂ after 70 hours.^{221, 222} Mann *et al.* also used TBABr (6 mol%) to carbonate epoxidized veronica oil at 100°C with 140 Bar of CO₂.²²³ They obtained a yield of 72% after 46 hours, and as desired a low viscosity carbonated oil.

By using supercritical carbonate dioxide (100 Bar CO₂ and 100°C), Doll *et al.* compared TBABr, tetrabutylammonium hydroxyl, LiBr and KBr at 0.5 mol% for the carbonation of methyl oleate and methyl linoleate.^{224, 225} The TBABr catalyst system shows the highest reactivity of 100% epoxy conversion after 40 hours (82% conversion after 10 hours), while tetrabutylammonium hydroxyl, LiBr and KBr demonstrate little even no activity probably due to their poor solubility in both epoxidized oil and supercritical carbon dioxide.

Other declinations of catalyst system have been used along the literature. For instance, carbonated soybean oil with a conversion of 89.2% can be synthesized using SnCl₄.5H₂O/TBABr composite catalyst, whereas only 71.3% of conversion was obtained with TBABr alone (20h, 10 Bar of CO₂).²²⁶ For the optimized reaction conditions, the ratio was 1:3 for the composite catalyst and 98.6% conversion was reached after 40 hours. In another case, a conversion of almost 98% of epoxidized soybean oil can be achieved after 120 hours of reaction at 60 Bar of CO₂ and 130°C using 18-crown-6 activated KI as catalyst.²²⁷ Recently, carbonated linseed oil has been prepared with either homogeneous 3.5 wt% TBABr catalyst, or silica supported 4-pyrrolidinopyridinium iodide.²²⁸ At 10 Bar and 140°C, lower reaction rate were obtained with silica supported 4-pyrrolidinopyridinium iodide than with TBABr. The time for completion was 50 hours and 20 hours respectively. However, the use of heterogeneous catalyst enables facile catalyst recovery by filtration. The authors also

compared different carbon dioxide pressure from 1 Bar, to 10 and 30 Bar. As expected, the epoxide conversion increased as the carbon dioxide pressure increased. Very recently, for the carbonation at 100°C with 5 mol% catalyst and 117 Bar of CO₂, Langanke *et al.* used simultaneous activation of substrates and CO₂ with a bi-functional catalytic system based on an organic halide and a polyoxometalates (POM).²²⁹ For methyl oleate the combination of both systems led to better epoxide conversion, but in the case of polyepoxidized oleochemicals the ammonium halide alone is better as side reactions occurred with POM. Following another strategy, Kenar *et al.* prepared carbonated methyl oleate from fatty acid ester chlorohydrins in 2.5 hours to 5.5 hours at 50-55°C with a yield of 85%.²³⁰

3.2.2- Non-isocyanate PHU networks from vegetable oil derivatives

Carbonated vegetable oils can easily react with amines to give the corresponding non-isocyanate PHU networks. The thermo-mechanical properties depend on the chemical structure of the amine and cyclic carbonate-based compounds as well as on the stoichiometric ratio between them, and the respective contents of unconverted epoxy groups and cyclic carbonates.

Tamami *et al.* prepared PHU networks by reacting carbonated soybean oil with different diamines (ethane-1,2-diamine and hexane-1,6-diamine) and triamine (triethylenediamine) at 70°C for 10 hours, then at 100°C for 3 hours.²²¹ With ethane-1,2-diamine, the Young modulus was decreasing as the stoichiometric ratio was taken away from 1. The same authors performed the model reaction at room temperature between carbonated soybean oil and hexylamine in THF at 10 mol.L⁻¹ and found a complete conversion after 12 hours without amide formation.²²¹ Another group prepared non-isocyanate PUs with tensile strength up to 6 MPa and Tg from 2.3°C to 22.5°C by reacting carbonated soybean oil with ethane-1,2-diamine, butane-1,4-diamine, or hexane-1,6-diamine.²³¹

Javni *et al.* used m-xylylenediamine, p-xylylenediamine and aliphatic or cycloaliphatic diamines for curing reactions of cyclic carbonated soybean oil.²³² The Tg from -6°C to 26°C were related to the amine:cyclic carbonate ratio, and to the amine structure. The aromatic nature of the xylylenediamine reagent and the cycloaliphatic structure of isophorone diamine resulted in an increase of the tensile strength with a decrease of the elongation at break compared to the aliphatic diamine.

Bahr *et al.* prepared both carbonated soybean and linseed oil.²²⁸ The carbonated content in linseed oil was substantially higher (20.2% compared to 26.8%). Copolymers of both carbonated compounds enable the variation of cyclic carbonate content in order to explore the influence of curing agents and the carbonate content on the thermal and mechanical properties of NIPU. The stiffness and glass transition temperature increased significantly while increasing the crosslink density. For instance with ethane-1,2-diamine, the Young modulus was 180 ± 30 MPa ($T_g=55^\circ\text{C}$) with carbonated linseed oil, whereas it was only of 4 ± 1 MPa ($T_g=20^\circ\text{C}$) with carbonated soybean oil alone. By using cycloaliphatic amine such as isophorone diamine, the glass transition can be improved by two ($T_g=40^\circ\text{C}$ with isophorone diamine compared to $T_g=17-20^\circ\text{C}$ with ethane-1,2-diamine and butane-1,4-diamine). These results are in accordance with those of Javni *et al.* A glass transition and Young modulus as high as 60°C and 1460 ± 120 MPa respectively can be reached. At the same time, the elongation at break decreased drastically.²²⁸

Carbonated linseed oil was also used to prepare bio-based non-isocyanate urethane with an alkylated phenolic amine from cardanol.²³³

In a different way, Parzuchowski *et al.* prepared a bisphenol A-based epoxy resin modified with carbonated soybean oil.²²⁷ The authors quantified the difference in reactivity between oxirane and cyclic carbonate using primary or secondary amines. Different polyamines as well as various carbonated soybean oil contents were tested and thus a range of properties were attained.²²⁷ They tried a one step (all reactants mixed together) and a two step procedure (pre-mix of carbonated soybean oil and the amine). In the one step procedure, the oxiranes react more rapidly with the amine than the carbonate soybean oil and thus a network from the epoxy groups and the polyamine is formed. The unreacted carbonated soybean oil, being insoluble in this network, the system became heterogeneous and a second phase of small domains of carbonated soybean oil was created. In contrast, no second phase was formed during the two-step method during which all cyclic carbonates are first converted by amines. The phase separation depends not only on the process used, but also on the amount of carbonated soybean oil. The average domain size was function of the amount of carbonated soybean oil added to the composition. Particles of 335 ± 50 nm diameter were obtained for the sample with 40% of carbonated soybean oil cured with triethylenetetraamine. While using 20% of carbonated soybean oil, smaller particles were observed (184 ± 30 nm). The use of a lower reactive diamine such as isophorone diamine, led to even smaller particles (70 ± 30 nm) even with high content of carbonated soybean oil.

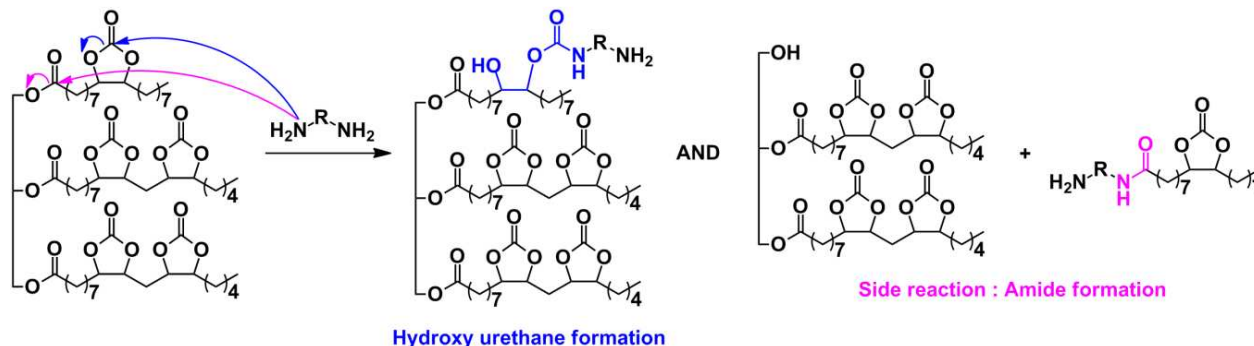
With both triethylenetetraamine and isophorone diamines, the T_g decreased with the increase of the carbonated soybean oil percentage, while using the one-step procedure. The evolution of the impact resistance with the content of carbonated soybean oil depended on the method used. Although higher content of carbonated soybean oil lead to higher impact resistance with the one-step procedure, it was not the case with the two-step procedure. Moreover, they found an optimum at 10% of carbonated soybean oil using the one-step method with a tensile strength of 69 ± 3 MPa and a corresponding elongation at break of 9.2%. This result was correlated with a phase separation.²²⁷

Following a similar strategy, which implies the difference in reactivity between epoxy groups and cyclic carbonates, partially carbonated soybean oil has been used for hybrid PHU networks.²²⁶ The optimal properties for high tensile strength were not obtained with complete conversion of the epoxy groups into cyclic carbonates but where in the range 73.3% to 85.1% conversion. The resultant materials have tensile strengths of 2.63-7.0 MPa, elongations at break of 163-232%, and a Shore A hardness of 84-93.²²⁶

Turunc *et al.* provided a route to prepare organic-inorganic nanostructured non-isocyanate hybrid PHUs.²³⁴ Various contents of cyclic carbonate modified silica particles were added into carbonated soybean oil and carbonated polypropylene glycol resin mixture to prepare PU-silica nanocomposite coatings using an aliphatic diamine as a curing agent. Using carbonated soybean oil, similar T_g , T_m and thermal stability were obtained with and without the carbonated silica particles. However, while increasing the carbonated silica particles to a certain extent, the Young modulus increases from 5.31 MPa to 9.36 MPa. The morphology studies indicated that carbonated silica nanoparticles could be better dispersed in carbonated PPG than in carbonated soybean oil-based formulations, thus an improvement of the thermal, mechanical, and coating properties can be obtained with nanocomposite coatings comprising carbonated soybean oil, PPG and silica particles.

These vegetable oil-based poly(cyclic carbonate)s are usually bearing ester groups due to the inherent structure of the triglycerides. A disadvantage is that the curing reaction is sometimes accompanied with the cleavage of the ester groups, thus reducing network density and lowering tensile strength.^{228, 231, 232} (Scheme II-1-18) For instance, Javni *et al.* demonstrated clearly in 2008 that during the curing the amine groups can react with the ester to form amide linkages.²³¹ Hence, cyclic carbonate compounds without ester linkages are preferred.⁵ This observation has not been found in cyclic carbonate compound presented in the petrochemical PHUs section. One reason to explain this behavior is the

electron-releasing effect of the fatty acid alkyl chain(s), which reduce the reactivity of the cyclic carbonates and thus amidation reaction can occur.



Scheme II-1-18- Amide side reaction occurring during PHU synthesis from carbonated soybean oil.

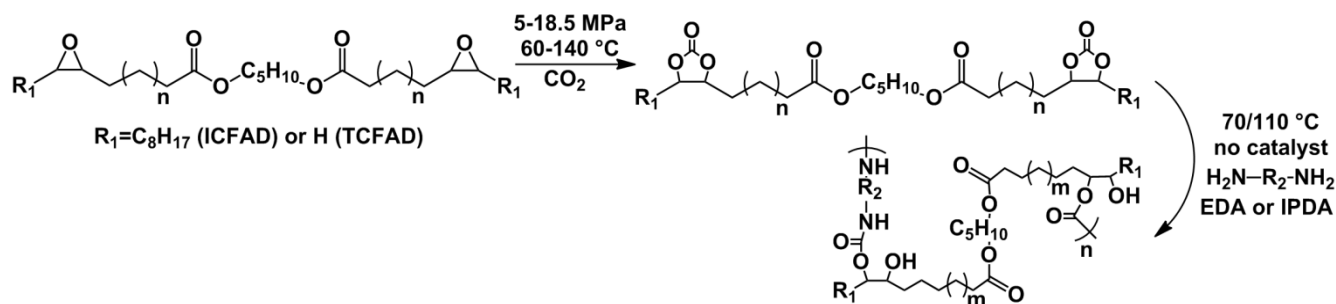
3.2.3- Fatty acid-based thermoplastic PHUs

Only one example relates the synthesis of thermoplastic PHUs from fatty acid derivatives. The fatty acid-based bis 5-membered cyclic carbonates were synthesized by a three step process composed of (1) a transesterification of fatty acid methyl esters, (2) an epoxidation of the double bonds and (3) a carbonation of the resulting epoxides. The solubility of the fatty acid or triglyceride-based mono-, bis- and poly-epoxides in supercritical CO₂ has been studied.²³⁵ Three different temperatures (40°C, 70°C and 100°C) and pressures ranging between 0.1 and 20 MPa have been investigated. The measurements were performed using an efficient in situ FTIR method that allows the determination of the variation of the concentration of each component in the two phases (CO₂ rich phase and vegetable oil-based epoxide rich phase) as a function of temperature and pressure. It appears that monoglyceride epoxide derivatives were found to be more soluble in CO₂ and more easily swelled by CO₂ in comparison to the di- and tri-glyceride epoxide derivatives.

Two bis 5-membered cyclic carbonates, internal carbonated fatty acid diester (ICFAD) and terminal carbonated fatty acid diester (TCFAD), prepared from methyl oleate and methyl undecenoate respectively, were polymerized with ethane-1,2-diamine and isophorone diamine to form TPUs containing hydroxyl moieties (Scheme II-1-19).^{236, 237} TBABr was used as the carbonation catalyst.

The TPUs presented molar masses up to 13 500 g.mol⁻¹ and exhibited relatively low glass transition temperatures ranging from -25°C to -13°C. As expected, TCFAD displayed a higher reactivity than ICFAD and poly(TCFAD) had slightly enhanced molar masses and T_g values compared to poly(ICFAD). Nevertheless, an amidation side reaction occurred between amine

functions and the ester linkages of the diester bis cyclic carbonates, giving amide groups. Thus the final polymer structure is affecting due to the competition with urethane linkage formation and the resulting distorted stoichiometry conditions, which can partly explain the low molar masses.^{236, 237}



*Scheme II-1-19- Bis cyclic carbonates and poly(hydroxyurethane)s from fatty acid or fatty acid methyl ester.*²³⁶

Besides, the cyclic carbonates being at the end of a long alkyl chain in vegetable oils derivatives, their reactivity were lower compared to petrochemical systems due to +I inductive effects. Remarkable long polymerization times have been reported as well in vegetable oils-based PHU networks.^{221, 228, 231}

3.3- Toward vegetable oils-based diamines

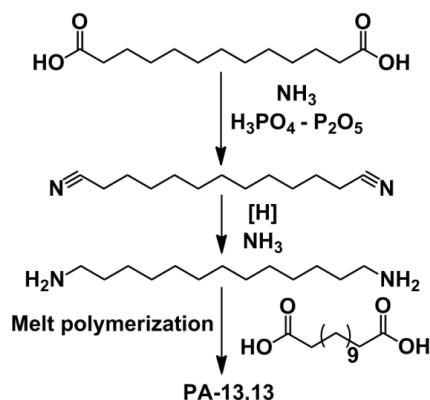
Bio-based amine compounds are nowadays definitely required notably in the polymer field for polyamides, epoxy resins and more particularly in non-isocyanate PHUs. Indeed, bio-based bis-cyclic carbonates have been widely prepared, while only few examples of vegetable oil-based amines have been reported in PA or epoxy resin synthesis. To the best of our knowledge, no reports refer to the use, in non-isocyanate PUs and TPUs, of vegetable oil-based diamines.

Vegetable oil-based amines have been prepared either (i) by bringing the amine moiety (or equivalent) via thiol-ene reaction, ring opening of triglycerides epoxy intermediates with an excess of diamines or metathesis reaction with acrylonitrile, or (ii) by the direct synthesis of the amine function into the triglyceride derivatives via the synthesis of nitrile, amide, acyl azide or bromo intermediates. In all cases, the synthesized amines were used in polyamides or epoxy resins preparation.

Concerning industrial amine-based compounds from fatty acid derivatives; the most prominent example is the AB-type fatty amino acid precursor of PA-11, which is produced from castor oil for nearly fifty years from ricinoleic acid by Arkema under the trade name Rilsan®.^{238, 239} The double bond of undecenoic acid is converted by HBr into the subsequent

bromo-based derivative, which is then transformed in ω -aminoundecanoic acid by reaction with ammonia.²⁴⁰ Another chemical company, Evonik, produced fully bio-based fatty acid-based PA from bio-based decane-1,10-diamine (VESTAMID® Terra, fully bio-based PA-10,10 and PA-10,12).

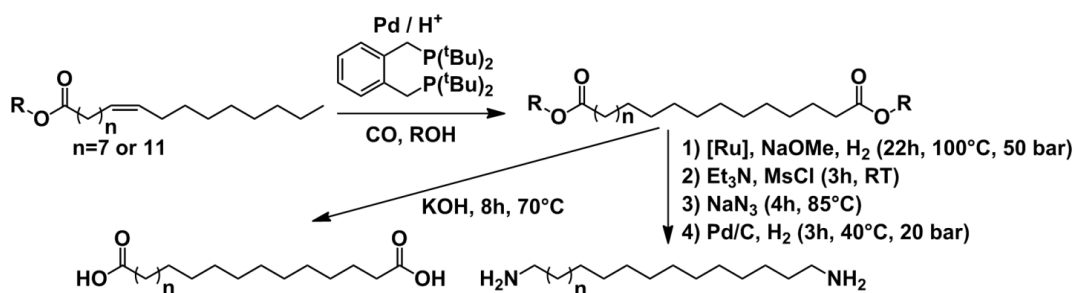
In the 1960s-1970s, the production of tridecane-1,13-diamine, from brassylic acid and of the corresponding PA have been investigated. The diamine synthesis has been performed via a dinitrile intermediate (See Scheme II-1-20) by reaction of brassylic acid with ammonia under specific conditions.^{241, 242}



Scheme II-1-20- Synthesis of PA-13,13 from brassylic acid.^{241, 242}

Very recently, PA-13,6 have been prepared from tridecane-1,13-diamine and adipic diacid.^{243, 244} The amine was synthesized by a multi-step reaction via acyl chloride and amide using thionyl chloride and aqueous ammonia respectively.

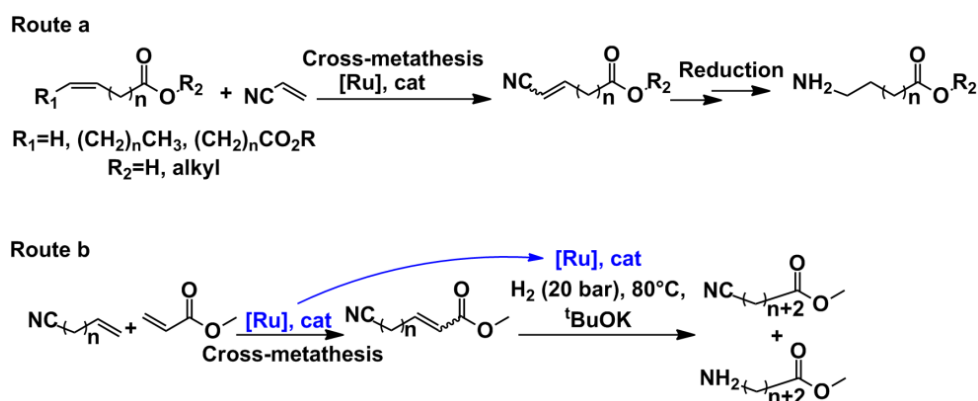
Mecking and coll. have reported on the isomerising alkoxyacylation of either methyl oleate and ethyl erucate followed by hydrolysis yielding C19 (dimethyl 1,19-nonadecanedioate) and C23 (diethyl 1,23-tricosanedioate) long-chain α,ω -diacid compounds in good purity.²⁴⁵ C19 and C23 diamines were obtained via a four-step reaction through diol then dimesylate and finally diazide compounds. (See Scheme II-1-21) The polycondensation of the diester compounds with their respective diamine derivatives resulted in PA with molar mass around 10 kg.mol⁻¹. PA-23,19 and PA-23,23, based on tricosane-1,23-diamine, exhibited a Tm of 156°C and 152°C respectively.



Scheme II-1-21- Synthesis of diacids and diamines from methyl oleate and erucate.²⁴⁵

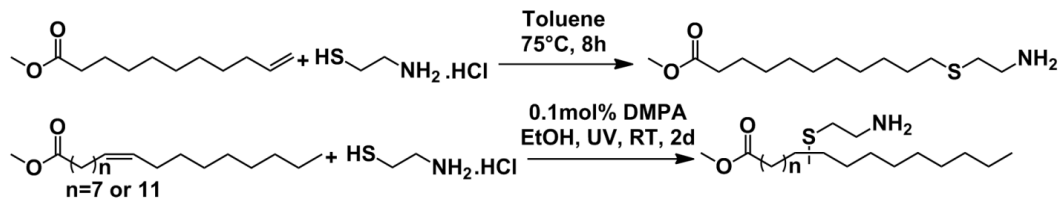
Walther *et al.* have also prepared the nonadecane-1,19-diamine by direct amination of the corresponding diol with excess ammonia at 140°C during 48h in the presence of a ruthenium phosphine catalyst.²⁴⁶ The diol was obtained from the dimethyl ester, directly obtained from the high-oleic sunflower oil via a parallel and/or subsequent sequence of transesterification / isomerization, and methoxycarbonylation. The corresponding polyamides were not prepared.

Another efficient way to produce PA is the polycondensation of aminocarboxylic acids. Greene *et al.* have synthesized 13-aminotridecanoic acid from erucic acid using various methods but PA-13 was not prepared.²⁴⁷ Dixneuf and coll. synthesized amino esters from methyl 10-undecenoate, dimethyl octadec-9-en-1,18-dioate and methyl ricinoleate using a two-step reaction involving a metathesis reaction between the unsaturated fatty acid derivatives and acrylonitrile followed by reduction to the amine formation (route a in Scheme II-1-22).²⁴⁸ The best protocol was based on the slow addition of catalyst, which allowed turnover numbers as high as 1900 (92% yield). In a second study, the same group analyzed a route involving the cross-metathesis of 10-undecenenitrile arising from castor oil with methyl acrylate (route b in Scheme II-1-22).²⁴⁹ Under optimal conditions a turnover number of 17200 (86% yield) of the fatty acid-based nitrile is obtained. Hydrogenation of the C-C double bond and the nitrile moieties finally gives access to the amino ester. This procedure was preferred to the cross metathesis between the fatty acid esters and the acrylonitrile due to higher turnover numbers. This amino ester, prepared by this sustainable way, could be useful for PA synthesis. Indeed, a single catalyst is introduced to perform three catalytic transformations (cross-metathesis, C-C double bond hydrogenation and nitrile reduction) from methyl acrylate and undecenenitrile, which are potentially bio-based substrates.



Scheme II-1-22- Synthetic routes to amino esters by sequential metathesis and hydrogenation reactions.^{248, 249}

Meier and coll. prepared fatty acid-based PA by AB polycondensation. The amine groups have been incorporated into methyl undecenoate, methyl oleate and methyl erucate by thiol-ene reaction with cysteamine hydrochloride, followed by subsequent neutralization (Scheme II-1-23).²⁵⁰ PA and copolyamides, with dimethyl adipate and hexane-1,6-diamine, were obtained with molar masses ranging from 4 kg.mol⁻¹ to 20 kg.mol⁻¹.



*Scheme II-1-23- Thiol-ene reaction with cysteamine hydrochloride on methyl undecenoate, oleate and erucate.*²⁵⁰

Very recently, Meier and coll. used the Wohl-Ziegler bromination to prepare brominated fatty acid derivatives, the latter being transformed into amine after reaction with NaN₃ and the subsequent reduction with H₂.²⁵¹ The AB monomers were then polymerized to obtain polyamides with 6500 and 7900 g.mol⁻¹ and dispersities of 1.4 and 1.49. The same group recently reported the reductive amination (NH₄Cl/NH₄OAc, Ra-Ni, 40 Bar H₂) of keto-fatty acid esters for the preparation of PAs and PA6,6 co-polyamides. The latter were synthesized by co-catalyst free Wacker oxidations of methyl oleate and methyl erucate.²⁵²

Conclusion

In this first chapter of the Part II, the literature toward more sustainable PUs has been reported. First the main different routes to non-phosgene or non-isocyanates have been presented briefly. In a second part, one of the most promising route to non-isocyanates and non-phosgene PHU has been developed in details, regarding the synthesis of cyclic carbonates and amines, the corresponding model reaction and polymerization (molar masses, catalysts, post-functionalization...). Vegetable oils have already been used to prepare cyclic carbonates for PHUs and amine compounds essentially for polyamides. However, it has been found that synthesizing the 5-membered cyclic carbonate from the double bond of vegetable oils lead to poor reactivity (+I inductive effect) of the obtained cyclic carbonate. Besides, in some cases, the formation of amide side reactions is observed due to the inherent presence of ester functions. In this context, we worked both on the preparation of amide-based bis 5-membered cyclic carbonates, more active bis 6-membered cyclic carbonates and diamines from vegetable oil derivatives.

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PART II - Chapter 2: Vegetable oils- based non-isocyanate PHUs *via* 5-membered cyclic carbonates

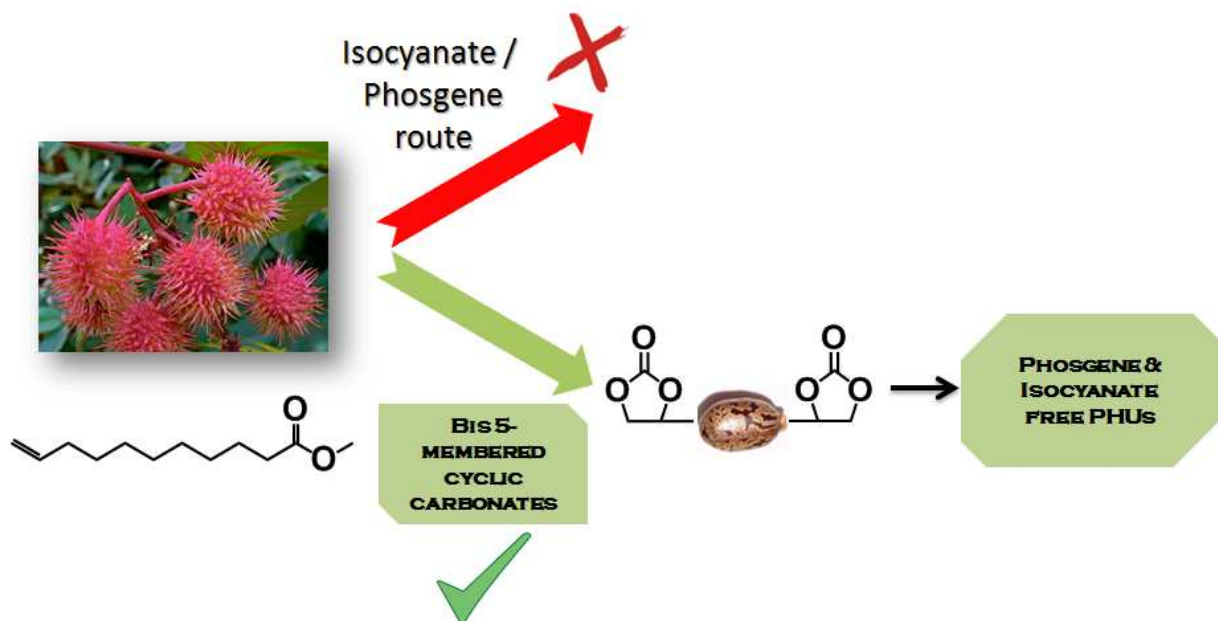


Table of contents

Introduction	150
1- Monomer synthesis	150
1.1- Bis epoxides intermediates	151
1.1.1- Transesterification and amidation	151
1.1.2- Epoxidation reaction	155
1.2- The bis 5-membered cyclic carbonate by carbonation with CO₂	155
2- Polymerization	159
2.1- Synthesis of PHUs and related molar masses	159
2.2- Thermo-mechanical properties	163
3- Catalysis of a model reaction	166
Conclusion and limitations	170
References	170
Experimental and supporting information	171

Introduction

This second chapter of Part II is dedicated to the design of fatty acid bis 5-membered cyclic carbonates bearing mainly stable amide linkages with the idea of preparing non-isocyanate thermoplastic PHUs with high molar masses and glass transition temperatures. Symmetrical bis 5-membered cyclic carbonates were prepared from methyl undecenoate by a sequence of (i) transesterification and/or amidation followed by (ii) epoxidation and (iii) carbonation reaction in CO₂, to synthesize linear PHUs with controlled properties from fatty acid derivatives. To achieve a large range of PHUs properties, various chemical structures of central blocks have been used. Besides, to lower the 5-membered cyclic carbonates melting points, co-reactants such as piperazine, N,N'-dimethylpropane-1,3-diamine and N,N'-dihexyldecane-1,10-diamine have been used. The so-formed monomers were characterized with FTIR-ATR, NMR and GC-FID.

By polyaddition of the bis cyclic carbonates and diamines, a plethora of linear fatty acid-based poly(hydroxy amide urethane)s have been synthesized without employing neither toxic and unstable diisocyanates, nor phosgene. FTIR-ATR, NMR, SEC, DSC and TGA were performed to investigate the PHUs chemical structures, molar masses, thermo-mechanical properties and thermal stabilities. Finally, with the idea of enhancing the polymerization rates and reducing the polymerization temperatures, the catalysis of a model reaction between propylene carbonate and hexylamine amine has been furthermore investigated by FTIR-ATR monitoring, as presented in the third part of this chapter.

1- Monomer synthesis

To synthesize linear PHUs from fatty acid derivatives, five bis 5-membered cyclic carbonates were prepared starting from methyl undecenoate by (i) transesterification and/or amidation followed by (ii) epoxidation and (iii) carbonation reaction. The Figure II-2-1 illustrates the chemical structures of the synthesized bis 5-membered cyclic carbonates. The central blocks of the 5-membered cyclic carbonates were of different nature so as to design PHUs with different thermo-mechanical properties. One bis 5-membered cyclic carbonate presents two ester groups (UndPdE-b5CC) and the others have two amide linkages. Amide functions were introduced into the 5-membered cyclic carbonates owing to their ability of strong hydrogen

bonding formation, but more particularly due to the possibility of amidation side reactions with ester functions. Among the diamide bis 5-membered cyclic carbonates, UndBdA-b5CC is issued from butane-1,4-diamine, which allows the formation of hydrogen bonds with the CONH group. In order to obtain diamide bis 5-membered cyclic carbonates with lower and lower melting point, piperazine (UndPipdA-b5CC), N,N'-dimethylpropane-1,3-diamine (UndPMedA-b5CC) and N,N'-dihexyldecane-1,10-diamine (UndDHexdA-b5CC) were used as central blocks. As it has been reported in literature that internal 5-membered cyclic carbonates were less reactive than terminal ones¹, methyl undecenoate was thus preferred as starting material. The chemical structure of the synthesized bis 5-membered cyclic carbonates and intermediates was evaluated by ¹H and ¹³C NMR and FTIR-ATR spectroscopies.

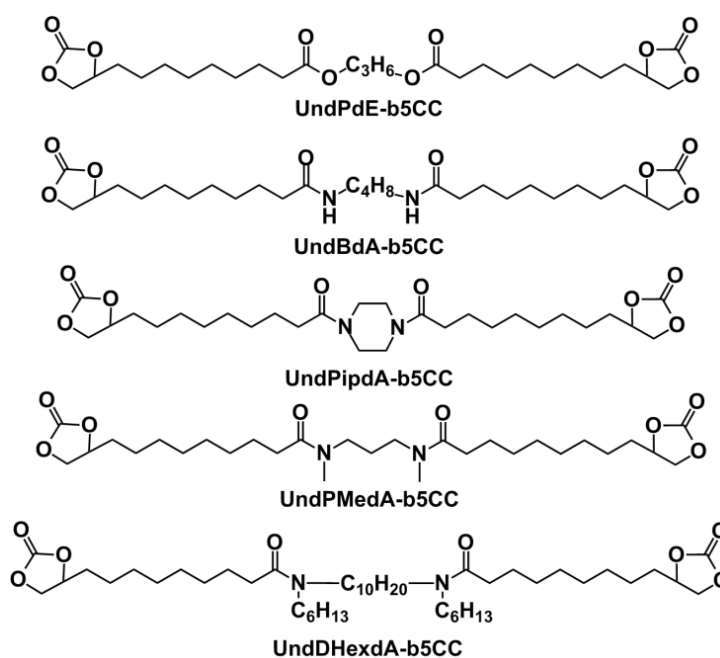
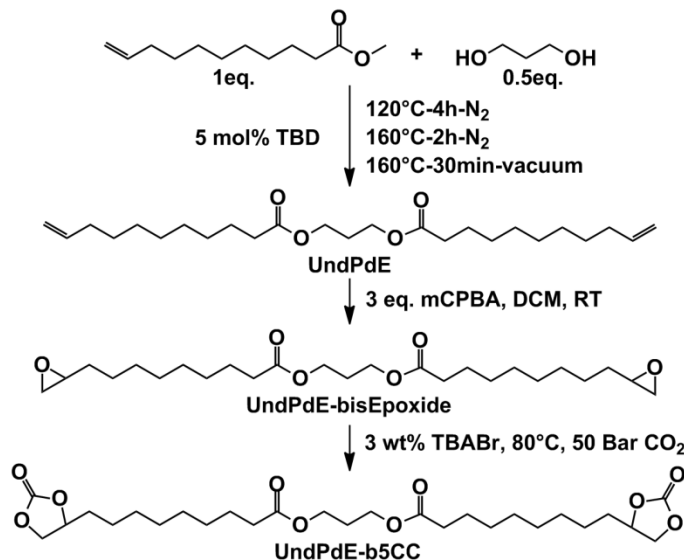


Figure II-2-1- Chemical structures of the synthesized bis 5-membered cyclic carbonates. Abbreviations used are as follows: [Und = from methyl undecenoate; [P = propyl, B = butyl, Pip= from piperazine, PMe= from N,N'-dimethylpropane-1,3-diamine, DHex= from N,N'-dihexyldecane-1,10-diamine]; [d = di-] and [E = ester, A = amide, b5CC=bis 5-membered cyclic carbonate].

1.1- Bis epoxides intermediates

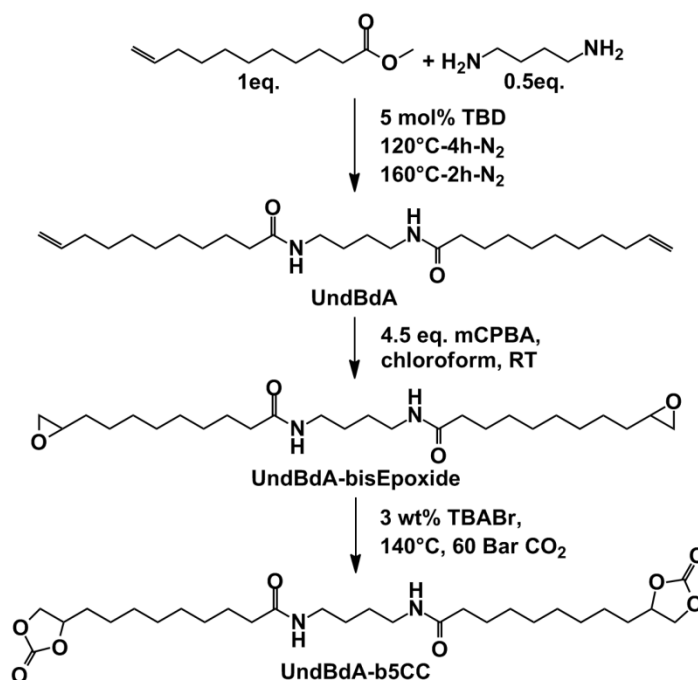
1.1.1- Transesterification and amidation

As presented in the Scheme II-2-1, the first step for the synthesis of UndPdE-b5CC is the transesterification of methyl undecenoate with 1,3-propanediol. This reaction has been performed in the same conditions as presented in the Part I - Chapter 2 and so will not be described again in this chapter.



Scheme II-2-1- Synthetic pathway to UndPdE-b5CC from methyl undecenoate, 1,3-propanediol and CO₂.

The Scheme II-2-2 illustrates the synthesis of UndBdA-b5CC from methyl undecenoate and butane-1,4-diamine. The syntheses of UndPipdA-b5CC, UndPMedA-b5CC and UndDHexdA-b5CC have been carried out in the same way with slight variations of the catalyst quantity, the solvent, the temperature and the pressure. (See experimental methods section). The amidation conditions of UndBdA are identical to the ones reported in the Part I - Chapter 2. For UndPipdA-b5CC and UndPMedA-b5CC, the amidation reactions were performed under inert atmosphere at 100°C (2h), then under nitrogen flow at 120°C (4h) and at 160°C (2h).



Scheme II-2-2- Synthetic strategy to UndBdA-b5CC from methyl undecenoate, butane-1,4-diamine and CO₂.

In the specific case of UndDHexdA-b5CC, the N,N'-dihexyldecane-1,10-diamine (SebHex-diamine) has first been prepared by the reduction of the corresponding diamide, which was obtained from sebacoyl chloride and hexylamine. Then the reaction between SebHex-diamine and methyl undecenoate was investigated but no conversion was observed probably due to the lower reactivity of the SebHex-diamine. This observation led to the use of more reactive undecenyl chloride instead of methyl undecenoate.

In all cases, the amidation reactions were monitored by means of FTIR-ATR and ^1H NMR spectroscopies. The stacked FTIR-ATR of the different steps to UndBdA-b5CC and of the synthesized bis 5-membered cyclic carbonates are given in Figure II-2-2 and Figure II-2-3 respectively. The FTIR-ATR of UndBdA showed two absorption bands at 1630 cm^{-1} and 1537 cm^{-1} , whereas as expected UndPipdA, UndPMedA and UndDHexdA FTIR-ATR spectra presents only the amide carbonyl stretching vibration in the range 1650 cm^{-1} - 1639 cm^{-1} . The ester carbonyl stretching ($\text{O}=\text{C}-\text{O}$) of the methyl undecenoate at 1720 cm^{-1} disappeared during all diamide syntheses. The UndBdA displayed also a band at 3295 cm^{-1} characteristic of N-H stretching vibrations. (See Figure II-2-2-(1) and Figure II-2-2-(2)) When necessary, the diamide was purified by flash chromatography to remove the unreacted methyl undecenoate and the monoamide formed.

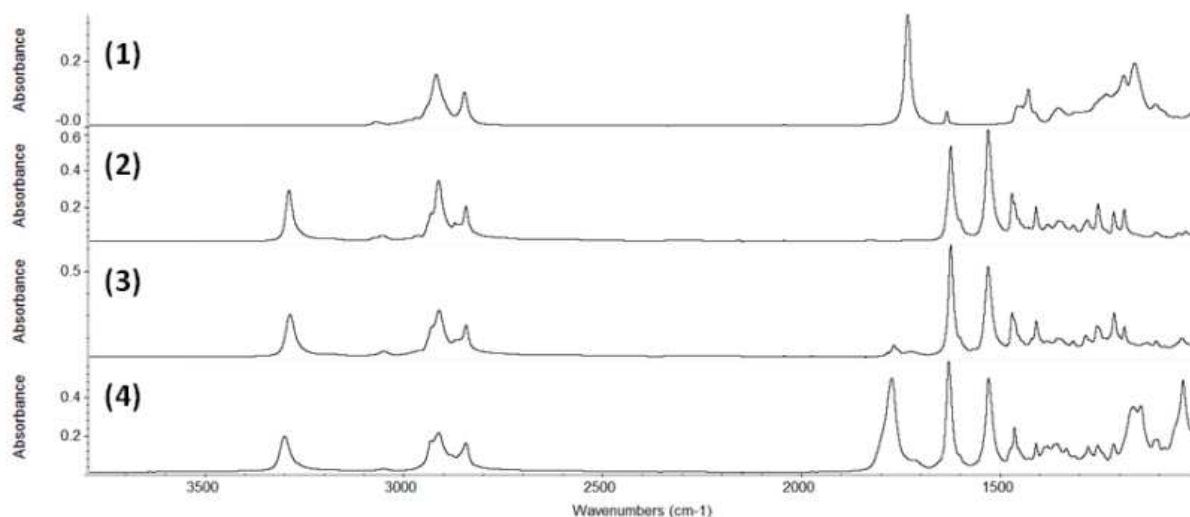


Figure II-2-2- Stacked FTIR-ATR spectra of (1) Methyl undecenoate, (2) UndBdA, (3) UndBdA-bisEpoxide and (4) UndBdA-b5CC.

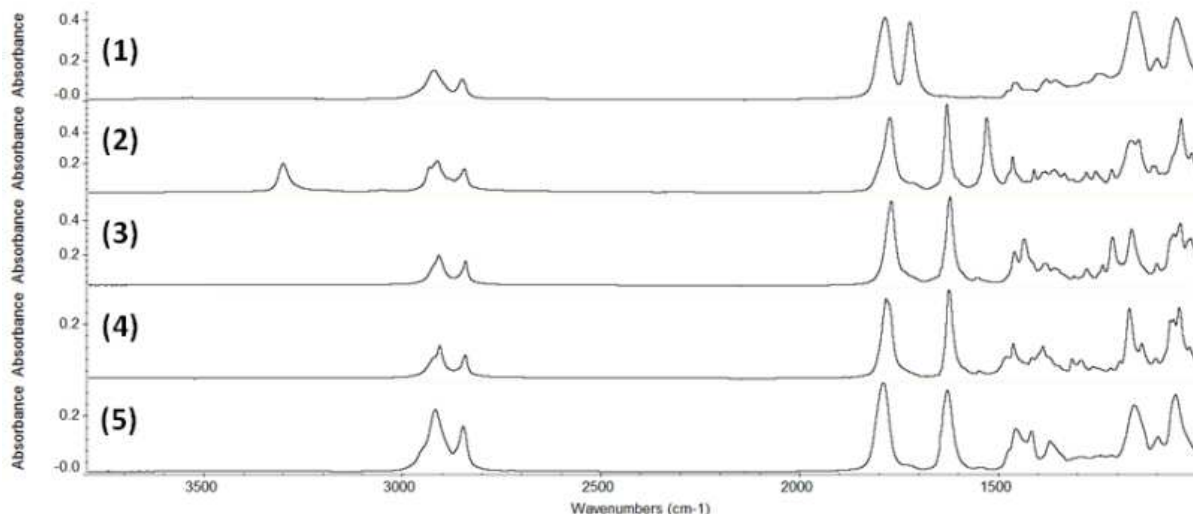


Figure II-2-3- Stacked FTIR-ATR spectra of (1) UndPdE-b5CC, (2) UndBdA-b5CC, (3) UndPipdA-b5CC, (4) UndPMedA-b5CC and (5) UndDHexdA-b5CC.

As an example, the stacked ^1H NMR spectra of the different steps for the synthesis of UndPipdA-b5CC are given in Figure II-2-4. The formation of the amide functions was confirmed in ^1H NMR, by the appearance of a triplet at 2.32 ppm, corresponding to the protons nearby the $\text{C}=\text{ONH}$. (See protons H2 in Figure II-2-4-(1) for UndPipdA) Moreover, the singlet at 3.66 ppm, which is characteristic of the ester moiety of methyl undecenoate, has disappeared.

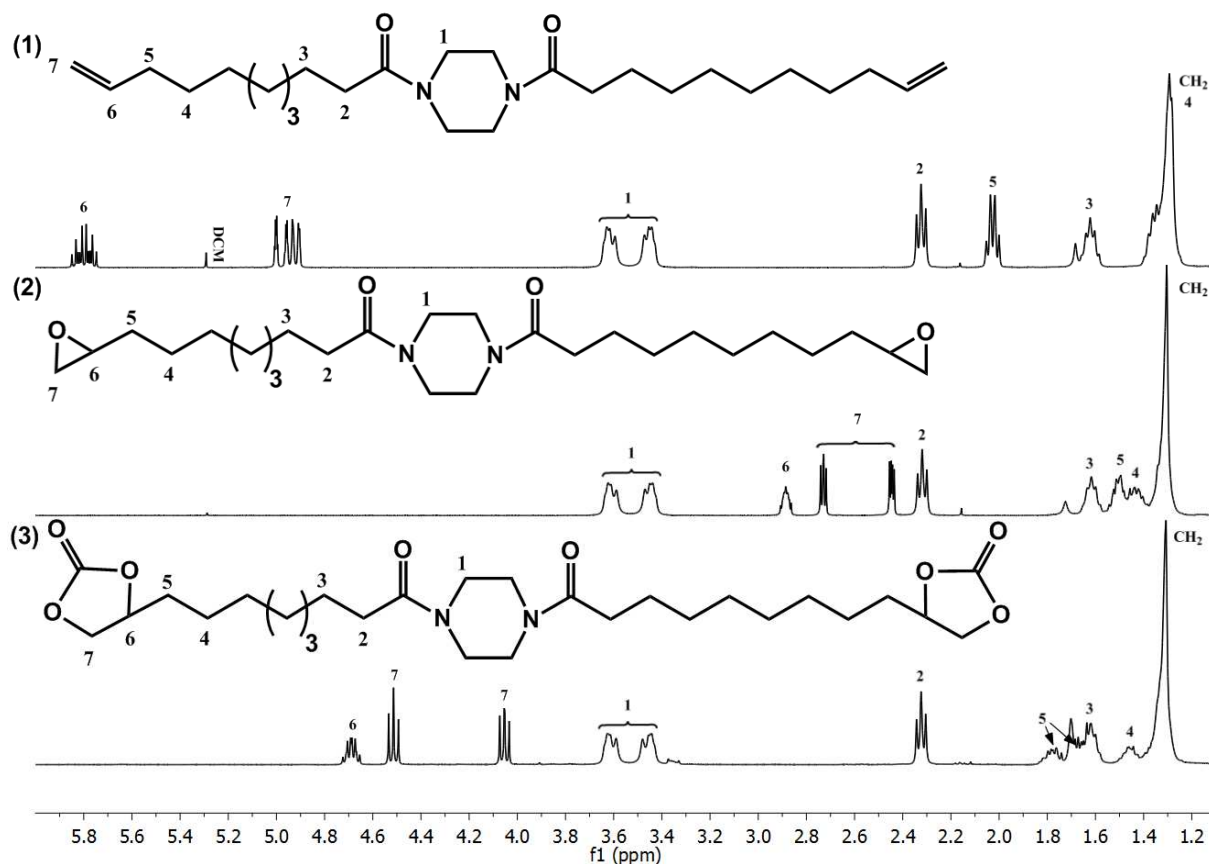


Figure II-2-4- Stacked ^1H NMR spectra of (1) UndPipdA, (2) UndPipdA-bisEpoxide and (3) UndPipdA-b5CC. (Analyses in CDCl_3)

1.1.2- Epoxidation reaction

The epoxidation reactions of the bis unsaturated precursors were performed with m-CPBA according to the previous literature.¹ The reaction progress was followed by the disappearance of double bond protons by ¹H NMR spectroscopy. The synthesis of the epoxide was attested by the formation of the epoxide characteristic peaks. As exposed in the Figure II-2-4-(2) for UndPipdA-bisEpoxide, the multiplets at 2.88 ppm, 2.73 ppm and 2.45 ppm (protons H6 and H7), revealed the formation of the epoxides.

After completion of the epoxidation, the reaction mixture was then successively washed with aqueous sodium sulfite, aqueous sodium bicarbonate and water. The washing with the aqueous solution of sodium sulfite allowed the transformation of the unreacted peroxide into acid. The latter was then neutralized by washings with aqueous sodium bicarbonate and water.

1.2- The bis 5-membered cyclic carbonate by carbonation with CO₂

As presented in the literature, various reaction conditions have been used for the carbonation of epoxide. As the melting point of UndBdA is high, two procedures have been investigated. In the first method, DMF was used as solvent and 2 wt% of LiBr was used. A temperature in the range 80°C-90°C and a pressure of CO₂ equal to 1 Bar were requested to obtain 70% conversion after 12 hours under those conditions. Following another strategy, full conversion was reached after the same time when the reaction was performed in bulk, with 3 wt% of TBABr at 140°C and 60 Bar of CO₂. Despite the need of high temperature and pressure in the second procedure, the first method was ruled out due to the use of toxic DMF as solvent and the difficulties to purify the reaction while using DMF.

Concerning the carbonation of fatty acid-based (poly-) epoxides, solubility studies have first been carried out by our partner from the *Institut des Sciences moléculaires (ISM)* at three different temperatures (40, 70 and 100°C) and pressures ranging between 0.1 and 20 MPa.¹
² The pressure–composition phase diagrams of the epoxidized vegetable oil/CO₂ binary mixtures have then been established. They demonstrated that the epoxidized fatty acid methyl esters were more soluble in CO₂ and more easily swelled by CO₂ in comparison to the di- and tri-glyceride derivatives. Nevertheless, a significant amount of CO₂ was incorporated at relatively moderate pressures in all these epoxidized vegetable oil derivatives.

For the carbonation of epoxides using CO_2 , numerous catalysts have been reported in the literature, as presented previously.³⁻⁶ In this thesis, in partnership with S. Foltran and T. Tassaing from the *ISM*, the use of three salts has been investigated on the carbonation of UndPdE-bisEpoxide. The latter presented the advantage to have a low melting point. The reactions were carried out at 80°C with 50 Bar of CO_2 and 3 wt% of catalysts. The progress of the carbonation was monitored by in situ FTIR in a home-made stainless steel cell by the disappearance of the band at 825 cm^{-1} (asymmetric stretching of the epoxide) and the appearance of the signal at 775 cm^{-1} (cyclic carbonate). (See Figure II-2-5). The Figure II-2-6 illustrates the appearance of the band at 775 cm^{-1} during the carbonation reaction of UndPdE-bisEpoxide at 80°C with 50 Bar of CO_2 and 3 wt% of different catalysts. While full conversion was obtained after 8 hours with the 1-methyl-3-methylimidazolium iodide salt (MMII) as catalyst, higher reaction times of 15 hours and 22 hours were necessary for the full conversion with the ammonium salt (tetra-*n*-butylammonium bromide - TBABr) and the guanidinium salt (1,5,7-triaza-bicyclo[4.4.0]dec-5-enium bromide - TBD.HBr) respectively. Due to the commercial availability and the relatively good reactivity of TBABr, this catalyst was preferred for all the carbonation reactions.

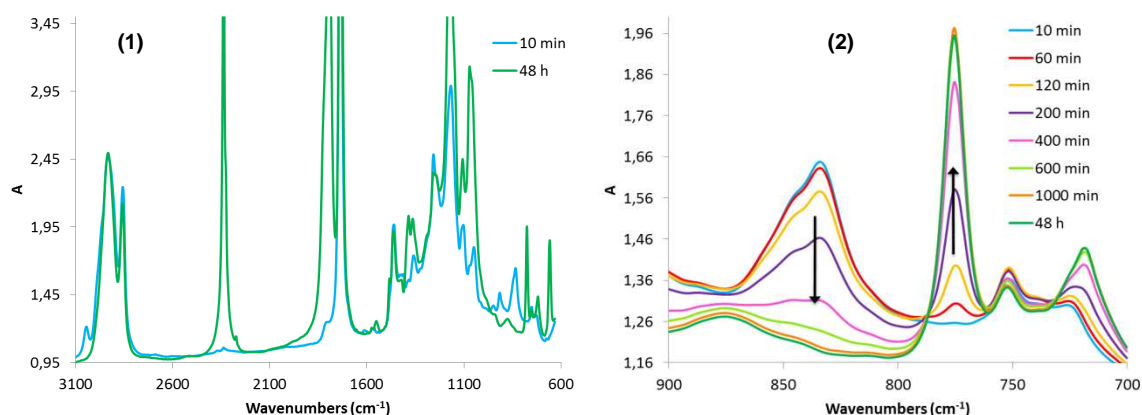


Figure II-2-5- Stacked FTIR spectra of the carbonation reaction of UndPdE-bisEpoxide at 80°C with 50 Bar of CO_2 and 3 wt% TBABr (1) at 10 min and 48 hours and (2) at different reaction times with a focus between 900 cm^{-1} and 700 cm^{-1} .

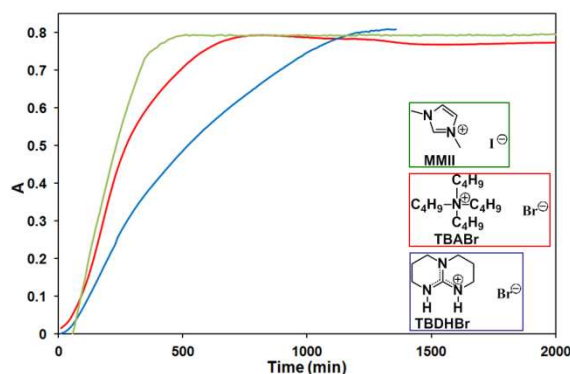
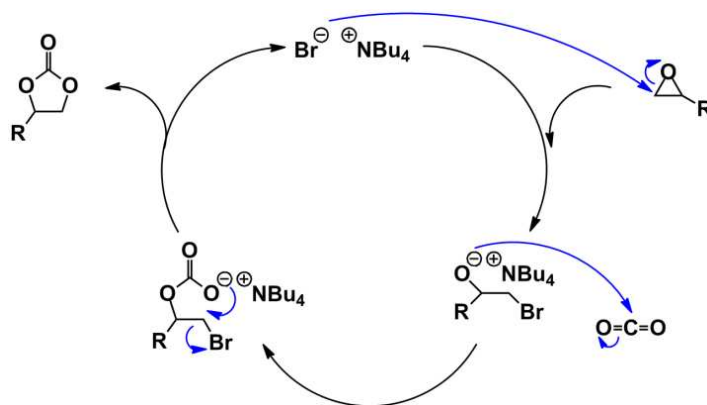


Figure II-2-6- Evolution of the absorbance of the band at 775 cm^{-1} during the carbonation reaction of UndPdE-bisEpoxide at 80°C with 50 Bar of CO_2 and 3 wt% catalyst.

The mechanism of the carbonation reaction of epoxides with CO₂ using TBABr has already been reported in the literature and is illustrated in Scheme II-2-3.^{3,4}



Scheme II-2-3- Reported plausible mechanism for the carbonation reaction of epoxide with CO₂ using TBABr.⁷

After 24 hours, full conversion was attained for all fatty acid-based bis epoxides using the following reaction conditions: 80°C / 50 Bar for UndPdE-bisEpoxide, UndPMedA-bisEpoxide and UndDHexdA-bisEpoxide, 135°C / 50 Bar for UndPipdA-bisEpoxide and 140°C / 60 Bar for UndBdA-bisEpoxide. Indeed, the study of UndBdA-bisEpoxide carbonation using the in situ FTIR revealed the need of a CO₂ pressure of 60 Bar to obtain a homogeneous mixture and a subsequent effective reaction. Therefore a pressure of 60 Bar was used for the carbonations of UndBdA-bisEpoxide in larger quantity.

After reaction, a band in the range 1795 cm⁻¹ - 1775 cm⁻¹, corresponding to the carbonyl vibration of the cyclic carbonate was visible for all synthesized 5-membered cyclic carbonates. (See Figure II-2-2-(4) and Figure II-2-3) The formation of the cyclic carbonate was also confirmed by ¹H NMR, as illustrated in the Figure II-2-7. For instance, the ¹H NMR spectra of UndPipdA-bisEpoxide and UndPipdA-b5CC clearly demonstrate the formation of the 5-membered cyclic carbonate. (See protons H6 and H7 in Figure II-2-4-(2) and Figure II-2-4-(3)) In the case of UndPMedA-b5CC, ¹H NMR has been performed at 60°C, 80°C and 90°C in order to confirm the chemical structure of the monomer. (See SI Figure II-2-1)

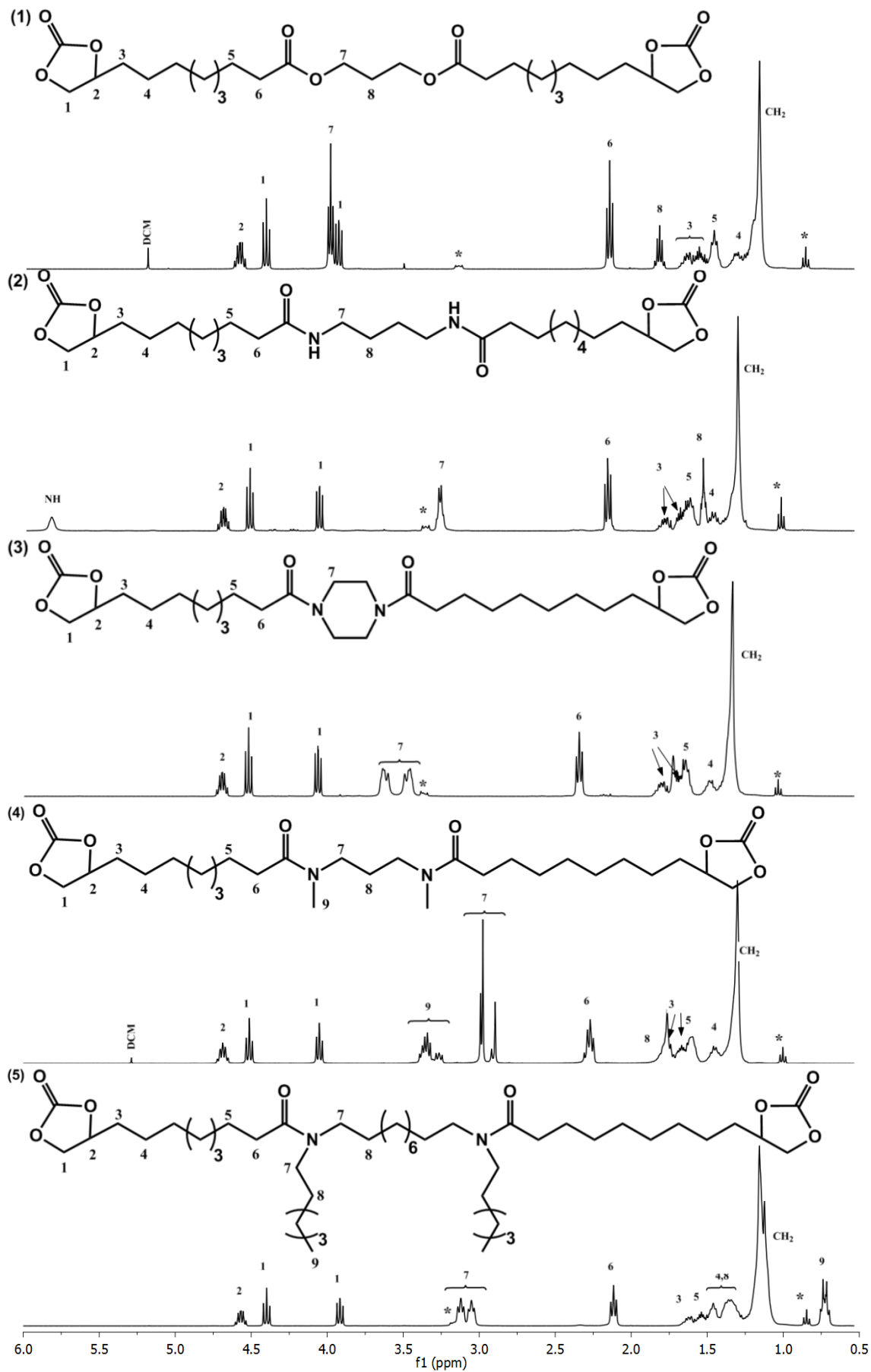


Figure II-2-7- Stacked ^1H NMR spectra of (1) UndPdE-b5CC, (2) UndBdA-b5CC and (3) UndPipdA-b5CC, (4) UndPMedA-b5CC and (5) UndHexdA-b5CC. (*) TBABr. (Analyses in CCl_3)

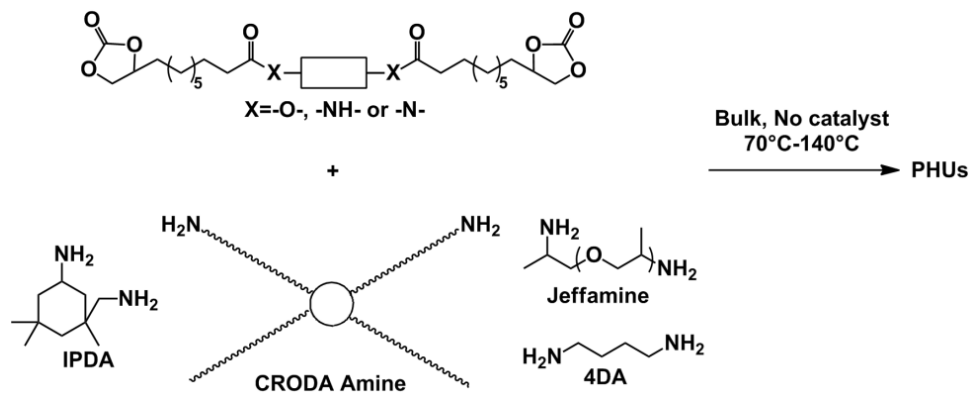
The purity (when possible) and melting points of the monomers, as well as the ^1H - ^{13}C HSQC-NMR analysis for UndPipdA-b5CC are given in supporting information (See SI Table II-2-1 and SI Figure II-2-2). Amide-containing 5-membered cyclic carbonates showed higher melting points than UndPdE-b5CC. While removing the possibility of H bond and bringing flexibility with pendent groups/chains to the central block, lower melting points were observed.

2- Polymerization

2.1- Synthesis of PHUs and related molar masses

To prepare a wide range of fatty acid-based non-isocyanates PHUs, the synthesized bis 5-membered cyclic carbonates were used in polyaddition with four diamines; butane-1,4-diamine (4DA), isophorone diamine (IPDA), CRODA diamine and Jeffamine 400. The diamines IPDA, CRODA and Jeffamine 400 were used to introduce flexibility in the PHUs, by increasing the free volume between the polymer chains. The Scheme II-2-4 illustrates the synthesis of PHUs. First polymerization tests were carried out in solvent, but the reactions were really too slow. Thus, the polyadditions were performed in bulk at a temperature depending on the melting point of the bis 5-membered cyclic carbonate used 140°C (for UndBdA-b5CC and UndPipdA-b5CC), 120°C (for UndPMedA-b5CC and UndDHexdA-b5CC) and 70°C or 110°C/120°C for UndPdE-b5CC). High temperatures were necessary to have homogeneous mixtures. However, even at high temperature; the blends were not fully homogeneous while using UndBdA-b5CC or IPDA, due to the hydrogen bonds and cyclo aliphatic structure.

The polymerizations were monitored with FTIR-ATR, and the obtained PHUs were brown to yellow and viscous to solid in nature. The Table II-2-1 gives the experimental details along with the abbreviations used for the PHUs, as well as the polymerizations results.



Scheme II-2-4- Synthesis of fatty acid-based poly(hydroxyurethane)s.

The chemical structures of the polymers were assessed by FTIR-ATR and ^1H NMR spectroscopies. The appearance of bands around 1700 cm^{-1} and 1539 cm^{-1} , corresponding to the vibrations of C=O-NH and CN respectively, attested to the formation of urethane linkage. Besides, a large band attributed to the NH and OH vibrations can be observed in the region 3656 cm^{-1} - 3123 cm^{-1} . The ester and amide moieties of the precursor bis 5-membered cyclic carbonates were well preserved. The FTIR-ATR spectra of PHU-BdA-1, PHU-PipdA-1, PHU-PMedA-1 and PHU-DHexdA-1 are given in Figure II-2-8.

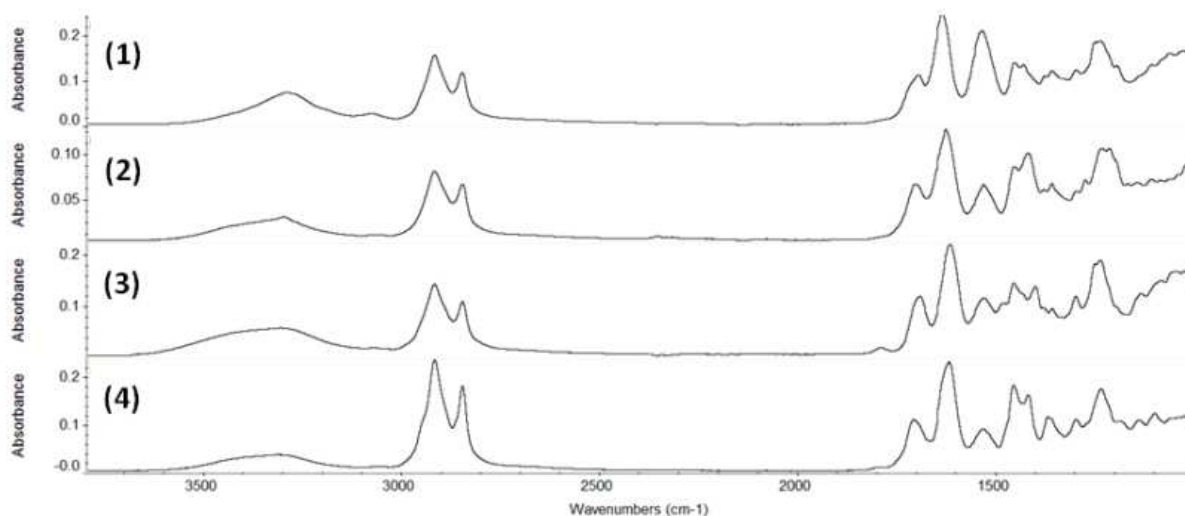


Figure II-2-8- Stacked FTIR-ATR spectra of PHU-BdA-1, PHU-PipdA-1, PHU-PMedA-1 and PHU-DHexdA-1.

As illustrated in the Figure II-2-9, the synthesis of PHU was assessed by the formation of a clearly visible peak at 3.15 ppm. Besides, the peaks corresponding to the cyclic carbonates decreased with conversion. The signals corresponding to the hydroxyl urethanes can be attributed, and one can notice the formation of around 50%:50% of the form with the primary alcohol and the one with the secondary alcohol. As an example, for PHU-PipdA-2 the ratio between the formation of primary and secondary alcohol was 43.8%:56.2%.

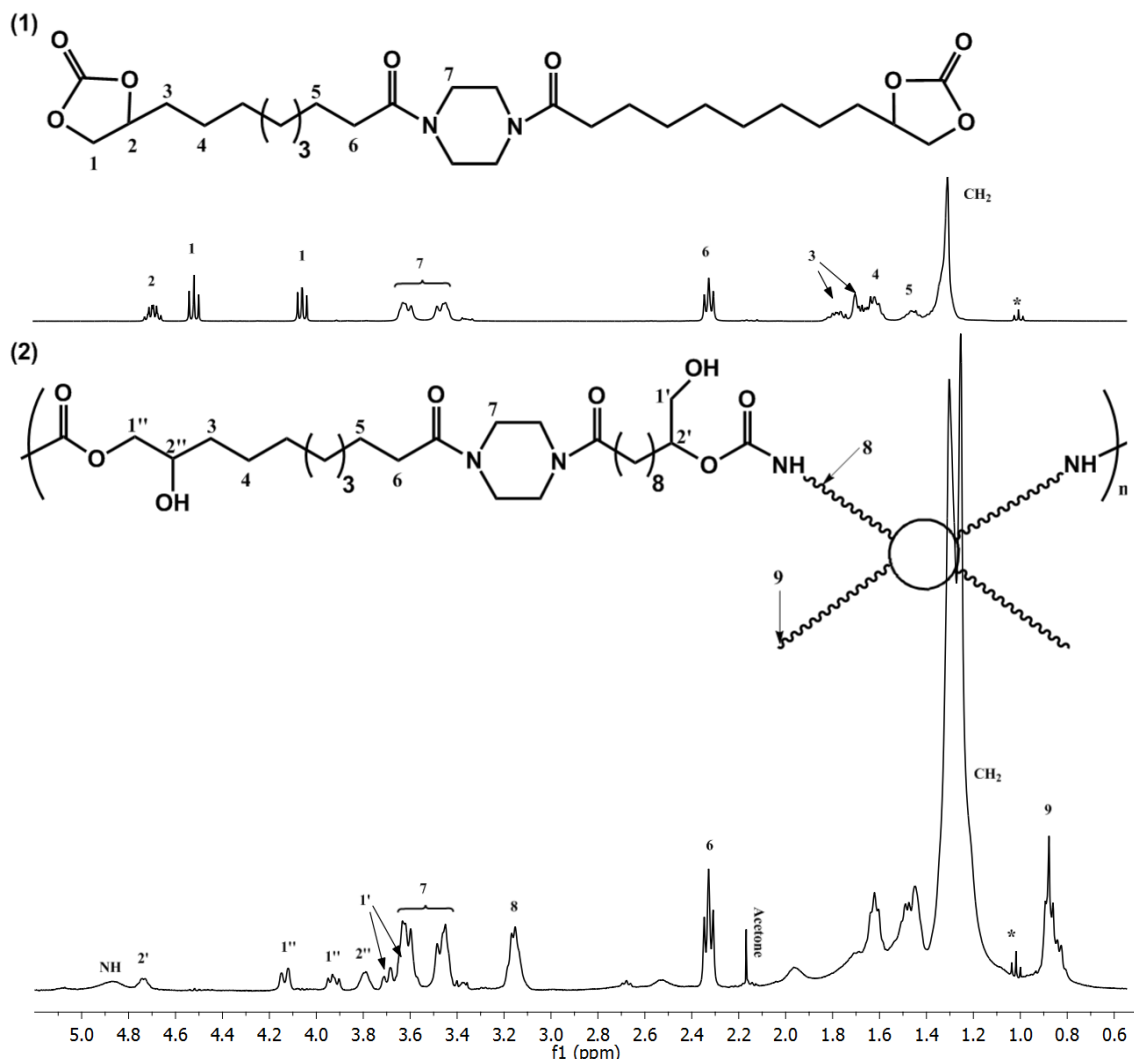


Figure II-2-9- Stacked ^1H NMR spectra of PHU-PipdA-2. $(^{21})$ TBABr. (Analyses in CDCl_3)

It can be noticed from the Table II-2-1 that the conversions were relatively fast at the beginning with conversions in the range 60%-95% after 5 hours. However, no full conversions were achieved in most of the cases even after long polymerization times. Besides, the polymerizations with CRODA amine were much faster than with IPDA and Jeffamine, probably due to the unhindered character of the amine.

SEC data, which are exposed in Table II-2-1, indicate the formation of PHUs with molar masses in the range 11 000 to 31 000 $\text{g}\cdot\text{mol}^{-1}$ after one to 12 days in bulk at the polymerization temperature (70°C to 140°C). However, the molar mass values provided by SEC should not be taken as absolute values as the SEC calibration was carried out in DMF using PS standards. As an example, the Figure II-2-10 illustrates the SEC analysis of PHU-PMedA-2. The molar mass dispersities were in the range of 1.2 to 2.9. The molar masses data given in the Table II-2-1 correspond to the main peak observable in SEC.

However, in almost all analyses, a smaller peak around 4 000 g.mol⁻¹ can be detected and could be attributed to the presence of cycles. In the MALDI-TOF MS analyses of the PHUs, the repeating unit was identifiable together with peaks of side products, which were not assigned.

Table II-2-1- Molar masses and dispersities of the PHUs from bis 5-membered cyclic carbonates polymerized in bulk.

Sample	Used b5CC	Diamine	Temperature (°C)	Time	Conversion (%) ¹	\bar{M}_n (g.mol ⁻¹) ²	Dispersity ²
PHU-dE-1	UndPdE-b5CC	4DA	70	1d	95.1	25 400	1.6
				3d	95.6	29 800	1.8
				7d	96.4	30 400	2.5
PHU-BdA-1	UndBdA-b5CC	IPDA	140	5h	64.1	15 300	1.3
				13d	97.6	18 900	2.4
PHU-BdA-2	UndBdA-b5CC	CRODA	140	5h	97.6	14 900	1.5
PHU-BdA-3		Jeffamine	140	5h	84.3	14 600	1.3
				6d	98.9	20 900	2.6
PHU-PipdA-1	UndPipdA-b5CC	IPDA	140	5h	76.3	16 500	1.5
				1d	87.0	18 200	1.5
PHU-PipdA-2	UndPipdA-b5CC	CRODA	140	5h	91.9	19 300	1.7
				1d	93.2	19 200	1.7
PHU-PipdA-3		Jeffamine	140	5h	46.7	11 200	1.2
				3d	91.5	23 300	2.9
PHU-PMedA-1	UndPMedA-b5CC	IPDA	120	5h	53.5	11 000	1.2
				12d	91.5	31 100	2.2
PHU-PMedA-2	UndPMedA-b5CC	CRODA	120	5h	87.6	mm ³	mm ³
				6d	94.4	28 700	1.7
PHU-PMedA-3		Jeffamine	120	5h	12.4	mm ³	mm ³
				6d	84.1	20 700	1.4
PHU-DHexdA-1	UndDHexdA-b5CC	IPDA	120	1d	ns	ns	ns
PHU-DHexdA-2		CRODA	120	1d	nd	nd	nd
PHU-DHexdA-3		Jeffamine	120	1d	nd	nd	nd
PHU-DHexdA-4		4DA	120	1d	nd	nd	nd

(1) Calculated by FTIR-ATR using the equation: $x = 100 - \frac{(H_{CC}/H_{Ad})_t}{(H_{CC}/H_{Ad})_{t=0}} * 100$, where x , t , H_{CC} and H_{Ad} are the conversion, the time, the height of the peaks corresponding to the cyclic carbonate and amide (or ester) carbonyls respectively. (2) SEC in DMF with 1 wt% LiBr - calibration PS standards. The analyses were performed on the soluble fraction. The given data correspond to the main peak in SEC. The results presented here are for the fraction at 5h and for the best molar masses fraction or the last soluble fraction observed for each sample. (3) Highly multi modal molar masses. ns=not soluble and nd=not determined.

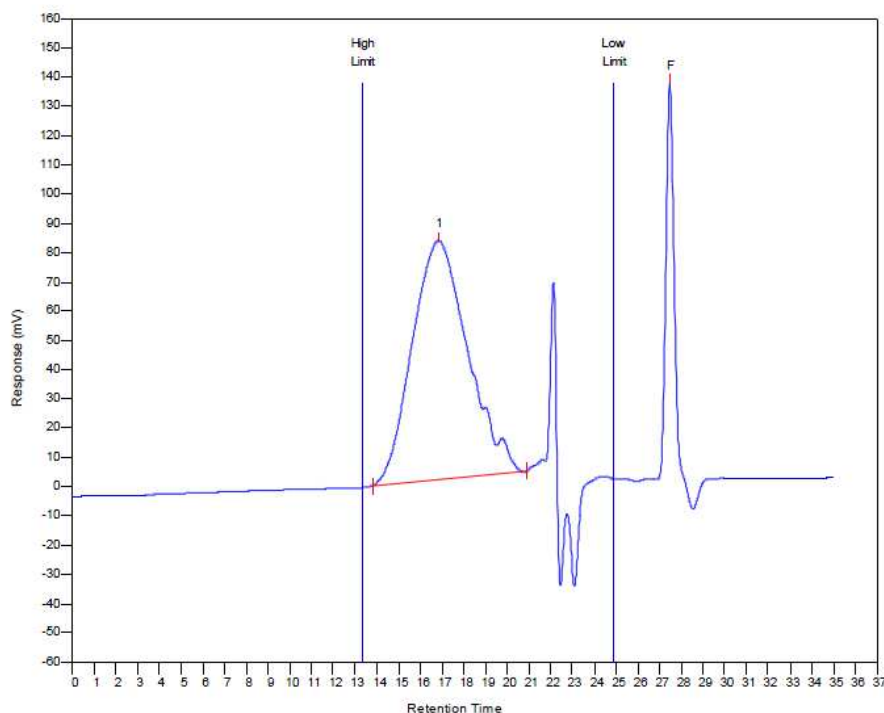


Figure II-2-10- SEC analysis of PHU-PMedA-2 (SEC in DMF with 1 wt% LiBr - calibration PS standards).

The fatty acid bis 5-membered cyclic carbonates are stabilized with the +I inductive effect of the alkyl chain and thus demonstrate low reactivity, even at high temperatures. No full conversions were achieved even after long polymerization times. Moreover, after long times at high temperature, side reactions started to occur. In FTIR-ATR, those side reactions could be attributed to ester or dialkyl carbonate formation. (See SI Figure II-2-3 for PHU-PMedA-2) The apparition of side reactions matched with slight decreases of the molar masses and of the glass transition temperature. (See SI Table II-2-2)

This observation explains the choice to decrease the melting points of the synthesized bis 5-membered cyclic carbonates to then polymerize them in bulk at lower temperature.

Afterwards, the synthesized fatty acid PHUs were analyzed, in terms of thermo-mechanical behavior. (See the next part) Moreover, with a view to reduce the polymerization times and temperatures, the catalysis of the model reaction between propylene carbonate and hexylamine has been examined. (See the third part)

2.2- Thermo-mechanical properties

As in the Part I - Chapter 2, the thermo-mechanical properties of the synthesized PHUs are correlated with their chemical structure. The Table II-2-2 summarized the glass transition and melting temperatures of the PHUs. Amorphous PHUs were obtained with UndPipdA-b5CC, UndPMedA-b5CC and UndDHexdA-b5CC. The cyclic structure of the central

block of UndPipdA-b5CC led to higher T_g. Moreover, the longer the alkyl dangling group or chain is, the lower the glass transition is. (See PHU-PipdA-1, PHU-PMedA-1 and PHU-DHexdA-1 in Figure II-2-11)

Table II-2-2- Thermo-mechanical properties of the synthesized PHUs.

Sample	Time	T _g (°C) ¹	T _m (°C) ¹
PHU-dE-1	1 d	-17	-
PHU-BdA-1	13 d	40	115 ²
PHU-BdA-2	6 d	2	115
PHU-BdA-3	6 d	-21	109
PHU-PipdA-1	6 d	55	-
PHU-PipdA-2	1 d	-2	-
PHU-PipdA-3	6d	-15	-
PHU-PMedA-1	6 d	32	-
PHU-PMedA-2	1 d	-4	-
PHU-PMedA-3	6 d	-17	-
PHU-DHexdA-1	6 d	3	-
PHU-DHexdA-2	1 d	-18	-
PHU-DHexdA-3	6 d	-29	-
PHU-DHexdA-4	1 d	-13	-

(1) Determined by DSC at 10°C.min⁻¹. (2) With crystallization upon heating.

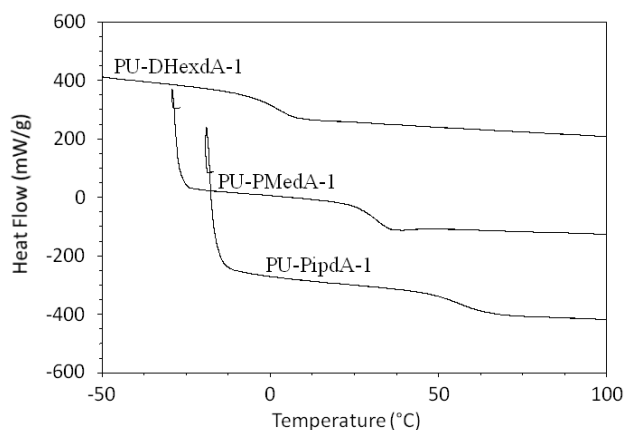


Figure II-2-11- DSC traces of amorphous PHU-PipdA-1, PHU-PMedA-1 and PHU-DHexdA-1.

With UndBdA-b5CC as comonomer, the PHUs obtained were semi-crystalline in nature. The presence of hydrogen bonds from the amide linkages of UndBdA-b5CC favored interactions between polymer chains and thus the crystallization of the resulting PHUs. The effect of the chemical structure of the amine can be observed from the Figure II-2-12 with UndBdA-b5CC. The use of a cyclic aliphatic amine induced the formation of a PHU with a glass transition temperature of 39.9°C. However, while using CRODA diamine, a lower glass transition temperature (2.4°C) was obtained. Indeed, the resulting dangling chains in the polymer

backbone, plasticize the final so-formed PHU. The PHU-BdA-3 with Jeffamine ($400 \text{ g}\cdot\text{mol}^{-1}$) as comonomer reached an even lower glass transition of -21°C , which can be explained by the polyether nature of the Jeffamine. The Figure II-2-12 illustrates the DSC thermograms of the semi-crystalline PHUs based on UndBdA-b5CC with various diamines.

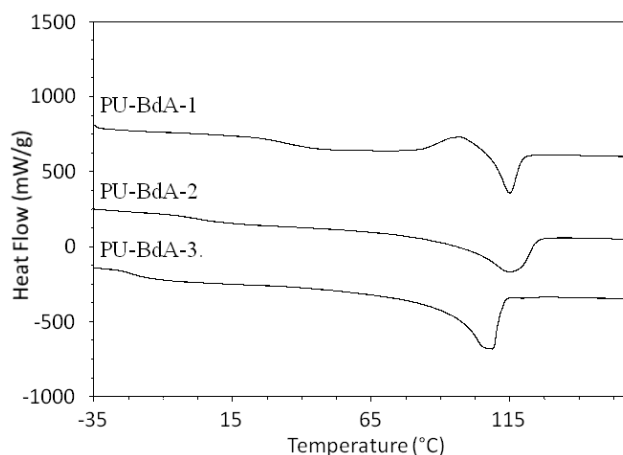


Figure II-2-12- DSC thermograms after second heating of semi-crystalline PHU-BdA-1, PHU-BdA-2 and PHU-BdA-3.

The properties of PHU-BdA-1 can be compared to some extent to the ones of PU-dA-1 synthesized by the classical route in the Part I - Chapter 2. (See Table II-2-3) Nevertheless, the effect of the hydroxyl generated in the PHU, prepared by the cyclic carbonate/amine route, can not be highlighted due to the presence of the sulfur atom (in the PU prepared by the classical alcohol/isocyanate route), as well as due to the probable difference in molar masses between the two polymers. Indeed, the molar masses are not comparable because PU-dA-1 was not analyzable by SEC due to solubility issues.

However, similar T_g and T_m can be observed. The PU-dA-1, synthesized by the classical alcohol/isocyanate route, demonstrated a T_g and a T_m of 47°C and 117°C respectively. In the case of PHU-BdA-1, synthesized by the cyclic carbonate/amine route, the T_g and T_m are 40°C and 115°C respectively.

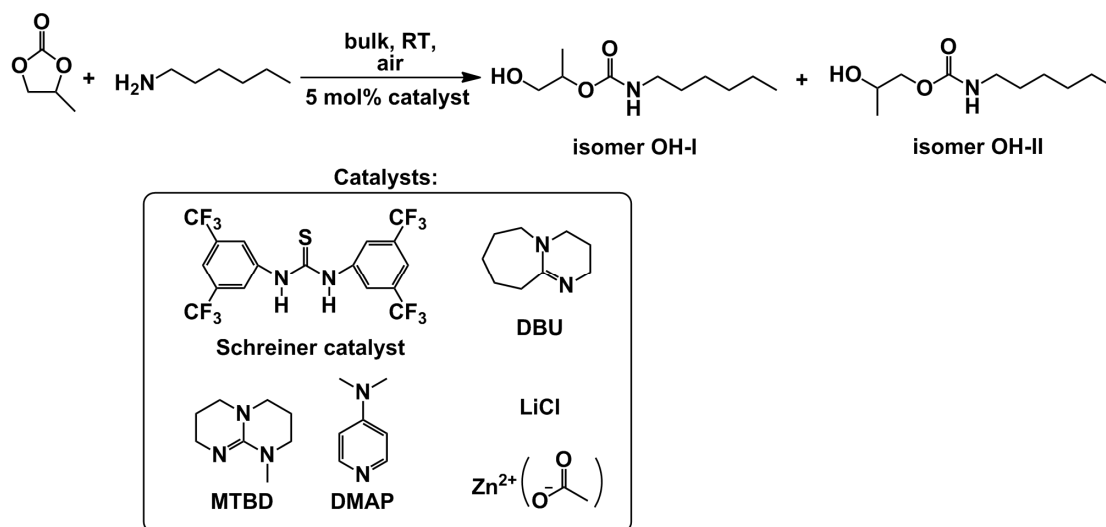
Table II-2-3- Comparison between PUs and PHUs.

Sample	Route	\bar{M}_n ($\text{g}\cdot\text{mol}^{-1}$) ¹	Dispersity	T_g ($^\circ\text{C}$) ²	T_m ($^\circ\text{C}$) ²
PU-dA-1 (Part I - Chapter 2)	alcohol / isocyanate	ns	ns	47	117
PHU-BdA-1 (Part II - Chapter 2)	cyclic carbonate / amine	18 900	2.4	40	115 ³

(1) SEC in DMF with 1 wt% LiBr - calibration PS standards. (2) Determined by DSC at $10^\circ\text{C}\cdot\text{min}^{-1}$. (3) With crystallization upon heating.

3- Catalysis of a model reaction

With the idea of reducing the polymerization temperature and time, the catalysis of the reaction between a 5-membered cyclic carbonates and an amine has been investigated. Various catalysts have been evaluated, and the kinetics were performed on a model reaction between equimolar ratio of propylene carbonate and hexylamine at room temperature without solvent and with 5 mol% of catalyst. (See Scheme II-2-5) The bulk condition was preferred due to really long reaction times reported in the literature for similar reactions in solvent.⁸ Indeed with the same reactants, 75% of conversion was reached after 50 days in toluene or DMSO at 70°C. The different catalysts that have been tested are presented in Scheme II-2-5. As it was found to be a successful bidentate hydrogen bonding catalyst⁹, the Schreiner thiourea catalyst was investigated alone and together in combination with tertiary amines. The guanidine MTBD and the amidine base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene - pKa=24.3) were also tested. Besides, nucleophile catalyst 4-dimethylaminopyridine (DMPA), salt LiCl and zinc acetate (ZnAc) were evaluated as well.



Scheme II-2-5- Model reaction of propylene carbonate and hexylamine as well as the various catalysts used.

The Figure II-2-13 exposes the kinetic data of the reaction between propylene carbonate and hexylamine with 5 mol% of the various catalysts. The reactions were monitored by FTIR-ATR following the disappearance of the carbonyl peak of the cyclic carbonate. The conversion was calculated using the equation: $= 100 - \frac{(H_{CC}/H_{CH_2})_t}{(H_{CC}/H_{CH_2})_{t=0}} * 100$, where x, t, H_{CC} and H_{CH₂} are the conversion, the time, the height of the peaks corresponding to the cyclic carbonate carbonyl and the unmodified CH₂ respectively.

The kinetic of hexylamine addition onto propylene carbonate is improved with the Schreiner catalyst alone as well as together with tertiary amines. The Schreiner catalyst was effective at the beginning of the reaction, however after 1 hour similar conversion to the uncatalyzed reaction was observed. This could be explained by the high hydrogen bonds density progressively formed, with the conversion, due to the generated hydroxyl groups. The same tendency observed with the Schreiner catalyst at room temperature was underlined at 80°C. (See Figure II-2-14)

For the uncatalyzed as well as the DBU and DMAP catalyzed reactions, an overall second order can correlate with the experimental data, having initial apparent reaction rate constants of $0.074 \text{ L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$, $0.134 \text{ L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ and $0.076 \text{ L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ respectively. However, the kinetic curves of the ZnAc and LiCl catalyzed reactions fit with an overall third order. The corresponding apparent initial reaction rate constants are: $0.189 \text{ L}^2\cdot\text{mol}^{-2}\cdot\text{h}^{-1}$ and $0.489 \text{ L}^2\cdot\text{mol}^{-2}\cdot\text{h}^{-1}$ respectively.

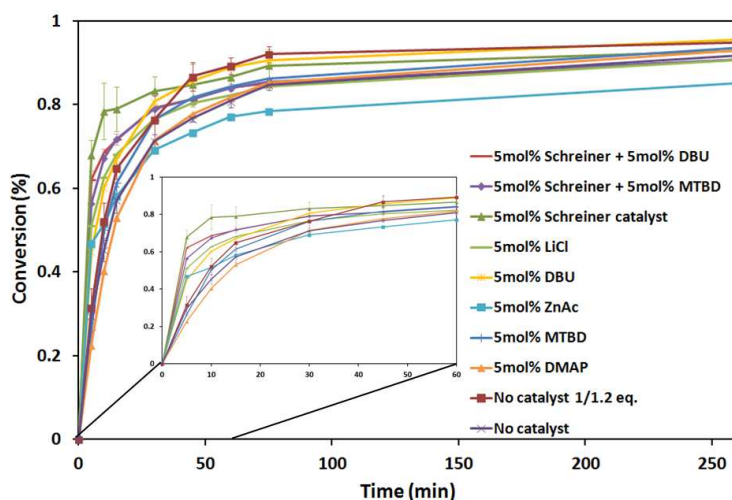


Figure II-2-13- Kinetic data of the model reaction with various catalysts at 25°C in bulk.

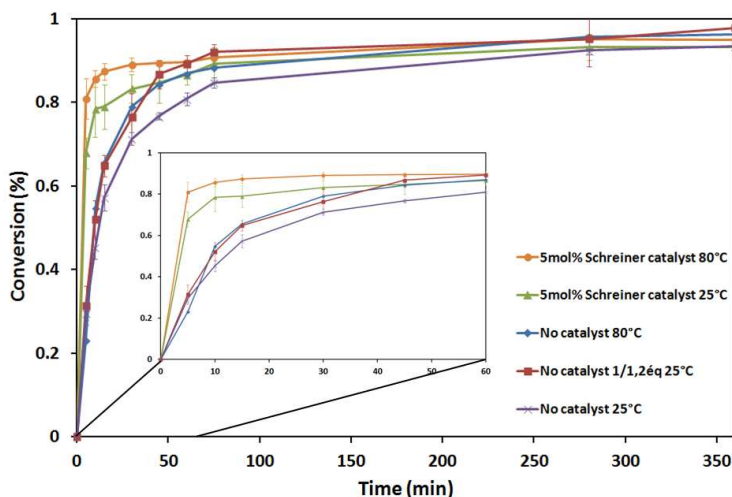


Figure II-2-14- Kinetic data of the model reaction with Schreiner catalyst at 25°C and 80°C in bulk.

The Figure II-2-15 presents the typical ^1H NMR analysis of the model reaction. The opening of the propylene carbonate with hexylamine can lead to two isomers; with a primary (isomer OH-I) or secondary (isomer OH-II) alcohol.

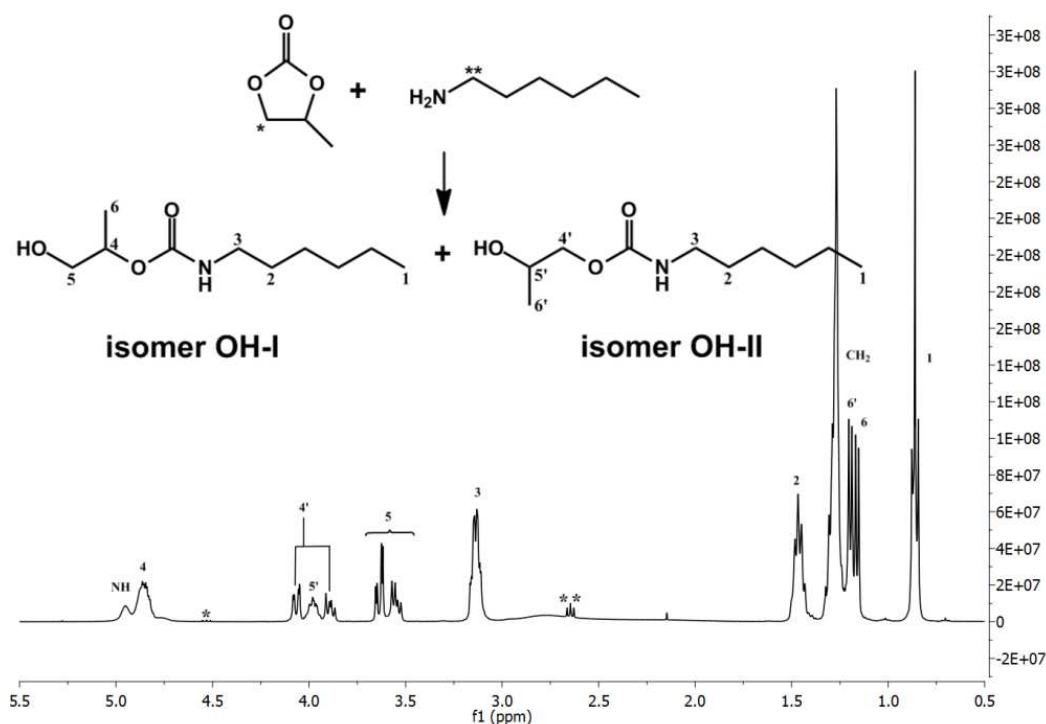


Figure II-2-15- ^1H NMR of the reaction between propylene carbonate and hexylamine without catalyst at RT after 11 days. (Analysis in CDCl_3)

For all model reactions, the ratio isomer OH-I / isomer OH-II was between 53:47 and 60:40. While more secondary hydroxyl groups were reported in the literature, more primary hydroxyl groups were favored in this study. (See Table II-2-4)

Table II-2-4- Analyses of the reactions between 5CCMe and hexylamine with different catalysts in bulk at RT.

Catalyst used	Catalyst quantity (mol%)	Ratio OH I : OH II ⁽¹⁾
No	/	58:42
DMAP	5	57 :43
MTBD	5	58 :42
ZnAc	5	60 :40
DBU	5	53 :47
LiCl	5	58 :42
Schreiner catalyst	5	59 :41
Schreiner catalyst + MTBD	5+5	57 :43
Schreiner catalyst + DBU	5+5	50 :50

(1) Calculated by ^1H NMR using the equation: $\% \text{OH I} = \frac{I_{\text{OH I}}}{I_{\text{OH I}} + I_{\text{OH II}}} * 100$, where % OH I, $I_{\text{OH I}}$ and $I_{\text{OH II}}$ are the % of the product with primary hydroxyl and the integrations of the peaks corresponding to the product with primary and secondary hydroxyl respectively.

Since its high initial activity for the addition of hexylamine onto propylene carbonate, the Schreiner catalyst has been tested in bulk polymerizations with UndPdE-b5CC and butane-1,4-diamine. As observed for the model reaction, similar conversions are detected by FTIR-ATR after 5 hours between the uncatalyzed and catalyzed polymerizations. (See Figure II-2-16)

Besides, after one day, similar molar masses and dispersity were obtained as detailed in the Table II-2-5. Further investigations are necessary to find an improved catalytic system for the polymerization of bis 5-membered cyclic carbonates and diamines. Indeed, the Schreiner catalyst is efficient only at the beginning of the polymerization, and an efficient co-catalyst should be found for the end of the polymerization.

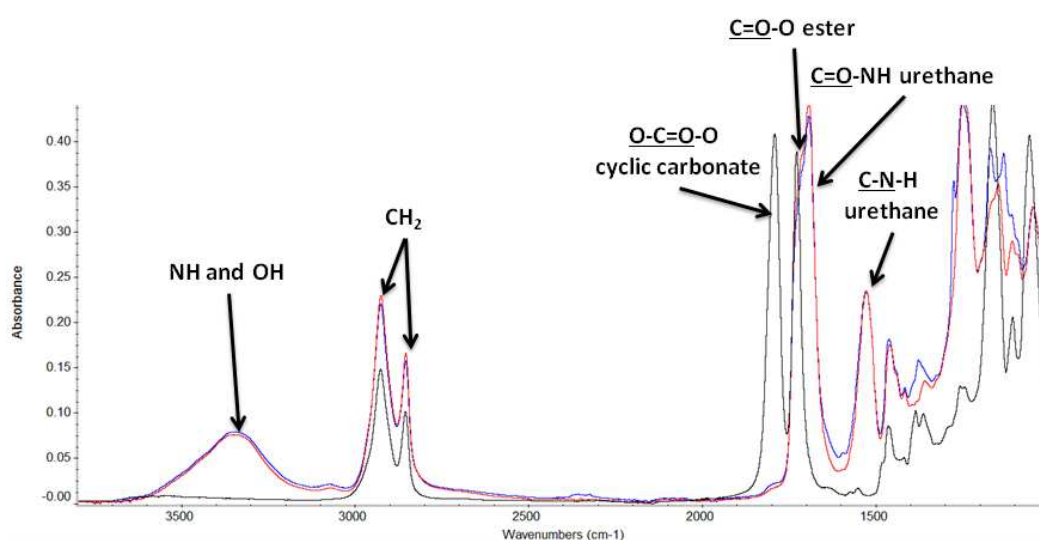


Figure II-2-16- Stacked FTIR-ATR spectra of UndPdE-b5CC (black), PHU-dE-1 after 1 day (red) and PHU-dE-1-cat after 1 day (blue).

Table II-2-5- Molar masses and dispersities for the uncatalyzed and catalyzed (Schreiner catalyst) polymerizations between UndPdE-b5CC and butane-1,4-diamine

Samples	Catalyst	Time	Conversion ¹	\bar{M}_n (g.mol ⁻¹) ²	\bar{M}_w (g.mol ⁻¹) ²	\bar{D}^2
PHU-dE-1	-	1 d	95.1	25 400	41 800	1.6
PHU-dE-1-cat	5 mol% Schreiner catalyst	1 d	94.9	24 700	37 000	1.5

(1) Conversion calculated by FTIR-ATR. (See the equation above) (2) SEC in DMF with 1 wt% LiBr - calibration PS standards.

Conclusion and limitations

Various 5-membered cyclic carbonates bearing ester or stable amide linkages have been synthesized following a three step procedure. The first stage was the transesterification or amidation of methyl undecenoate. Then the cyclic carbonates have been introduced by epoxidation of the double bonds and subsequent carbonation with CO₂. PHUs with molar masses up to 31 000 g.mol⁻¹ have been prepared by polyaddition of these bis 5-membered cyclic carbonates with different diamines.

Some drawbacks have been pointed out such as the stability and thus low reactivity of the fatty acid-based 5-membered cyclic carbonate due to +I inductive effect. High temperatures and long polymerization reaction times were requested and lead to unavoidable side reactions. Thus, the catalysis of the reaction between propylene carbonate and hexylamine amine has been furthermore investigated by FTIR-ATR monitoring. Additional investigations are necessary to find an efficient catalytic system. Regarding the catalysis of the reaction between 5-membered cyclic carbonate and amine is on key to improve the kinetic of PHU synthesis. Another possibility is the use of more reactive cyclic carbonates such as 6-membered ones for instance, as presented in the next chapter.

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Experimental and supporting information

Experimental methods

5CC synthesis and characterizations

The purities of the compounds are given when the analysis was possible.

1- Transesterification and amidation reactions

Transesterification step. Methyl undecenoate (20 g, 101 mmol), propanediol (3.8 g, 50 mmol), TBD (702 mg, 5 mmol) (1: 0.5: 0.05) were stirred under nitrogen flow at 120°C (4h), at 160°C (2h) then under vacuum at 160°C (30 min). The reaction mixture was dissolved in ethyl acetate (200 mL) and washed with water (3 x 50 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and solvent was removed on rotary evaporator. Yield=73%. **UndPdE:** ¹H NMR (CDCl₃, 25°C, 400 MHz) δ (ppm): 5.78 (m, 2H), 4.93 (m, 4H), 4.12 (t, 4H), 2.27 (t, 4H), 2.02 (m, 4H), 1.93 (m, 2H), 1.59 (m, 4H), 1.34 (m, 4H), 1.26 (m, 16H). IR (cm⁻¹): 2924, 2853, 1735, 1161, 906.

Amidation step. The diamides were prepared with different method according to the chemical structure of the diamine.

Methyl undecenoate (20 g, 101 mmol), butane-1,4-diamine (4.4 g, 50 mmol) and TBD (702 mg, 5 mmol) (1: 0.5: 0.05) were stirred under nitrogen flow at 120°C (4h) then at 160°C (2h). The reaction flask was cooled down at 90°C and NMP (60 mL) was added to end up with an homogeneous phase. The required UnddA was slowly precipitated by reaching room temperature. A filtration and washes with methanol were performed. Yield=83%. **UndBdA:** ¹H NMR (CDCl₃, 50°C, 400 MHz) δ (ppm): 5.79 (m, 2H), 4.98 (m, 4H), 3.26 (m, 4H), 2.15 (t, 4H), 1.99 (m, 4H), 1.65 (m, 4H), 1.53 (m, 4H), 1.40 (m, 4H), 1.32 (m, 16H). IR (cm⁻¹): 3295, 2918, 2847, 1630, 1537.

For UndPipdA and UndPMedA diamides, the amidation reactions were as followed. Methyl undecenoate, diamine and TBD (1: 0.5: 0.05) were stirred in a round-bottom flask equipped with a bubbling system under inert atmosphere at 100°C (2h), then under nitrogen flow at

120°C (4h) and at 160°C (2h). The diamides were purified by column chromatography and obtained as a yellow viscous liquid.

UndPipdA: Methyl undecenoate (20 g, 101 mmol), piperazine (4.3 g, 50 mmol) and TBD (702 mg, 5 mmol). UndPipdA was purified by column chromatography to eliminate completely the monoamide (eluent: cyclohexane / ethyl acetate with increasing percentage of ethyl acetate from 20% to 60%). Yield = 68.2%. ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 5.79 (m, 2H), 4.94 (m, 4H), 3.62 (m, 4H), 3.44 (m, 4H), 2.32 (t, 4H), 2.03 (m, 4H), 1.63 (m, 4H), 1.35-1.29 (m, 20H). IR (cm^{-1}): 2918, 2847, 1650, 906.

UndPMedA: Methyl undecenoate (20 g, 101 mmol), N,N'-dimethylpropane-1,3-diamine (5.2 g, 50 mmol) and TBD (702 mg, 5 mmol). UndPMedA was purified by column chromatography to eliminate completely the monoamide (eluent: heptane / ethyl acetate with increasing percentage of ethyl acetate from 20% to 60%). Yield = 79.3%. ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 5.80 (m, 2H), 4.95 (m, 4H), 3.35-3.25 (m, 4H), 2.98-2.89 (s, 6H), 2.26 (m, 4H), 2.01 (m, 4H), 1.75 (m, 2H), 1.59 (m, 4H), 1.34-1.28 (m, 20H). IR (cm^{-1}): 2924, 2850, 1639, 906.

Concerning the preparation of UndDHexdA, the diamine (SebHex-diamine) used as central block was synthesized in a first step, and then the amidation was performed. The SebHex-diamine was obtained by the reduction of the corresponding diamide issued from sebacoyl chloride and hexylamine. Hexylamine (9 g, 86.4 mmol, 2.05 eq.), triethylamine (20.7 mL, 143.3 mmol, 3.41 eq.), then chloroform (125 mL) were introduced in a round-bottom flask. Afterwards, the sebacoyl chloride (10 g, 42 mmol, 1 eq.) was added dropwise. The formation of a white precipitate due to the generation of triethylamine hydrochloride salt revealed the progress of the reaction. After filtration and washes with hot water, the organic phase was dried over anhydrous sodium sulfate, filtered and the chloroform was removed on rotary evaporator. After drying, the diamide was reduced by LiAlH_4 (3 eq. per function) in dried THF under reflux overnight. Then, an aqueous solution of potassium sodium tartrate at $1 \text{ mol}\cdot\text{L}^{-1}$ (200mL) was added to the reaction mixture placed into an ice bath. The SebHex-diamine was recovered after filtration followed by extraction of the filtrate with ethyl acetate. SebHex-diamine was purified by column chromatography (eluent: ethyl ether / methanol with increasing percentage of methanol from 0% to 31%). Yield = 84.6%. **SebHex-diamine:** ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 2.57 (1, 8H), 1.46 (m, 8H), 1.27 (m, 24H), 0.81 (t, 6H).

To SebHex-diamine (8.4 g, 25 mmol), dried THF (100 mL) and triethylamine (5.5 g, 55 mmol, 1.1 eq.) were added. Then undecenyl chloride (10 g, 49 mmol) was added dropwise. The reaction mixture was then stirred at room temperature for 2 hours. UndDHexdA was purified by filtration of the formed salt, followed by column chromatography to eliminate completely the monoamide (eluent: heptane / ethyl acetate (95/5)). Yield = 91.3%. **UndDHexdA:** ^1H NMR (CDCl_3 , 50°C , 400 MHz) δ (ppm): 5.80 (m, 2H), 4.94 (m, 4H), 3.27 (m, 4H), 3.19 (m, 4H), 2.27 (t, 4H), 2.02 (m, 4H), 1.62 (m, 4H), 1.51 (m, 8H), 1.36-1.28 (m, 40H), 0.88 (m, 6H). IR (cm^{-1}): 2924, 2851, 1642, 906.

2- Epoxidation reaction

The diester or diamide and m-CPBA (3 eq. and 4.5 eq. for UndBdA) were stirred at room temperature in DCM (20mL/g of product) or chloroform (for UndBdA). After 1 day, the conversion of the double bonds, monitored by ^1H NMR spectroscopy, were in the range 84% to 100%. The reaction mixture was then thoroughly washed with aqueous Na_2SO_3 (3 x 50 mL), aqueous NaHCO_3 (4 x 50 mL) and water (4 x 50 mL) until neutral pH. The organic layer was dried over anhydrous sodium sulfate filtered and solvent was removed on rotary evaporator to obtain the bis epoxides.

UndPdE-bisEpoxide: UndPdE (17 g, 42 mmol) and m-CPBA (21.5 g, 125 mmol, 3 eq.). The purity of UndPdE-bisEpoxide (92.8%) was determined by GC-FID. Yield=95.9%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 4.12 (t, 4H), 2.90 (m, 2H), 2.74 (t, 2H), 2.45 (m, 2H), 2.29 (t, 4H), 1.95 (m, 2H), 1.61 (m, 4H), 1.51 (m, 4H), 1.44 (m, 4H), 1.30 (m, 16H). IR (cm^{-1}): 2927, 2856, 1732, 1161.

UndBdA-bisEpoxide: UndBdA (12.7 g, 30 mmol) and m-CPBA (23.4 g, 136 mmol, 4.5 eq.). The purity of UndBdA-bisEpoxide (80.4%) was determined by GC-FID. Yield=97%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 5.79 (s, 2NH), 3.26 (m, 4H), 2.89 (m, 2H), 2.74 (t, 2H), 2.46 (m, 2H), 2.16 (t, 4H), 1.71 (m, 4H), 1.61-1.53 (m, 12H), 1.31 (m, 16H). IR (cm^{-1}): 3292, 2912, 2851, 1631, 1537.

UndPipdA-bisEpoxide: UndPipdA (13.2 g, 31 mmol) and m-CPBA (16.3 g, 95 mmol, 3 eq.). The purity of UndPipdA-bisEpoxide (97.9%) was determined by GC-FID. Yield=84.5%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 3.61 (m, 4H), 3.45 (m, 4H), 2.88 (m, 2H), 2.73 (t, 2H), 2.45 (m, 2H), 2.32 (t, 4H), 1.61 (m, 4H), 1.49-1.44 (m, 8H), 1.34-1.30 (m, 16H). IR (cm^{-1}): 2913, 2848, 1651.

UndPMedA-bisEpoxide: UndPMedA (20 g, 46 mmol) and m-CPBA (23.8 g, 138 mmol, 3 eq.). The purity of UndPMedA-bisEpoxide (93.9%) was determined by GC-FID. Yield=83.9%. ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 3.37 (m, 4H), 3.00-2.92 (s, 6H), 2.90 (m, 2H), 2.75 (t, 2H), 2.46 (m, 2H), 2.31 (m, 4H), 1.79 (m, 2H), 1.61 (m, 4H), 1.51 (m, 4H), 1.42 (m, 4H), 1.29 (m, 16H). IR (cm^{-1}): 2924, 2854, 1639.

UndDHexdA-bisEpoxide: UndDHexdA (10 g, 15 mmol) and m-CPBA (7.7 g, 44 mmol, 3 eq.). Yield=54.4%. ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 3.28 (m, 4H), 3.19 (m, 4H), 2.89 (m, 2H), 2.73 (t, 2H), 2.46 (m, 2H), 2.27 (t, 4H), 1.62 (m, 4H), 1.43 (m, 16H), 1.31 (m, 40H), 0.88 (m, 6H). IR (cm^{-1}): 2924, 2853, 1637.

3- Synthesis of 5-membered cyclic carbonates

The bis-epoxide was first pre-mixed with TBABr (3 wt%). Then the mixture was placed in a reactor and heated up at the selected temperature (80°C for UndPdE-bisEpoxide, UndPMedA-bisEpoxide and UndDHexdA-bisEpoxide, 135°C for UndPipdA-bisEpoxide and 140°C for UndBdA-bisEpoxide). Once the temperature got stabilized, CO_2 was slowly introduced into the reactor until 50 Bar or 60 Bar in the case of UndBdA-bisEpoxide. After 24 hours, the reactor was cooled down to room temperature and slowly depressurized to the atmospheric pressure. All the ^1H NMR of all products revealed quantitative conversion by the disappearance of the protons of the epoxide.

UndPdE-CC: UndPdE-bisEpoxide (3 g, 6.8 mmol) and TBABr (0.09 g, 0.28 mmol, 3 wt%). The purity of UndPdE-bisEpoxide (99.1%) was determined by SEC. Yield=97%. ^1H NMR (CDCl_3 , 25°C, 400 MHz) δ (ppm): 4.68 (m, 2H), 4.50 (t, 2H), 4.11 (t, 4H), 4.04 (t, 2H), 2.27 (t, 4H), 1.94 (m, 2H), 1.76 (m, 2H), 1.66 (m, 2H), 1.58 (m, 4H), 1.45 (m, 4H), 1.28 (m, 16H). ^{13}C NMR (CDCl_3 , 25°C, 100 MHz) δ (ppm): 173.81 (COO), 155.20 (OCOO), 77.21 ($\underline{\text{C}}\text{H-OCOO}$), 69.51 ($\underline{\text{C}}\text{H}_2\text{-OCOO}$), 60.93 ($\underline{\text{C}}\text{H}_2\text{-OCO}$), 34.28 ($\underline{\text{C}}\text{H}_2\text{-COO}$), 33.95 ($\underline{\text{C}}\text{H}_2\text{-CH-OCOO}$), 29.21-29.13 (CH_2), 28.10 ($\underline{\text{C}}\text{H}_2\text{-CH}_2\text{-OCO}$), 24.94 ($\underline{\text{C}}\text{H}_2\text{-CH}_2\text{-COO}$), 24.44 ($\underline{\text{C}}\text{H}_2\text{-CH}_2\text{-CH-OCOO}$). IR (cm^{-1}): 2927, 2856, 1792, 1727, 1163.

UndBdA-b5CC: UndBdA-bisEpoxide (3 g, 6.6 mmol) and TBABr (0.09 g, 0.28 mmol, 4.5 wt%). Yield=95%. ^1H NMR (CDCl_3 , 25°C, 400 MHz) δ (ppm): 5.83 (s, 2NH), 4.70 (m, 2H), 4.53 (t, 2H), 4.06 (t, 2H), 3.26 (m, 4H), 2.16 (t, 4H), 1.78 (m, 2H), 1.62 (m, 6H), 1.53 (m, 4H), 1.47 (m, 4H), 1.30 (m, 16H). ^{13}C NMR (CDCl_3 , 25°C, 100 MHz) δ (ppm): 173.81 (CONH), 155.27 (OCOO), 77.22 ($\underline{\text{C}}\text{H-OCOO}$), 69.54 ($\underline{\text{C}}\text{H}_2\text{-OCOO}$), 39.20 ($\underline{\text{C}}\text{H}_2\text{-NHCO}$), 36.65 ($\underline{\text{C}}\text{H}_2\text{-CONH}$), 33.94

($\underline{\text{C}}\text{H}_2\text{-CH-OCOO}$), 29.17 (CH_2), 26.91 ($\underline{\text{C}}\text{H}_2\text{-CH}_2\text{-NHCO}$), 25.84 ($\underline{\text{C}}\text{H}_2\text{-CH}_2\text{-CONH}$), 24.43 ($\underline{\text{C}}\text{H}_2\text{-CH}_2\text{-CH-OCOO}$). IR (cm^{-1}): 3309, 2918, 2850, 1778, 1637, 1535.

UndPipdA-b5CC: UndPipdA-bisEpoxide (5 g, 11.1 mmol) and TBABr (0.15 g, 0.46 mmol, 3 wt%). Yield=98%. ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 4.69 (m, 2H), 4.51 (t, 2H), 4.06 (t, 2H), 3.62 (m, 4H), 3.45 (m, 4H), 2.32 (t, 4H), 1.76 (m, 2H), 1.70-1.63 (m, 8H), 1.47 (m, 2H), 1.31 (m, 16H). ^{13}C NMR (CDCl_3 , 25°C, 100 MHz) δ (ppm): 172.00 (C=O-N), 155.15 (OCOO), 77.12 ($\underline{\text{C}}\text{H-OCOO}$), 69.47 ($\underline{\text{C}}\text{H}_2\text{-OCOO}$), 45.41 and 41.61 ($(\underline{\text{C}}\text{H}_2)_2\text{-N-C=O}$), 33.93 ($\underline{\text{C}}\text{H}_2\text{-CH-OCOO}$), 33.29 ($\underline{\text{C}}\text{H}_2\text{-C=O-N}$), 29.25 (CH_2), 25.20 ($\underline{\text{C}}\text{H}_2\text{-CH}_2\text{-C=O-N}$), 24.42 ($\underline{\text{C}}\text{H}_2\text{-CH}_2\text{-CH-OCOO}$). IR (cm^{-1}): 2915, 2847, 1775, 1628.

UndPMedA-b5CC: UndPMedA-bisEpoxide (5 g, 10.7 mmol) and TBABr (0.15 g, 0.46 mmol, 3 wt%). The purity of UndPMedA-bisEpoxide (88.6%) was determined by GC-FID. Yield=96%. ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 4.69 (m, 2H), 4.51 (t, 2H), 4.05 (t, 2H), 3.34-3.27 (m, 4H), 2.98-2.89 (s, 6H), 2.27 (m, 4H), 1.79 (m, 6H), 1.61 (m, 6H), 1.47 (m, 2H), 1.30 (m, 16H). ^{13}C NMR (CDCl_3 , 25°C, 100 MHz) δ (ppm): 173.12 ($\underline{\text{C}}\text{ONCH}_3$), 155.20 (OCOO), 77.16 ($\underline{\text{C}}\text{H-OCOO}$), 69.51 ($\underline{\text{C}}\text{H}_2\text{-OCOO}$), 47.76-45.50 ($\underline{\text{C}}\text{H}_2\text{-NCH}_3\text{CO}$), 35.51-33.08 (NCH_3CO), 33.92 ($\underline{\text{C}}\text{H}_2\text{-CH-OCOO}$), 33.65-33.38 ($\underline{\text{C}}\text{H}_2\text{-CONCH}_3$), 29.52-24.46 (CH_2), 26.53 ($\underline{\text{C}}\text{H}_2\text{-CH}_2\text{-NCH}_3\text{CO}$). IR (cm^{-1}): 2913, 2847, 1787, 1631.

UndDHexdA-b5CC: UndDHexdA-bisEpoxide (3 g, 4.2 mmol) and TBABr (0.09 g, 0.28 mmol, 3 wt%). Yield=88.7%. ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 4.67 (m, 2H), 4.50 (t, 2H), 4.04 (t, 2H), 3.25 (m, 4H), 3.17 (m, 4H), 2.24 (t, 4H), 1.75 (m, 2H), 1.65-1.60 (m, 6H), 1.45 (m, 12H), 1.29 (m, 40H), 0.87 (m, 6H). ^{13}C NMR (CDCl_3 , 25°C, 100 MHz) δ (ppm): 173.10 ($\underline{\text{C}}\text{ONCH}_3$), 155.14 (OCOO), 76.97 ($\underline{\text{C}}\text{H-OCOO}$), 69.27 ($\underline{\text{C}}\text{H}_2\text{-OCOO}$), 47.73-45.56 ($\underline{\text{C}}\text{H}_2\text{-NCO}$), 33.59 ($\underline{\text{C}}\text{H}_2\text{-CH-OCOO}$), 32.77 ($\underline{\text{C}}\text{H}_2\text{-CON}$), 31.27-22.30 (CH_2), 13.78 (CH_3). IR (cm^{-1}): 2924, 2854, 1795, 1634.

Polymers synthesis and characterizations

The bis 5-membered cyclic carbonates (UndPdE-b5CC, UndBdA-b5CC, UndPipdA-b5CC, UndPMedA-b5CC and UndDHexdA-CC) and the diamines (butane-1,4-diamine (4DA), isophorone diamine (IPDA), Jeffamine 400 $\text{g}\cdot\text{mol}^{-1}$, CRODA diamine) were weighted in a test tube. The polymerization reactions were conducted in bulk under static nitrogen. The mixture was stirred at the selected temperature: 140°C (for UndBdA-b5CC and

UndPipdA-b5CC), 120°C (for UndPMedA-b5CC and UndDHexdA-b5CC) and 70°C or 110°C/120°C for UndPdE-b5CC. No catalysts were added for the polymerization reactions.

PHU-dE-1 [UndPdE-b5CC+4DA] : 3655-3127, 2924, 2854, 1714-1691, 1528.

PHU-BdA-1 [UndBdA-b5CC+IPDA] : 3536-3132, 2922, 2852, 1700, 1642, 1539.

PHU-DHexdA-1 [UndDHexdA-b5CC+IPDA] : 3595-3128, 2922, 2852, 1713, 1626, 1535.

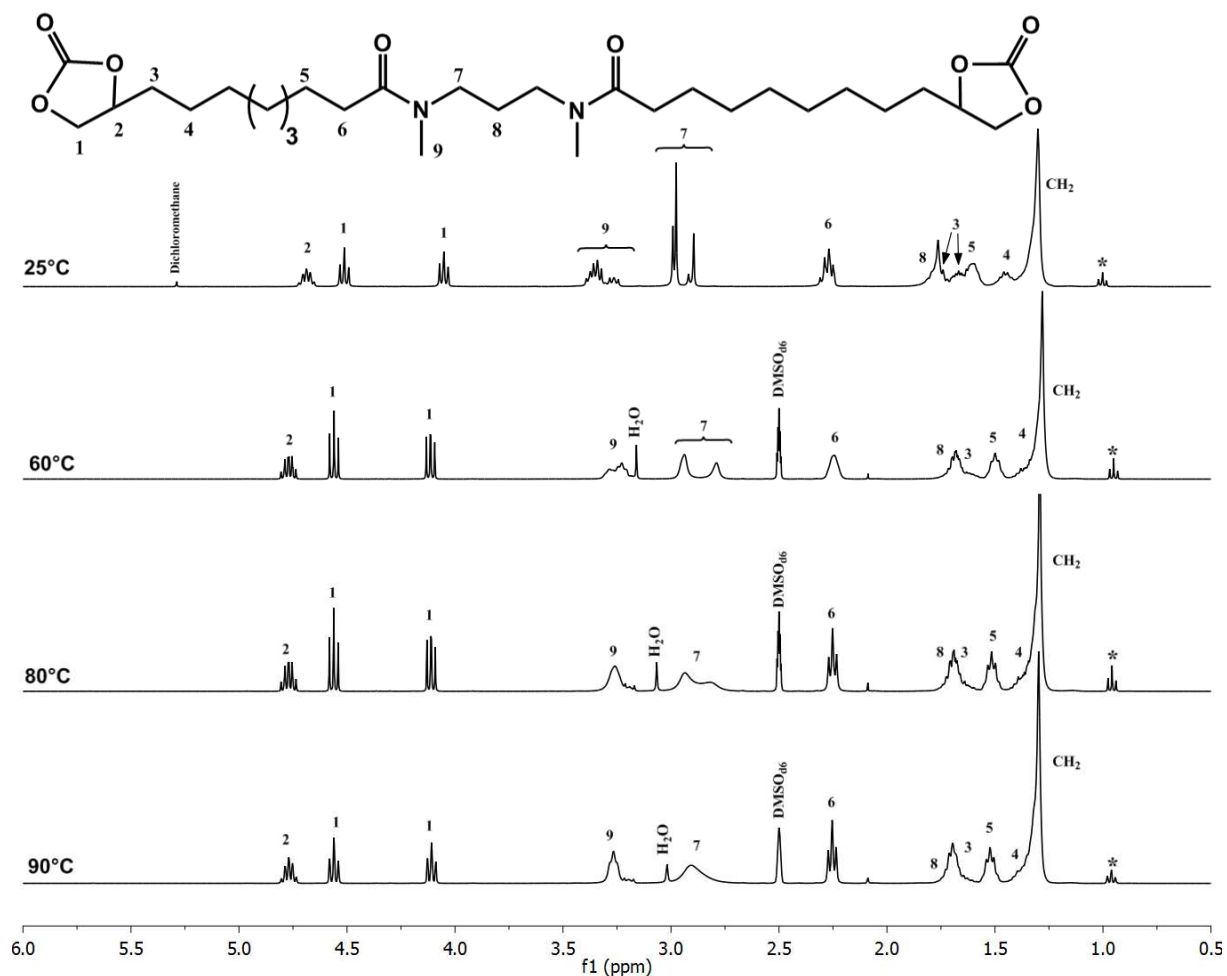
Kinetic experiments monitored by FTIR-ATR of the cyclic carbonate-amine reaction

The kinetic experiments were performed in bulk at 25°C with a ratio 1:1 between the propylene carbonate and hexylamine, using 5 mol% of catalyst. For some experiments, higher temperature (80°C) was also investigated. For instance; propylene carbonate (5CC) (0.25 g, 2.4 mmol) and MTBD (18.7 mg, 0.12 mmol, 5 mol%) were weighted in a test tube. Then, hexylamine (0.25 g, 2.4 mmol) was added to the reaction mixture. The reaction was monitored with FTIR-ATR spectroscopy with the disappearance of the carbonyl band of the cyclic carbonate. Two isomers are obtained; one with a primary alcohol (isomer OH-I) and one with a secondary alcohol (isomer OH-II).

PCC+hexylamine-isomer OH-II: ^1H NMR (CDCl_3 , 25°C, 400 MHz) δ (ppm): 4.97 (NH), 4.05 (m, 1H), 3.98 (m, 1H), 3.91 (m, 1H), 3.14 (m, 2H), 1.47 (m, 2H), 1.27 (m, 6H), 1.15 (d, 3H), 0.86 (t, 3H). ^{13}C NMR (CDCl_3 , 25°C, 100 MHz) δ (ppm): 156.98 (OCONH), 72.69 ($\underline{\text{C}}\text{H-OCONH}$), 66.52 ($\underline{\text{C}}\text{H}_2\text{-OH}$), 41.17 ($\underline{\text{C}}\text{H}_2\text{-NHCOO}$), 29.94 ($\underline{\text{C}}\text{H}_2\text{-CH}_2\text{-NHCOO}$), 31.54-22.64 (CH_2), 16.70 ($\underline{\text{C}}\text{H}_3\text{-CH-OCONH}$), 14.08 ($\text{CH}_2\text{-}\underline{\text{C}}\text{H}_3$). IR (cm^{-1}): 3321, 2929, 2856, 1687, 1533.

PCC+hexylamine-isomer OH-I: ^1H NMR (CDCl_3 , 25°C, 400 MHz) δ (ppm): 4.97 (NH), 4.85 (m, 1H), 3.63-3.55 (m, 2H), 3.14 (m, 2H), 1.47 (m, 2H), 1.27 (m, 6H), 1.17 (d, 3H), 0.86 (t, 3H). ^{13}C NMR (CDCl_3 , 25°C, 100 MHz) δ (ppm): 156.98 (OCONH), 70.21 ($\underline{\text{C}}\text{H}_2\text{-OCONH}$), 66.61 ($\underline{\text{C}}\text{H-OH}$), 41.17 ($\underline{\text{C}}\text{H}_2\text{-NHCOO}$), 29.94 ($\underline{\text{C}}\text{H}_2\text{-CH}_2\text{-NHCOO}$), 31.54-22.64 (CH_2), 19.17 ($\underline{\text{C}}\text{H}_3\text{-CH-OH}$), 14.08 ($\text{CH}_2\text{-}\underline{\text{C}}\text{H}_3$). IR (cm^{-1}): 3321, 2929, 2856, 1687, 1533.

Supporting information

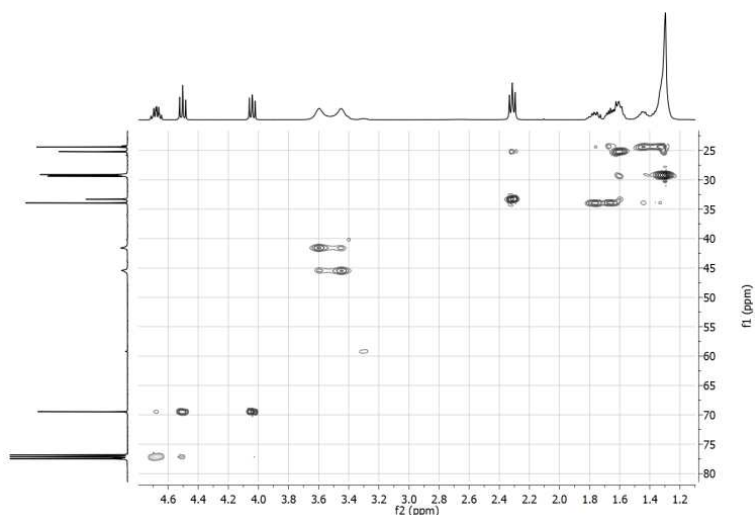


SI Figure II-2-1-¹H NMR of UndPMedA-b5CC at 25°C (in CDCl₃), 60°C, 80°C and 90°C. (in DMSO-d₆)

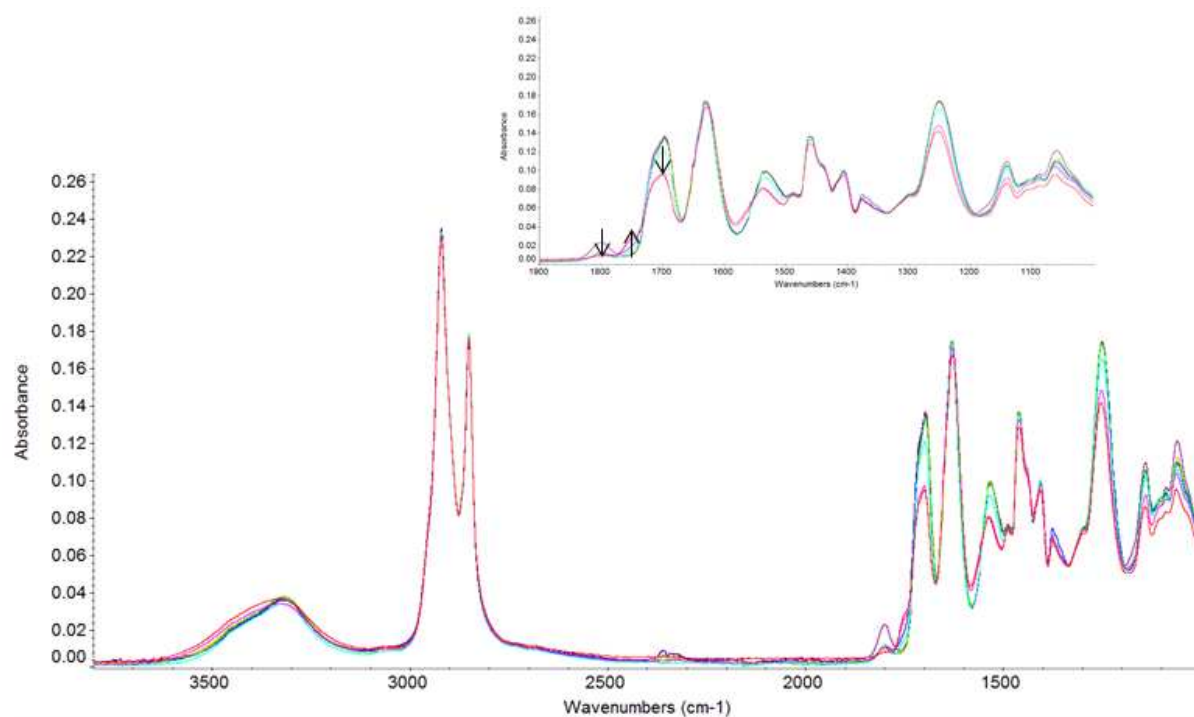
SI Table II-2-1- Characterizations of the synthesized 5-membered cyclic carbonates.

Synthesized b5CC	%purity	T _m (°C) ³
UndPdE-b5CC	99.1 ¹	L
UndBdA-b5CC	nd	137.4
UndPipdA-b5CC	nd	132.6
UndPMedA-b5CC	88.6 ²	102.5 ⁴
UndDHexdA-b5CC	nd	L

(1) Determined by SEC, (2) Determined by GC-FID and (3) Determined by DSC 10°C/min under N₂, (4) Crystallization while heating, nd=not determined, L=liquid at room temperature.



SI Figure II-2-2- ^1H - ^{13}C HSQC-NMR of UndPipdA-b5CC. (Analysis in CDCl_3)



SI Figure II-2-3- FTIR-ATR evidence of the presence of side reactions during the polymerization in bulk at high temperature of PU-PMedA-2.

SI Table II-2-2- Decrease of the molar mass and of the glass transition temperature during the polymerization in bulk at high temperature of PU-PMedA-2.

Time (d)	\bar{M}_n (g.mol $^{-1}$)	\bar{M}_w (g.mol $^{-1}$)	\bar{D}	Tg ($^{\circ}\text{C}$)
1d	28 100	41 400	1.47	-4.5
6d	28 700	47 500	1.66	nd
15d	17 200	27 800	1.61	-11.5

SEC in DMF with 1 wt% LiBr - calibration PS standards.

PART II - Chapter 3: Toward vegetable oil-based non-isocyanate PHUs from more reactive 6-membered cyclic carbonates

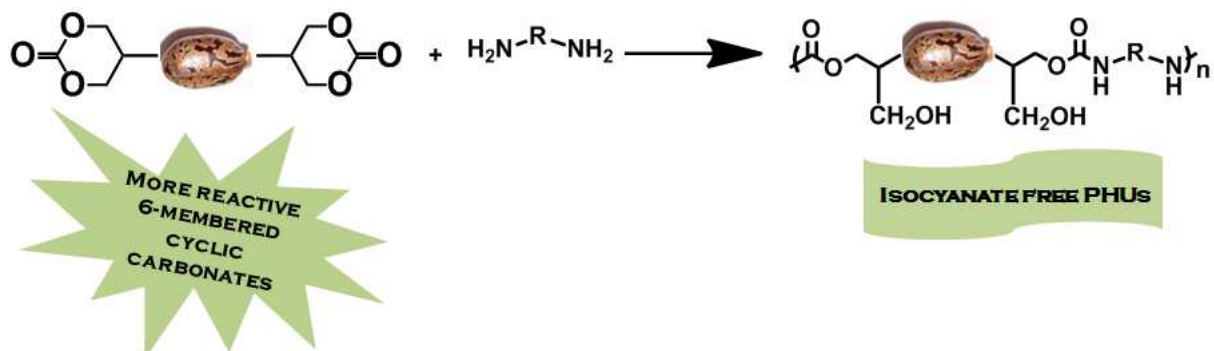


Table of contents

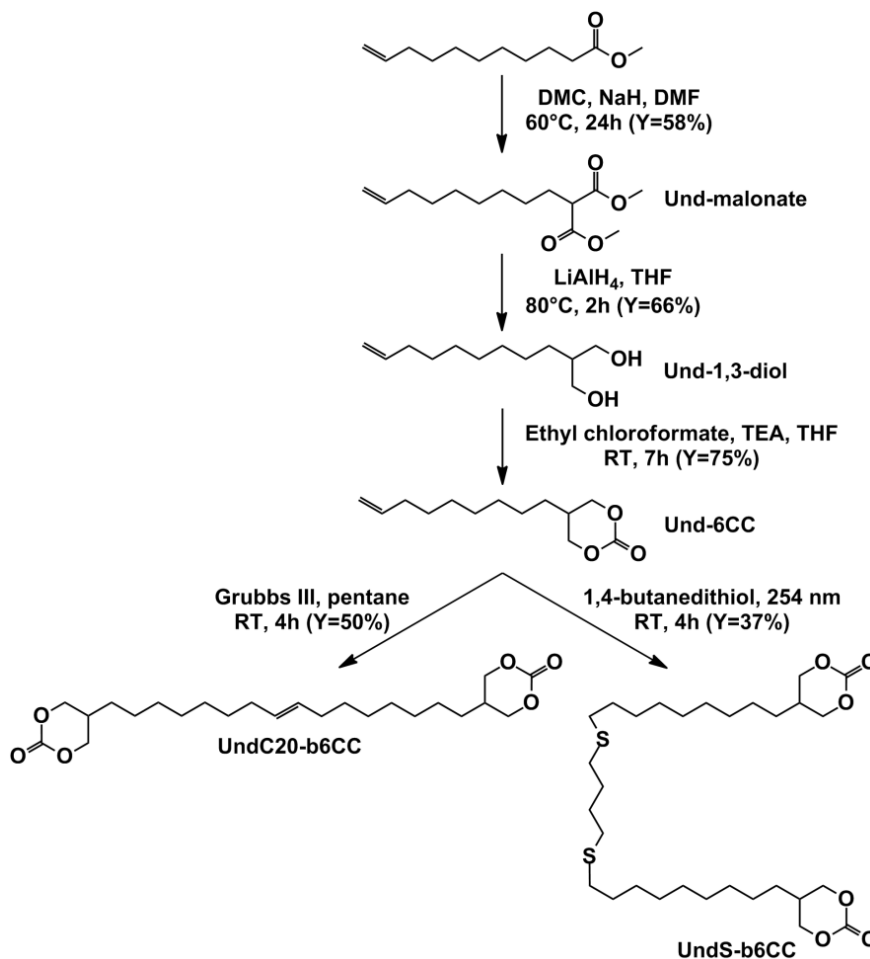
Introduction	182
1- Bis 6-membered cyclic carbonate (b6CC) synthesis	182
1.1- Synthesis of the 6-membered cyclic carbonate (Und-6CC)	183
1.2- Coupling reactions	187
2- Comparison of different cyclic carbonates reactivity	190
3- Polymerization	199
3.1- Synthesis of PHUs and related molar masses	199
3.2- Thermal stability and thermo-mechanical properties	206
Conclusion	207
References	208
Experimental and supporting information	209

Introduction

To our knowledge, while vegetable oil-based 5-membered cyclic carbonates have been studied as PHUs precursors, no literature has been published on the preparation of more reactive vegetable oil-based bis 6-membered cyclic carbonates. In the present chapter, the synthesis of 6-membered cyclic carbonate from methyl undecenoate (Und-6CC) is reported via malonate and 1,3-diol intermediates. To prepare the fatty acid-based malonate, the approach developed by Meier and coll. was preferred due to the use of non-toxic DMC, the synthesis of which potentially avoids phosgene and its derivatives.^{1, 2} The coupling of Und-6CC was done under mild conditions, by metathesis or thiol-ene reactions allowing the preparation of bis 6-membered cyclic carbonates: UndC20-b6CC and UndS-b6CC respectively. In the second part of the study, the increased reactivity of Und-6CC has been proved by model reactions with hexylamine. The bis 6-membered cyclic carbonates were then examined in polymerization with dodecane-1,12-diamine in solution. The synthesized PHUs were characterized through FTIR-ATR, NMR, MALDI-TOF MS, DSC and TGA.

1- Bis 6-membered cyclic carbonate (b6CC) synthesis

As illustrated in the Scheme II-3-1, the Und-6CC compound was synthesized using a three step strategy via a malonate (Und-malonate) and a 1,3-diol (Und-1,3-diol) intermediates. The chemical structures of the synthesized Und-6CC, UndC20-b6CC and UndS-b6CC compounds as well as the different intermediates were assessed by ¹H and ¹³C NMR, ¹H-¹H COSY, ¹H-¹³C HSQC and FTIR-ATR spectroscopy. The Und-6CC compound and intermediates are also of interest as potential precursors for the synthesis of polyesters (Und-malonate & Und-1,3-diol), PUs using the alcohol/isocyanate route (Und-1,3-diol) and polycarbonates (Und-1,3-diol & Und-6CC), but those possibilities will not be discussed in this manuscript.



Scheme II-3-1- General synthetic route to Und-6CC, UndC20-b6CC and UndS-b6CC.

1.1- Synthesis of the 6-membered cyclic carbonate (Und-6CC)

The synthesis of Und-6CC involved three steps which are (i) the malonate (Und-malonate) synthesis from methyl undecenoate, (ii) the reduction of the malonate into a 1,3-diol (Und-1,3-diol) and finally (iii) the cyclization into a 6-membered cyclic carbonate (Und-6CC). The Figure II-3-1 and Figure II-3-2 present the stacked FTIR-ATR and ¹H NMR respectively for the different steps from methyl undecenoate to Und-6CC. After optimization of reported conditions on dimethyl sebacate, Und-malonate was synthesized at 60°C for 24 hours from methyl undecenoate using 40 eq. of DMC, 2.5 eq. of NaH and 1 eq. of DMF. The Table II-3-1 presents the optimization of the conditions on dimethyl sebacate. It has been demonstrated by Meier and coll. that the large excess of DMC is needed to avoid Claisen-condensation side-product and that anhydrous DMF can accelerate considerably the deprotonation in α-position of the ester by increasing the solvation of the reactants and/or the intermediates.² Besides, the NaH excess was requested due to the more acidic character of the formed

malonate compared to the methyl undecenoate precursor, which induce an unfavorable deprotonation on the latter compound.²

Table II-3-1- Optimization of the conditions for the malonate synthesis at 60°C on dimethyl sebacate (SebdE).

SebdE (eq.)	DMC (eq./ester)	NaH _{60% disp.} (eq.)	DMF (eq./ester)	Time (h)	Malonate conversion ¹
1	20	2.5	1	10	26
1	30	2.5	1	15	50*
1	40	2.5	1	24	80
1	40	2.5	1	40	71

(1) Estimated by ¹H NMR. (*) Claisen side products.

In FTIR-ATR, a double peak at 1753 cm⁻¹-1735 cm⁻¹ assignable to the C=O of the malonate was clearly observable after the first step reaction. (See Figure II-3-1-(1) and II-3-1-(2))

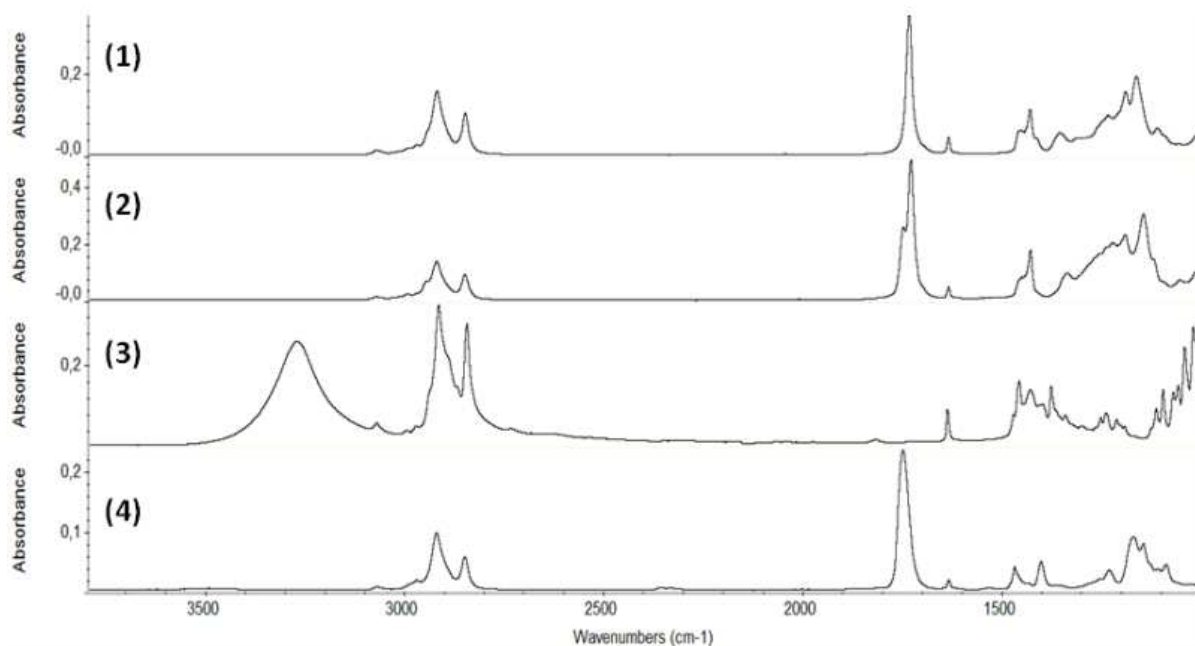


Figure II-3-1- Stacked FTIR-ATR spectra of (1) methyl undecenoate, (2) Und-malonate, (3) Und-1,3-diol and (4) Und-6CC.

The conversion of methyl undecenoate into Und-malonate was confirmed by ¹H NMR spectroscopy. The integration of the methylene protons nearby the ester linkage of methyl undecenoate (See Figure II-3-2-(1), H6 protons at 3.66 ppm) has decreased with reaction time. In addition, a triplet at 3.35 ppm and a multiplet at 1.88 ppm, corresponding to the methylene proton close to the malonate group, confirm the synthesis of Und-malonate. Besides, a large singlet at 3.73 ppm was observed, which corresponds to the malonate methylene protons of Und-malonate. After the work up, the percentage of unreacted methyl undecenoate (26.7%) was determined through ¹H NMR. Moreover, the Claisen-condensation side product was detected in proportion between 2.4% and 3% depending on the batch using the optimized conditions. The SI Figure II-3-1 illustrates the evidence of the presence of the Claisen-condensation product in a flash chromatography aliquot.

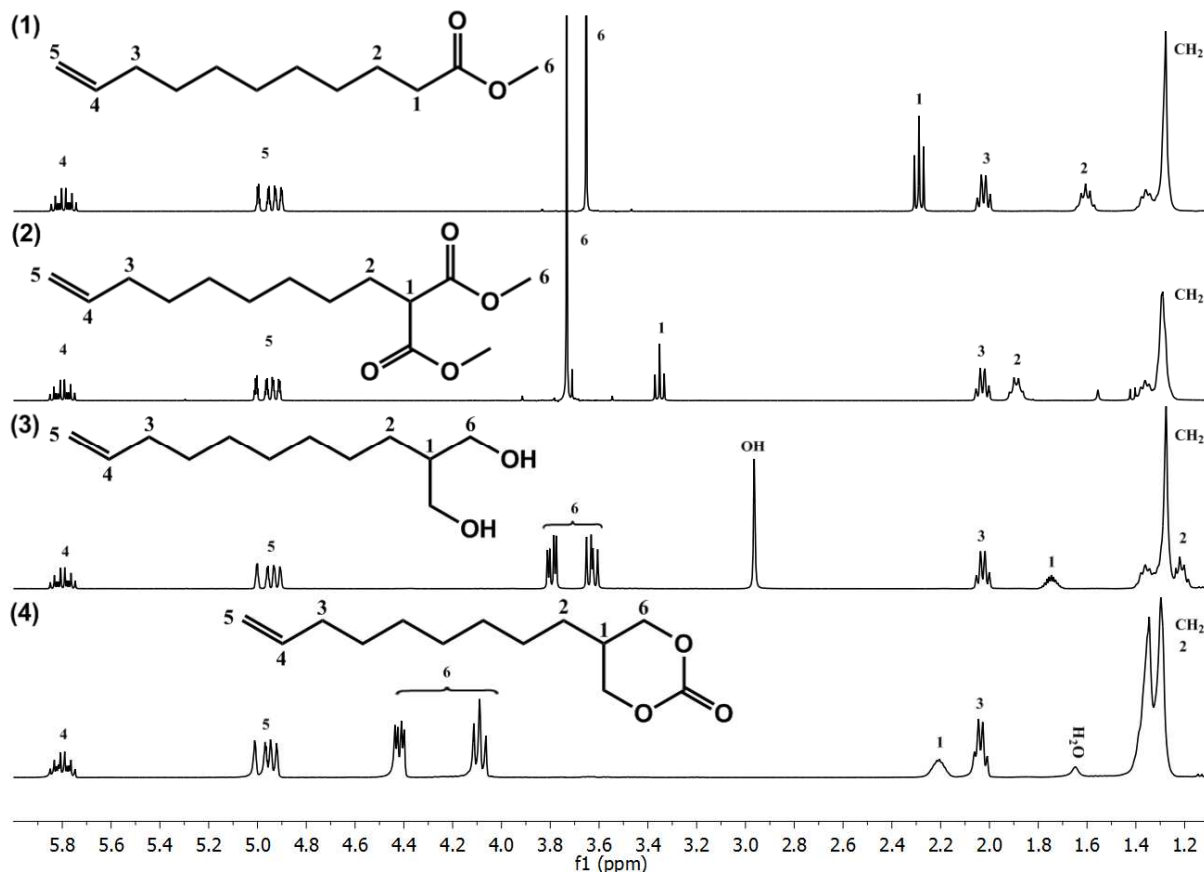


Figure II-3-2- Stacked ^1H NMR spectra of (1) methyl undecenoate, (2) Und-malonate, (3) Und-1,3-diol and (4) Und-6CC.
(All analyses were performed in CDCl_3 .)

After purification, the proton number ratios were in agreement with the resonance intensity ratios. (See Figure II-3-2-(2)). The smallest singlet at 3.71 ppm could be assignable to the enol form, even if this attribution has not been validated due to the low amount present. (3% compared to the malonate in the purified Und-malonate)

The reduction of Und-malonate was carried out under reflux for 2 hours using 4.1 eq. of LiAlH_4 in dried THF. In FTIR-ATR, the disappearance of the band corresponding to the carbonyl and the appearance of a large band around 3277 cm^{-1} clearly indicate the reduction of the malonate into the diol. (See Figure II-3-1-(3)) The synthesis of Und-1,3-diol was also confirmed by ^1H NMR with the disappearance of the singlet at 3.73 ppm and the triplet at 3.35 ppm. (See Figure II-3-2-(3)) Besides, it has been demonstrated that the two multiplets at 3.78 ppm and 3.63 ppm correlate with the same carbon in ^1H - ^{13}C HSQC and can be assigned to the methylene protons nearby the hydroxyl group. The synthesis of Und-1,3-diol is thus confirmed. In the literature, it is mentioned that the reduction of pure malonates afford the 1,3-diol as the principal reduction product, whereas the reduction of the corresponding enolate results in a mixture of products containing mainly allylic alcohol along

with lesser amounts of aldehyde and saturated alcohol.^{3, 4} As the amount of the enol derivative was low in Und-malonate, the Und-1,3-diol was obtained as the major product. As presented in the Part II - Chapter 1, various methods have been developed to cyclize 1,3-diols and then obtain 6-membered cyclic carbonates. The cyclization of the Und-1,3-diol into Und-6CC has been managed using ethyl chloroformate and a stoichiometric amount of TEA at room temperature in THF and diluted conditions. This method was preferred over non phosgene route due to the compared high conversion obtained on the model reaction with 1,3-propanediol. (See Table II-3-2 and Figure II-3-3) However, non phosgene routes can be also largely feasible as reported in the literature.⁵⁻¹³ After the reaction, remaining ethyl chloroformate and Und-1,3-diol (3%) as well as side products formed (16% of the open carbonate obtained by the reaction of Und-1,3-diol and 1 eq. ethyl chloroformate) were removed by flash chromatography. The purity of the final Und-6CC was 99.5% as determined by GC-FID. (See SI Figure II-3-3 and II-3-2 for the NMR and GC analyses respectively of purified Und-6CC) The preliminary method was the direct use of dimethyl sebacate to obtain a dimalonate, then a tetra-ol and the subsequent bis cyclic carbonate. However, the herein reported strategy, from methyl undecenoate with further coupling, was preferred due to the increase of side products during the cyclization of the tetra-ol.

Table II-3-2- Optimization of the conditions on 1,3-propanediol for the synthesis of 6-membered cyclic carbonate. (TEA= triethyl amine, ECF=Ethyl chloroformate and DCM=dimethyl carbonate ; (1) RT, THF ; (2) 80°C, toluene ; (3) Estimation)

1,3-propanediol (eq.)	Additive	Carbonation agent	Concentration (mol.L ⁻¹)	Oligomers (SEC in THF)	% 6CC (¹ H NMR ³)
1	TEA (2 eq.)	ECF (2 eq.)	12 ¹	++	
1	TEA (2 eq.)	ECF (2 eq.)	0.13 ¹	+	45.1 (2h)
1	TEA (2 eq.)	ECF (2 eq.)	0.13 ¹		44.5 (2h)
1	TEA (2.5 eq.)	ECF (2 eq.)	0.13 ¹		50.5 (2h)
1	TBD (5 wt%)	DMC (1 eq.)	0.13 ²		3.3 (7h)

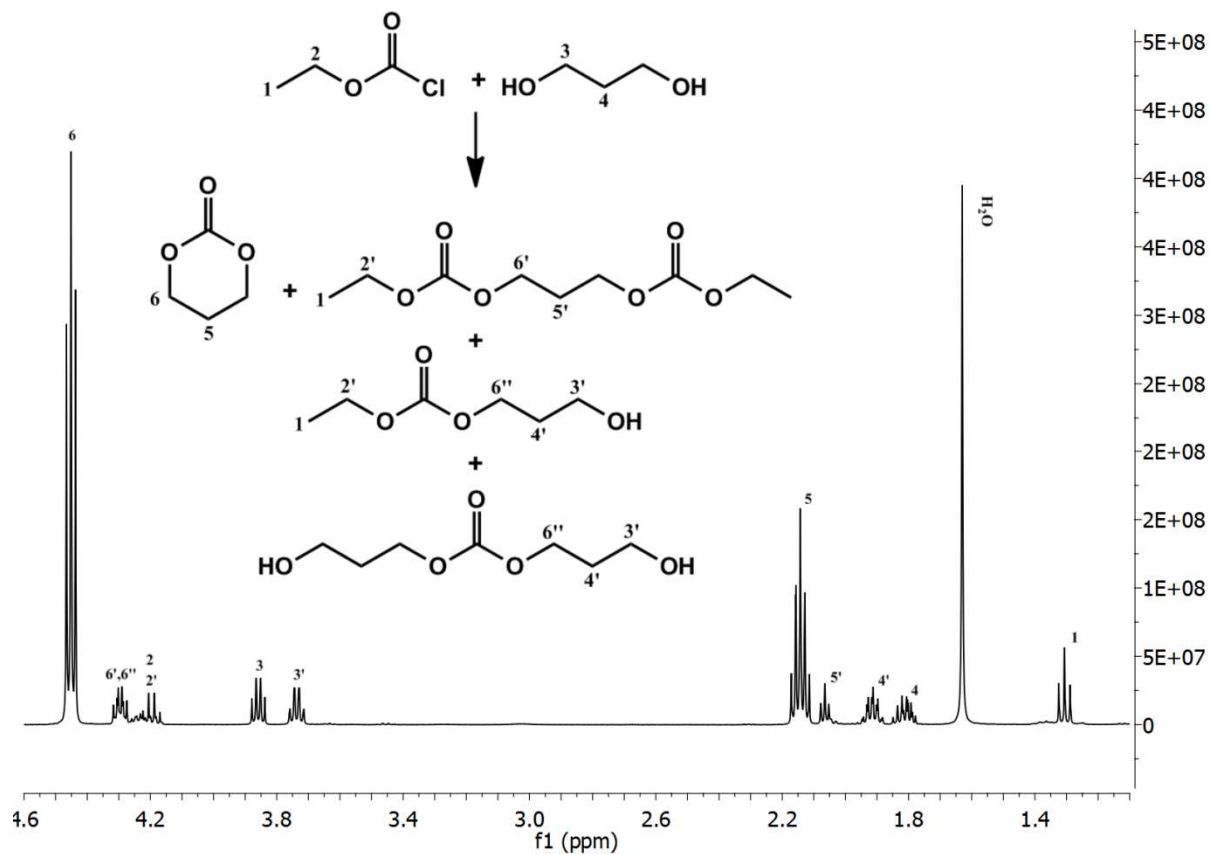


Figure II-3-3- Synthesis of 6-membered cyclic carbonate from 1,3-propanediol. (Analysis in $CDCl_3$)

1.2- Coupling reactions

The monofunctional Und-6CC, synthesized in the first part, was coupled thanks to the terminal double bond on its long alkyl chain, by metathesis (UndC20-b6CC) and thiol-ene (UndS-b6CC) reactions. (See Steps d and e respectively in Scheme II-3-1) These reactions have gained attention in the last decades as green methodologies and were chosen due to the mild conditions required. The Figure II-3-4 presents the stacked 1H NMR respectively for the purified Und-6CC, UndC20-b6CC and UndS-b6CC.

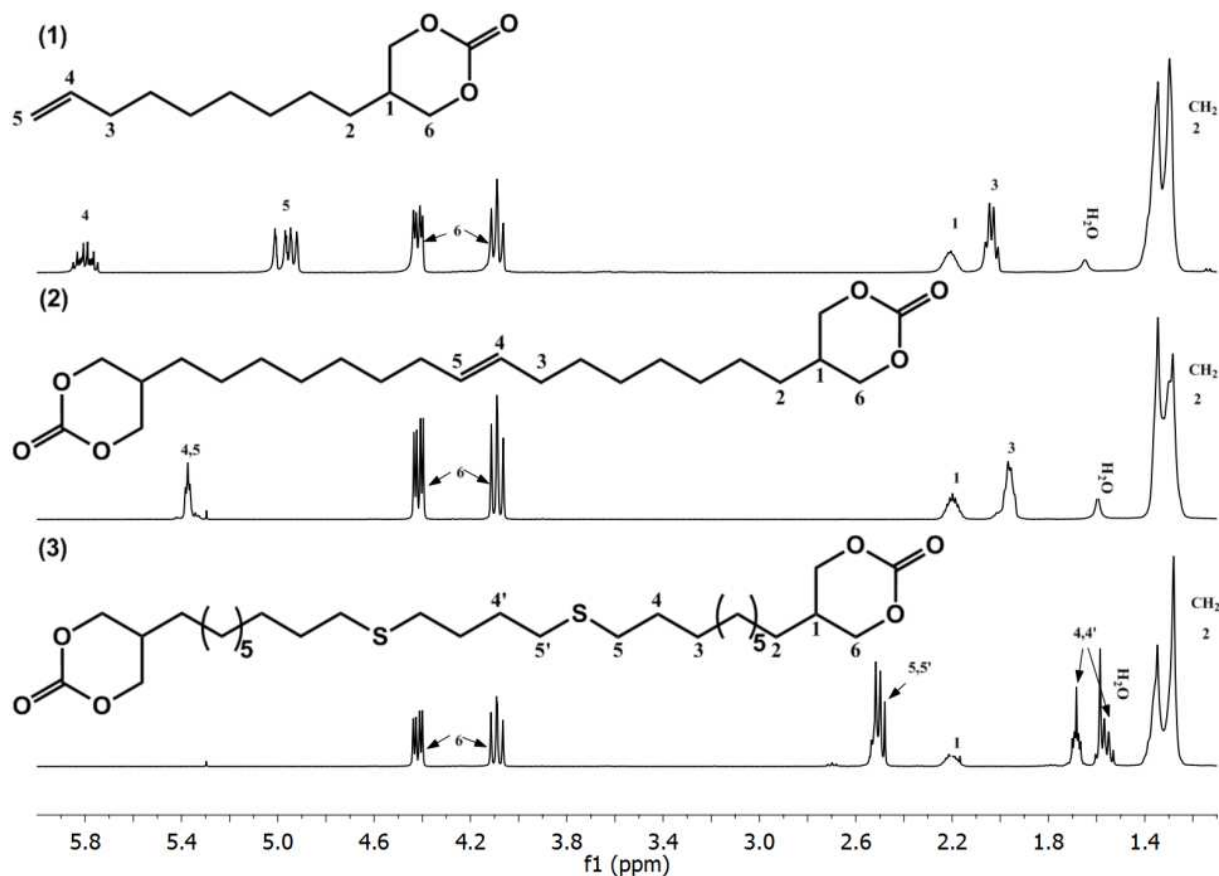


Figure II-3-4- Stacked ^1H NMR spectra of (1) Und-6CC, (2) UndC20-b6CC and (3) UndS-b6CC. (Analyses in CDCl_3 .)

The metathesis reaction of Und-6CC was performed at room temperature in dried pentane with 3rd generation Grubbs catalyst (1/200). The equilibrium was driven thanks to the precipitation of the formed product. A conversion of 67.0% was achieved after 4 hours as estimated by ^1H NMR. The reaction was confirmed by the simultaneous disappearance of the multiplet at 5.81 ppm and 4.96 ppm, and the appearance of the multiplet at 5.37 ppm. (See protons H4 and H5 in Figure II-3-4-(2)) As can be calculated from the integration of the peak corresponding to the CH_2 , isomerizations occurred during the metathesis. This observation has been validated by MALDI-TOF MS analyses. (See the polymer part) The product was then purified with flash chromatography using a mixture of cyclohexane and ethyl acetate as eluent to eliminate the isomerized side products. Indeed, the flash chromatography was a preferred purification method since a recrystallization test of UndC20-b6CC in methanol, the 6-membered cyclic carbonates got opened. (See Figure II-3-5)

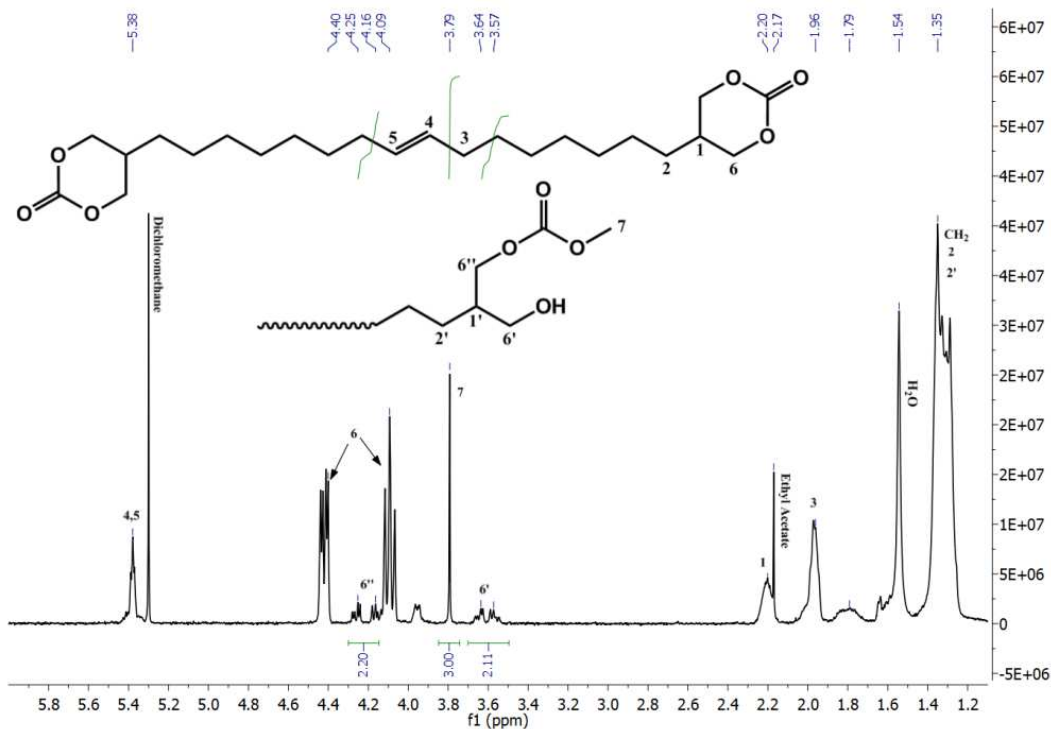


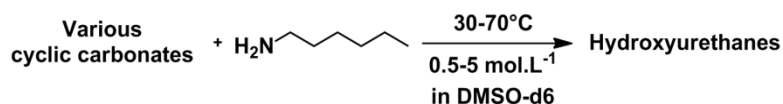
Figure II-3-5- Evidence for the ring opening of the 6-membered cyclic carbonates of UndC20-b6CC while a test of recrystallization in methanol. (Analysis performed in $CDCl_3$.)

In the line with the environmentally friendly and high efficiency process, the click chemistry thiol-ene addition, which has already been valorized with vegetable oil derivatives¹⁴, was also tried for the coupling of Und-6CC. The thiol-ene reaction was carried out under UV irradiations at room temperature. The reaction was monitored with 1H NMR spectroscopy with the disappearance of the double bond protons. The poor yield ($Y=37\%$) for the thiol-ene reaction step can be explained by the formation of side products. Indeed, compounds with higher molar masses were present in the mixture as observed in SEC. These side products are suspected to be the consequence of the ring opening of the 6-membered cyclic carbonates with Und-1,3-diol, regenerated by the reaction of Und-6CC with water and subsequent release of CO_2 . This hypothesis can be supported by the fact that the test of recrystallization of UndC20-b6CC (See above) and UndS-b6CC in methanol leads to the opening of the 6-membered cyclic carbonates by the methanol, but can not be confirmed by 1H NMR. Indeed, low amount of side products are detected and the formation of disulfide bridge is not excluded.

The UndC20-b6CC and UndS-b6CC samples were subjected to a thermal treatment in DSC ($10^\circ C \cdot min^{-1}$ to $120^\circ C$ then an isotherm of 15 minutes at this temperature) in order to evaluate their thermal stabilities by analyzing them after the treatment by 1H NMR. No thermal degradation was noticed in both cases.

2- Comparison of different cyclic carbonates reactivity

In order to identify precisely the difference in reactivity between 6-membered and 5-membered cyclic carbonates, kinetic experiments have been performed. (See Scheme II-3-2) The monitoring of the kinetic of the reaction was carried out directly in NMR apparatus at the selected temperature. For the different substrates, the conversions were calculated from the decrease of the peaks corresponding to the cyclic carbonates. The influence of the ring size of the carbonate, the substituents, the total reactants concentration, the temperature and the amine ratio were investigated. The presence of additives such as triethylamine and acetic acid were also examined. Then, based on the resulting kinetic curves, the orders of the reactions were determined together with the reaction rate constants.



Scheme II-3-2- Model reaction of various cyclic carbonates with hexylamine in different conditions.

Various cyclic carbonate substrates such as trimethylene carbonate (6CC), Und-6CC, ethylene carbonate (5CC), vinyl ethylene carbonate (5CCvinyl), glycerol carbonate (5CChydroxyl) and propylene carbonate (5CCMe) have been investigated on the reaction with hexylamine at 50°C and 1 mol.L⁻¹ in DMSO-d₆, using TCB as a reference. Otherwise mentioned, the ratio between cyclic carbonate and amine was 1:1. With the ¹H NMR spectra at the initial times, a ratio of 1:1.0 to 1:1.18 was confirmed. To compare the reactivity between 5- and 6-membered cyclic carbonates with a long alkyl chain, Dec-5CC has also been synthesized from 1,2-epoxy-9-decene, which is commercially available. The NMR analyses of the different model reactions are presented in Figure II-3-6, Figure II-3-7 and Figure II-3-8. With Und-6CC for instance, as the reaction was going, the signals for the protons nearby the cyclic carbonate at 4.40 ppm and 4.09 ppm decreased. Moreover, three signals at 3.94 ppm (CH₂-OCONH), 3.41 ppm (CH₂-OH) and 2.98 ppm (CH₂-NHCOO), corresponding to the formation of the urethane appeared. As can be seen from the Figure II-3-6-(2), the peak corresponding to the generated OH between 3 ppm and 4 ppm was detected after 4 hours. In FTIR-ATR, a band at 1705 cm⁻¹ also confirmed the formation of urethane.

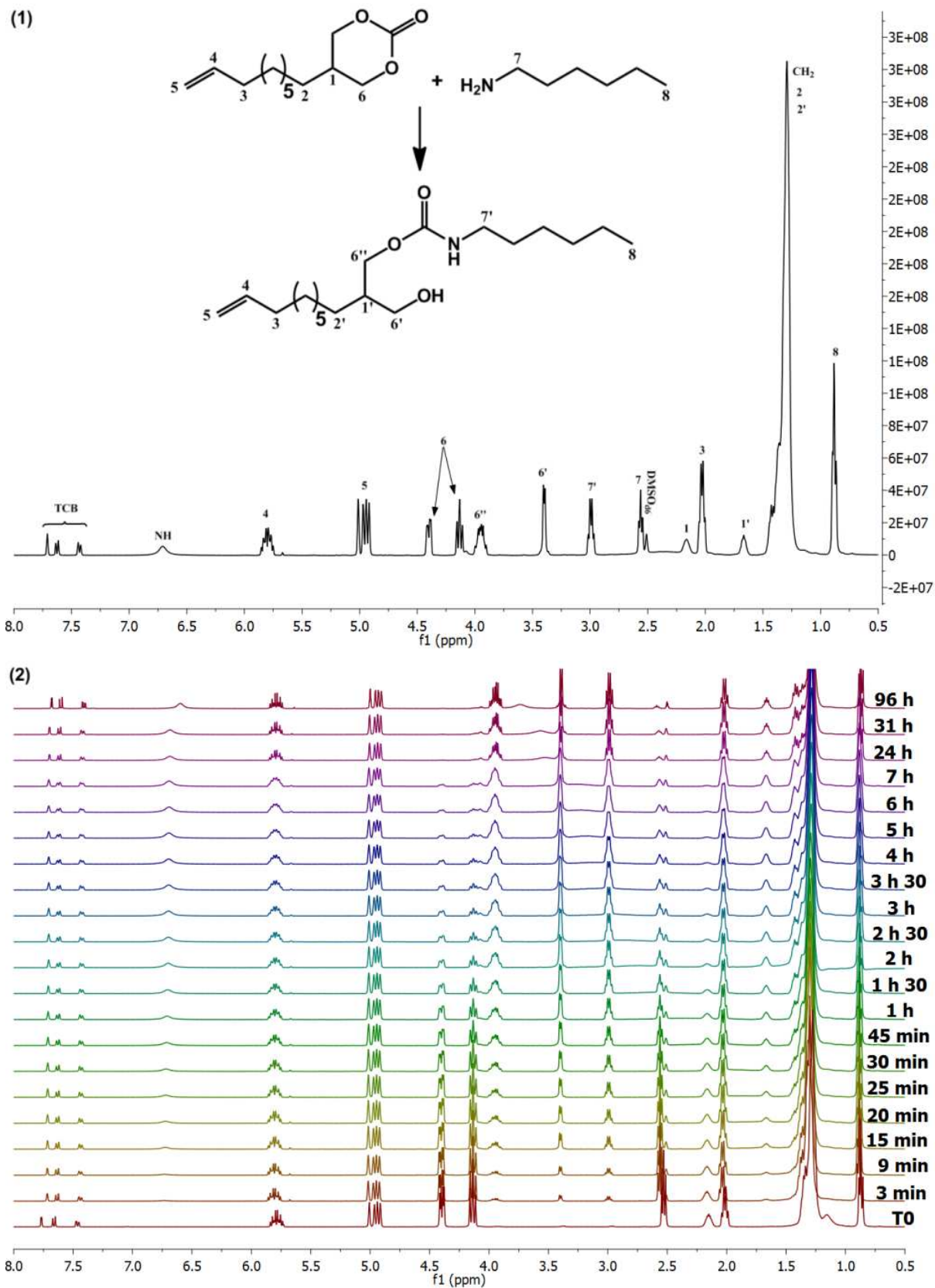


Figure II-3-6- Reaction between Und-6CC and hexylamine at 70°C in DMSO-d₆ at 1 mol.L⁻¹, with a ratio 1:1. (1) ¹H NMR after 1 hour and (2) Stacked ¹H NMR monitoring.

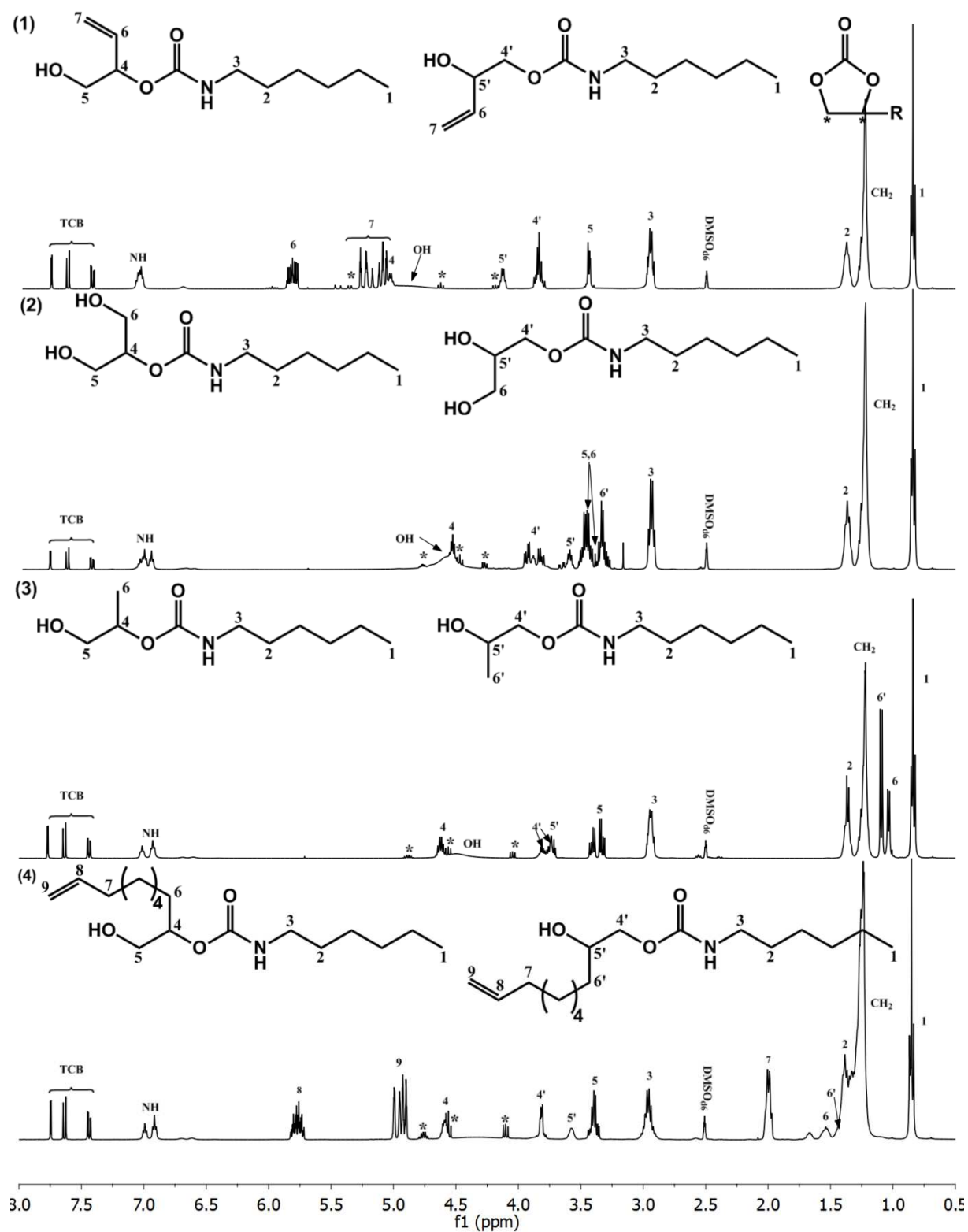


Figure II-3-7- Stacked ^1H NMR of the different model reaction performed with hexylamine at 50°C in DMSO-d_6 at $1\text{ mol}\cdot\text{L}^{-1}$. (1) from vinyl ethylene carbonate, (2) from glycerol carbonate, (3) from propylene carbonate and (4) from Dec-5CC. (*) Correspond to the protons of the starting carbonate.

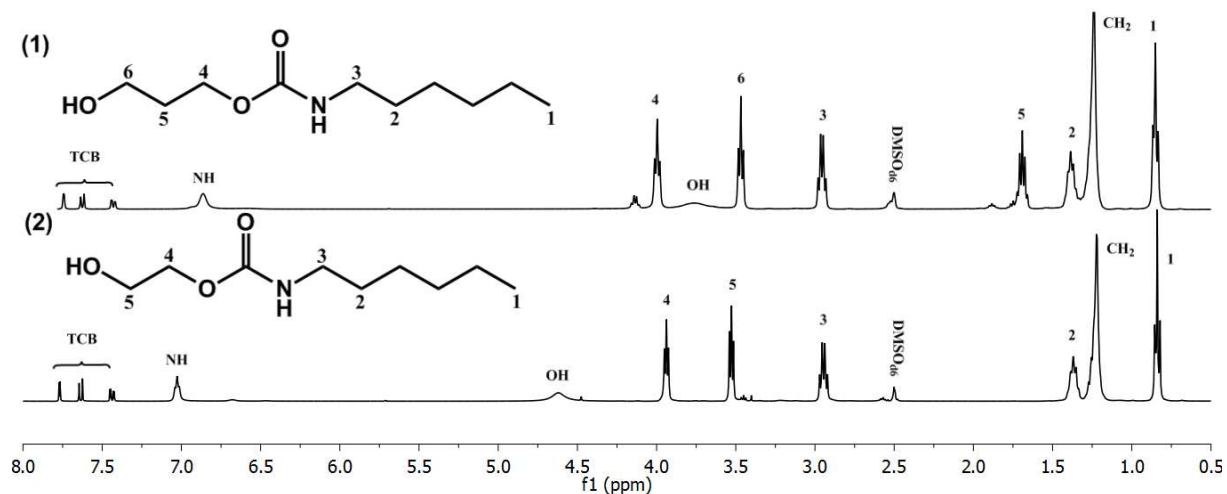


Figure II-3-8- Stacked ^1H NMR of the different model reaction performed with hexylamine at 50°C in DMSO-d_6 at 1 mol.L^{-1} .
¹. (1) from trimethylene carbonate and (2) from ethylene carbonate.

The Figure II-3-9 illustrates the difference in reactivity of the various cyclic carbonates; 5- and 6-membered ones. The conversion was calculated by ^1H NMR using the equation:

$$x = 100 - \frac{(I_c/I_{\text{TCB}})_t}{(I_c/I_{\text{TCB}})_{t=0}} * 100, \text{ where } x, t, I_c \text{ and } I_{\text{TCB}} \text{ are the conversion, the time, the}$$

integrations of the peaks corresponding to the cyclic carbonate and TCB respectively.

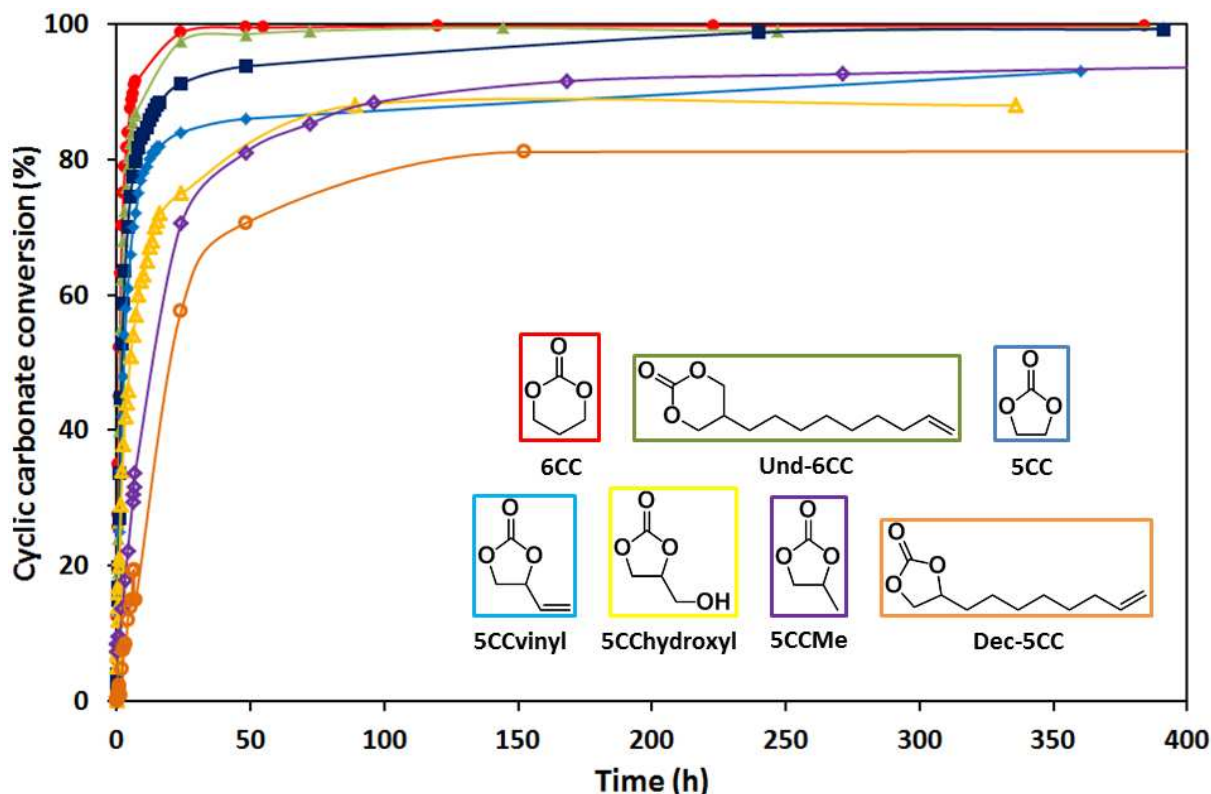


Figure II-3-9- Effect of various cyclic carbonates chemical structures on the kinetic of the reactions with hexylamine. (50°C , 1 mol.L^{-1} in DMSO-d_6 , ratio 1:1)

Regarding the reaction order of the reactions, better fits were obtained considering a second order in all cases, as mostly reported in the literature. Indeed, as depicted in Figure II-3-10, the relationships between the reaction time and $x/(1-x)$ (in which x is represent the cyclic carbonate conversion after a certain time) are initially linear.

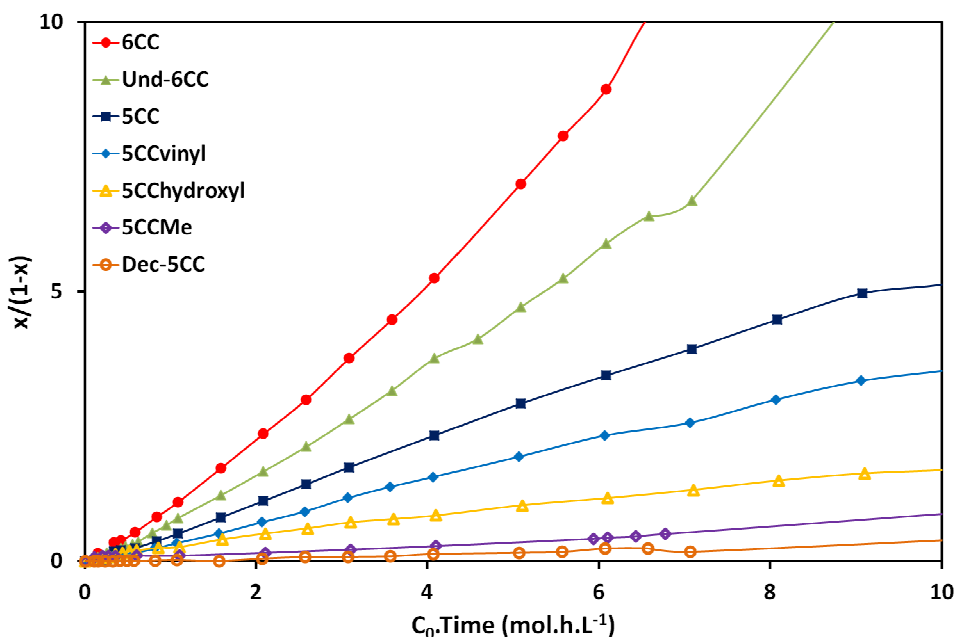


Figure II-3-10- Verification of the second order kinetic law: Time- $(x/(1-x))$ relationships for the reactions of cyclic carbonates with hexylamine, at 50°C and in DMSO- d_6 (1 mol.L⁻¹).

The equation (E5) was used to estimate the reaction rate constants in the case of the ratio 1:1 between cyclic carbonate and amine. In the equation (E1), $[CC]$ and $[A]$ are the concentrations at a certain time of cyclic carbonate and amine respectively, and $[CC]=[A]$. In the equation (E4), x is the conversion. The initial concentration of cyclic carbonate (C_0) is equal to 0.2, 1 or 5 mol.L⁻¹. The reaction rate constants are calculated from the first 8 hours.

$$-\frac{d[CC]}{dt} = k_{app}[CC][A] = k_{app}[CC]^2 \quad (E1)$$

$$-\frac{d[CC]}{[CC]^2} = k_{app}dt \quad (E2)$$

$$\frac{1}{[CC]} - \frac{1}{C_0} = k_{app}\Delta t \quad (E3)$$

$$\text{or } [CC] = C_0 - C_0x = C_0(1 - x) \quad (E4)$$

$$\frac{x}{1-x} = k_{app}C_0\Delta t \quad (E5)$$

The Table II-3-3 gives the estimated initial apparent reaction rate constants k_{app} obtained from the slopes of the curves in Figure II-3-9 and Figure II-3-10 for the different cyclic carbonates.

Table II-3-3- Reaction rate constants obtained for the different model reactions.

Cyclic carbonate	[CC] (mol.L ⁻¹)	T (°C)	Additives (7 mol%)	k _{app} (L.mol ⁻¹ .h ⁻¹)	Ratio OH I : OH II ¹
Und-6CC	1	30	/	0.46	/
	1	50	/	0.93	/
	1	70	/	1.92	/
	0.2	50	/	0.15	/
	5	50	/	1.77	/
trimethylene carbonate	1	50	/	1.41	/
	1	50	TEA	1.86	/
	1	50	acetic acid	1.39	/
ethylene carbonate	1	50	/	0.56	/
vinyl ethylene carbonate	1	50	/	0.37	42:58
glycerol carbonate	1	50	/	0.17	32:68*
propylene carbonate	1	50	/	0.08	59:41
Dec-5CC	1	50	/	0.03	57:43

(1) Calculated by ¹H NMR using the equation: % OH I = $\frac{I_{OH I}}{I_{OH I} + I_{OH II}} * 100$, where % OH I, I_{OH I} and I_{OH II} are the % of the product with primary hydroxyl and the integrations of the peaks corresponding to the product with primary and secondary hydroxyl respectively. (*) Only estimation due to peak overlaps.

As reported in the literature, trimethylene carbonate was much more reactive than ethylene carbonate. These reactivity differences for the various size rings can also be underlined while comparing Dec-5CC and Und-6CC. The Und-6CC demonstrated a higher reactivity than the Dec-5CC, with reaction rate constants of 0.93 L.mol⁻¹.h⁻¹ and 0.03 L.mol⁻¹.h⁻¹ respectively. The difference in reactivity between trimethylene carbonate and Und-6CC is quite low. In the case of 6-membered cyclic carbonate, the effect of an alkyl group with +I inductive effect seems limited. However, the difference between the kinetic curves of ethylene carbonate, propylene carbonate and Dec-5CC clearly demonstrated the effect of a +I inductive effect substituent on the reactivity of the 5-membered cyclic group. This observation explains the low reactivity of the fatty acid-based 5-membered cyclic carbonates developed in the Part II - Chapter 2. The kinetics diverged from the second order after a certain time: for the 6-membered cyclic carbonates the reaction was accelerated, whereas for the 5-membered ones, the reactions were slow down.

Moreover, the acceleration (deviation from the 2nd order) observed with the 6-membered cyclic carbonates after a certain time could be the result of a positive effect of the hydroxyl urethanes formed. Indeed, the primary hydroxyl can be considered as hydrogen bonds donors which could activate the carbonyl of the cyclic urethane. For the deviation from the

2nd order for the 5-membered cyclic carbonates, the decrease of the amine concentration along the reaction can explain the decrease in reactivity.

Different ratio of regioisomers (primary OH generated (%): secondary OH generated (%)) were obtained: 42:58 from vinyl ethylene carbonate, 32:68* from glycerol carbonate, 59:41 from propylene carbonate and 57:43 for Dec-5CC. (* estimation due to peak overlaps) For vinyl ethylene carbonate and glycerol carbonate, those ratios were in accordance with the ones reported in the literature. One can noticed that more primary alcohols were generated for propylene carbonate comparing to the literature, which was also the case in the catalysis part of the Part II - Chapter 2. The reactivity of vinyl ethylene carbonate and glycerol carbonate are better than propylene carbonate. However, even after 3 weeks, these reactions with propylene carbonate, vinyl ethylene carbonate and glycerol carbonate did not reach full conversions, but conversions in the range 91%-94% were calculated.

An increase of the initial reactant concentration and temperature leads to an increase of the kinetic of the reaction between Und-6CC and hexylamine. (See Figure II-3-11 and Figure II-3-12 respectively) The reaction rate constants are 0.15, 0.93 and 1.77 L.mol⁻¹.h⁻¹ at 0.2, 1 and 5 mol.L⁻¹ respectively. The higher the initial concentration is, the faster the kinetic of the reaction is. However at low conversion, k_{app} can be considered as a constant and the previous calculations are still valid. Moreover, a slight deviation from the 2nd order can be observed at 5 mol.L⁻¹.

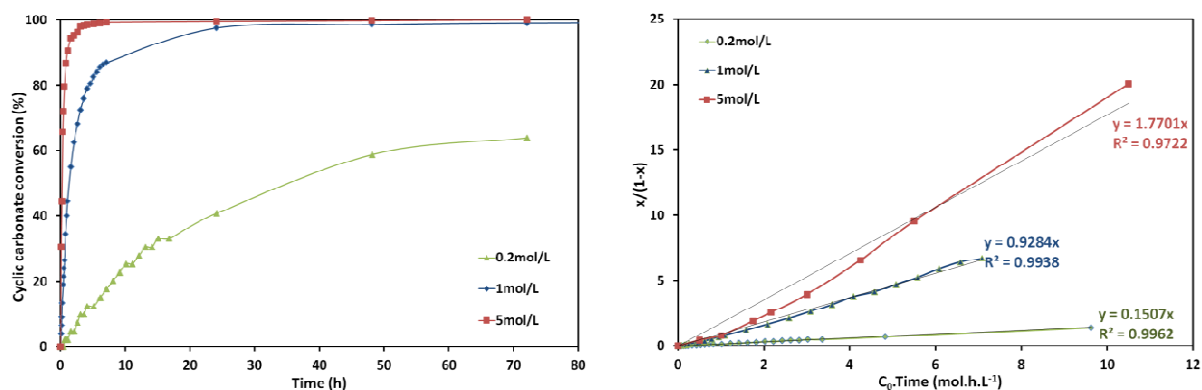


Figure II-3-11- Effect of the reactant concentrations on the kinetic of the reactions between Und-6CC and hexylamine. (50°C, in DMSO-d₆, ratio 1:1)

The reaction rate constants are 0.46, 0.93 and 1.92 L.mol⁻¹.h⁻¹ at 30, 50 and 70°C respectively. From the Arrhenius plot, the activation energy (E_a) can be estimated as 20.7 kJ.mol⁻¹ for Und-6CC. In the literature, Endo and coll. reported activation energies of 10.1 and 24.6 kJ.mol⁻¹ for 5- and 6-membered cyclic carbonates having an unsaturated alkyl chain substituent.¹⁵ Further experiments at other temperatures would allow a more precise

calculation of the activation energy. Besides, as for the concentration increase, a slight deviation from the second order can also be noticed at higher temperature such as 70°C.

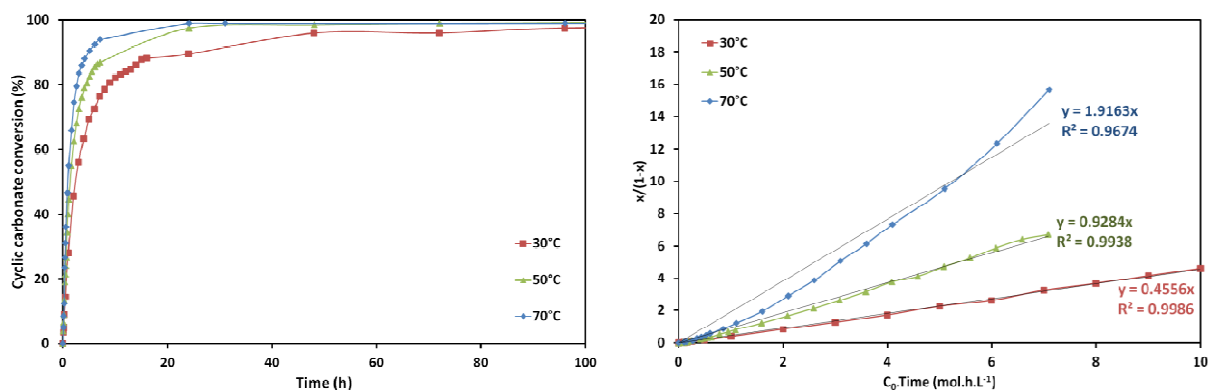


Figure II-3-12- Effect of the temperature on the kinetic of the reactions between Und-6CC and hexylamine. (1 mol.L⁻¹ in DMSO-d₆, ratio 1:1)

The ratio of amine has also an influence on the kinetic of the reaction between Und-6CC and hexylamine. While increasing the ratio of amine, the kinetic diverge from the second order and a third order can not fit with the experimental data. As the starting concentration of amine is higher, the reaction rates increase. Indeed as can be seen from the Figure II-3-13, the positive effect of the amine on the kinetic can be underlined.

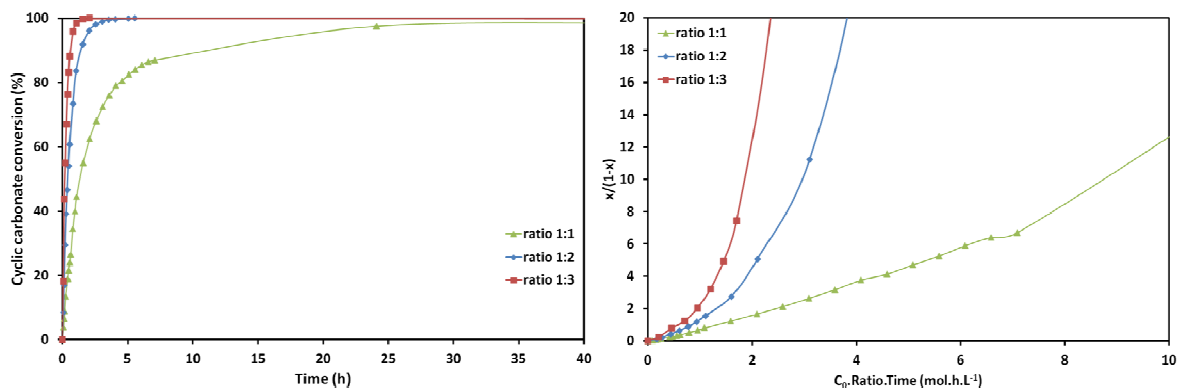


Figure II-3-13- Effect of the cyclic carbonate to hexylamine ratio on the kinetic of the reactions with Und-6CC. (50°C, 1 mol.L⁻¹ in DMSO-d₆)

As can be observed from the Figure II-3-14, triethylamine and acetic acid have limited influence on the reaction between trimethylene carbonate and hexylamine.

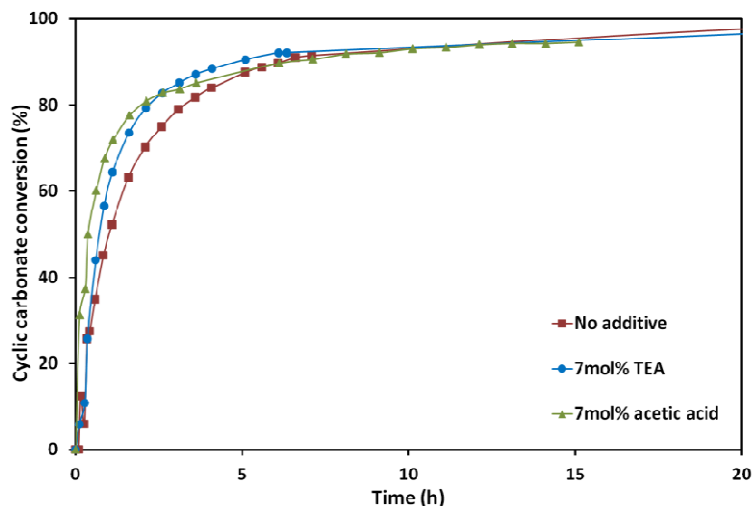


Figure II-3-14- Effect of additives on the kinetic of the reactions between trimethylene carbonate and hexylamine. (50°C, 1 mol.L⁻¹ in DMSO-d₆, ratio 1:1)

In some of these model reactions with 6-membered cyclic carbonates, side products were detected by ESI-TOF MS. In case of the reaction between trimethylene carbonate and hexylamine, the formation of around 17% of a urethane-carbonate alcohol was observed. This side product comes from the ring opening of trimethylene carbonate by the expected hydroxyurethane. While performing the reaction at different temperatures (30°C, 50°C and 70°C), no side products were noticed for the reactions of Und-6CC and hexylamine at 1 mol.L⁻¹. However, the ESI-TOF MS analysis of the reactions at 0.2 mol.L⁻¹ and 5 mol.L⁻¹ show around 15% and 2% respectively of similar urethane-carbonate alcohol. The given percentages from ESI-TOF MS are based on the hypothesis of a comparable ionization of the products, which is coherent due to chemical structure similarities.

As side reactions between the generated primary alcohols and the remaining cyclic carbonates were suspected, the reaction between Und-6CC and octanol was conducted. When the reaction was carried at 50°C and 1 mol.L⁻¹ of Und-6CC in DMSO-d₆ and that 25 eq. of octanol was added, the 6-membered cyclic carbonate got opened with a conversion of 35.3% after 24 hours. The formation of around 11% of dialkyl carbonates and 3% of bis dialkyl carbonates was observed by ESI-TOF MS analysis of the reaction mixture. These products are obtained by the ring opening of Und-6CC by Und-1,3-diol, the latter being regenerated by the reaction of Und-6CC with moisture. However, no reaction occurred in assessable amount, in the same concentration conditions with 5 eq. and 0.1 eq. of octanol. Besides, while performing the reaction at 50°C and 1 mol.L⁻¹ of total reactants in DMSO-d₆ with 25 eq. of octanol, no reaction was either observed, even if the presence of a small amount of water was also detected in ¹H NMR for those reactions. In Figure II-3-15, the kinetic curve of the ring opening of the 6-membered cyclic carbonate of Und-6CC is

compared to the reaction between Und-6CC and hexylamine (1:1). To conclude, it seems that specific conditions such as concentration and polarity lead to side products generated by the ring opening of the 6-membered cyclic carbonates with the hydroxyurethanes or other alcohol.

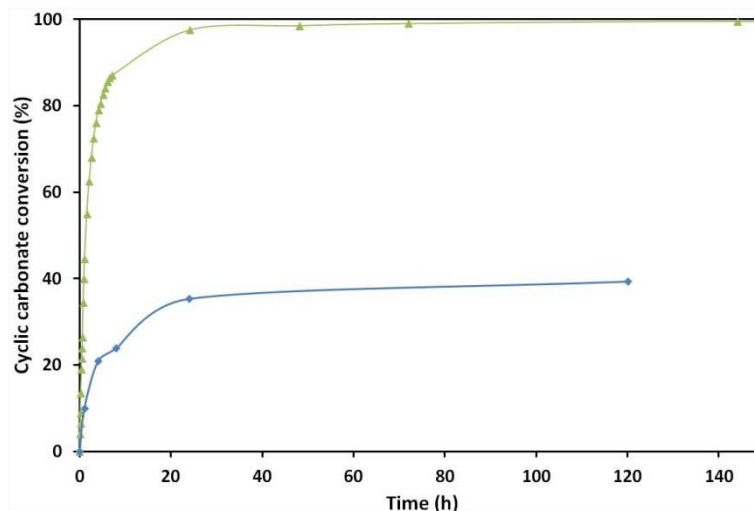
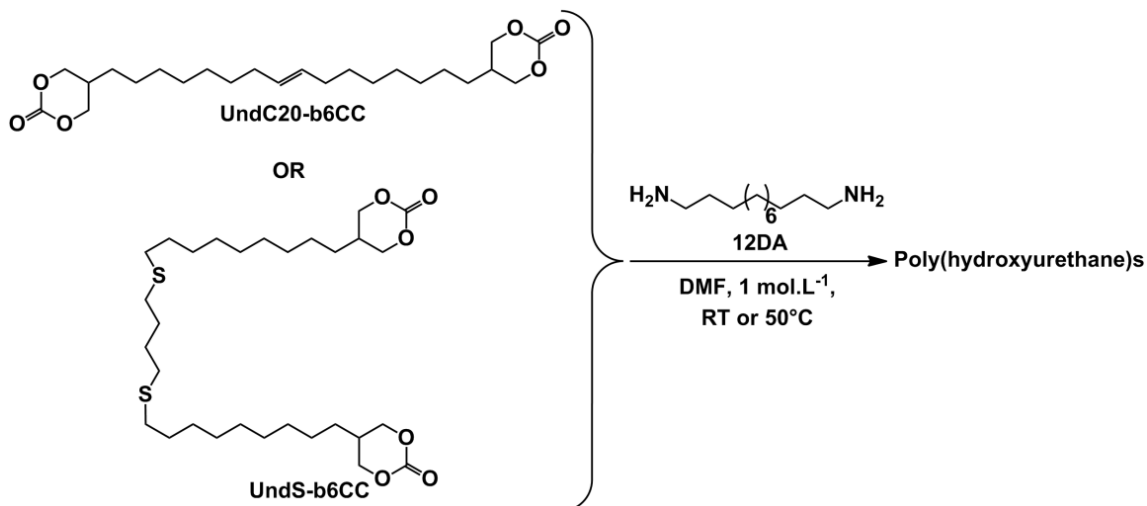


Figure II-3-15- Comparison of the 6-membered cyclic carbonate conversion with hexylamine (green) and in the case of water traces and large amount of octanol (blue). (50°C, 1 mol.L⁻¹ of Und-6CC in DMSO-d₆, ratio 1 :1 for the hexylamine and 1:25 for the octanol)

3- Polymerization

3.1- Synthesis of PHUs and related molar masses

PHUs were synthesized from the two bis 6-membered cyclic carbonates: UndC20-b6CC or UndS-b6CC and dodecane-1,12-diamine (12DA) as comonomer. (See Scheme II-3-3) The polymerizations were performed in DMF at 1 mol.L⁻¹, at RT or 50°C. The kinetic experiments were performed in DMSO but for solubility reason, DMF was used for the polymerizations.



Scheme II-3-3- Poly(hydroxyurethane) synthesis from UndC20-b6CC or UndS-b6CC and dodecane-1,12-diamine (12DA).

The PHU formation was confirmed by FTIR-ATR by the appearance of bands at 1686 cm⁻¹ and 1534 cm⁻¹, which correspond to the urethane linkage C=O and CN vibrations respectively. Besides, a large band at 3620 cm⁻¹-3158 cm⁻¹ was attributed to the NH and OH vibrations. The generation of primary hydroxyl was also proved by the bands at 1266 cm⁻¹, 1244 cm⁻¹ and 1027 cm⁻¹. The FTIR-ATR spectra of UndC20-b6CC and the corresponding PHU with 12DA (PHU-2) are given in Figure II-3-16.

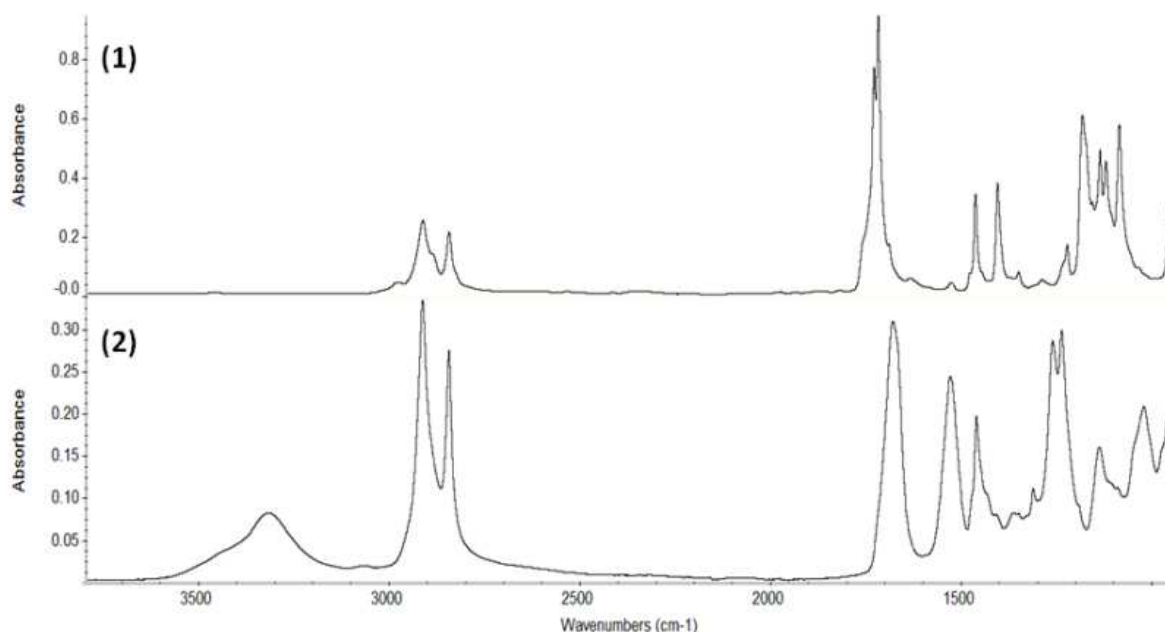


Figure II-3-16- Stacked FTIR-ATR spectra of (1) UndC20-b6CC and (2) the corresponding poly(hydroxyurethane)s with dodecane-1,12-diamine (PHU-2).

The chemical structures of the PHUs were also supported by NMR analyses, as illustrated in Figure II-3-17 for PHU-2. The signals for the protons corresponding to the opening of the 6-membered cyclic carbonate appeared in the ranges 4.00-4.15 ppm and 3.42-3.50 ppm. The formation of the urethane linkage was confirmed by the presence of the signal at 3.11 ppm,

which corresponds to the protons nearby the nitrogen atom of the urethane function. In Figure II-3-18 the evolutions of the cyclic carbonate conversions calculated by FTIR-ATR and by ^1H NMR are plotted for the polymerization of UndC20-b6CC and UndS-b6CC with 12DA. A good agreement between the two manners to estimate the conversion can be observed. Due to solubility patterns, the conversion by ^1H NMR cannot be given after 24 hours for the polymerizations performed at 50°C . The conversion x was calculated by ^1H NMR using the equation: $x = 100 - \frac{(I_{\text{CC}}/I_{\text{TCB}})_t}{(I_{\text{CC}}/I_{\text{TCB}})_{t=0}} * 100$, where t , I_{CC} and I_{TCB} are the time, the integrations of the peaks corresponding to the cyclic carbonate and the reference TCB respectively. Using FTIR-ATR, the conversion x was calculated using the equation: $x = 100 - \frac{(H_{\text{CC}}/H_{\text{CH}_2})_t}{(H_{\text{CC}}/H_{\text{CH}_2})_{t=0}} * 100$, where t , H_{CC} and H_{CH_2} are the time, the height of the peaks corresponding to the cyclic carbonate and CH_2 respectively.

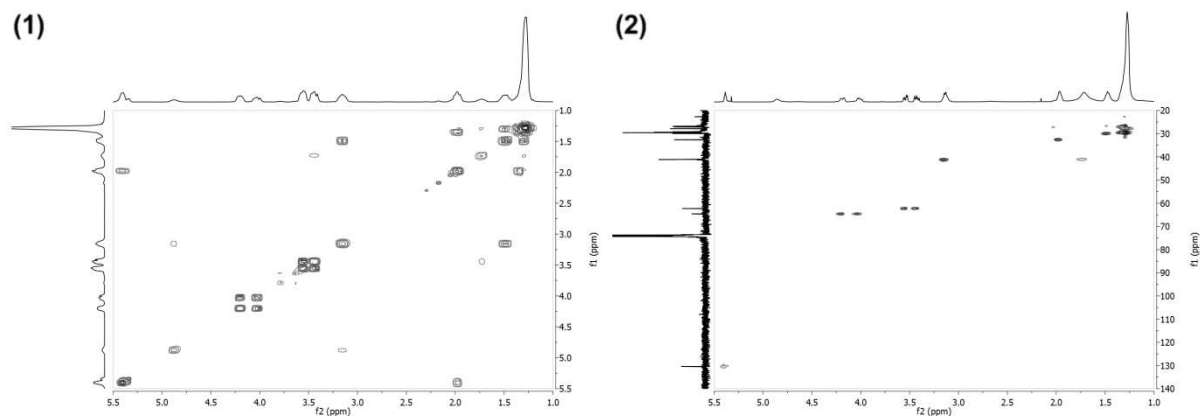


Figure II-3-17-(1) ^1H - ^1H COSY and (2) ^1H - ^{13}C HSQC-NMR spectra of PHU-2 from UndC20-b6CC and 12DA after quenching and DMF evaporation. (Analyses in TCE)

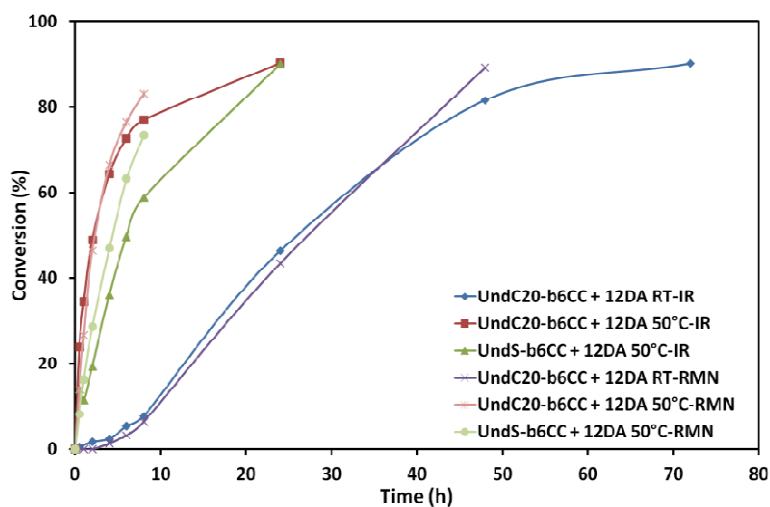


Figure II-3-18- Evolution of the polymerization kinetics at room temperature and 50°C by FTIR-ATR and ^1H NMR for UndC20-b6CC and UndS-b6CC with dodecane-1,12-diamine.

In order to notice in details whether or not side reactions occurred during the polymerization, MALDI-TOF MS analyses were carried out on the PHUs.

When the samples were quenched with hexylamine, the formation of urea was detected as describe below. After one day at 50°C, the polymerization mixtures appeared as gels and were not soluble anymore, which can be explained by the formation of side reactions between the hydroxyl groups present in the polymer backbone and the remaining cyclic carbonates, as describe in the previous part. After quenching with hexylamine, the mixture was soluble again and characterized by MALDI-TOF MS. Moreover the generated diol was also easily observable in ^1H NMR and MALDI-TOF MS.

The MALDI-TOF MS of quenched PHU-2 and PHU-3 are presented in Figure II-3-19 and Figure II-3-20 respectively. While analyzing the different signals, the three PHU families were detected (See Table II-3-4): (F1) terminated with two cyclic carbonates quenched, (F2) with one cyclic carbonate quenched and one amine and (F3) with two amines. In the particular case of PHU-2, the isomerizations that have taken place during the metathesis were clearly visible with peaks sets separated by 14. The repeated unit was clearly visible for both PHU-2 ($M_{\text{unit}} = 624 + x \cdot M_{\text{CH}_2} \text{ g.mol}^{-1}$) and PHU-3 ($M_{\text{unit}} = 775 \text{ g.mol}^{-1}$). Moreover, smaller signals assignable to urea side reactions were also observable, corresponding both to the formation of urea (F*) and the generation of the alcohol (F**) from F1 and F2 families. (See Scheme II-3-4) The fact that the F3* was not visible confirmed that the side reactions occur during the quenching of the sample.

For non quenched PHU-1 and for the soluble fractions of PHU-2 and PHU-3, the repeated units: $M_{\text{unit}} = 624 + x \cdot M_{\text{CH}_2} \text{ g.mol}^{-1}$ (PHU-1 and PHU-2) and $M_{\text{unit}} = 775 \text{ g.mol}^{-1}$ (PHU-3) were also found.

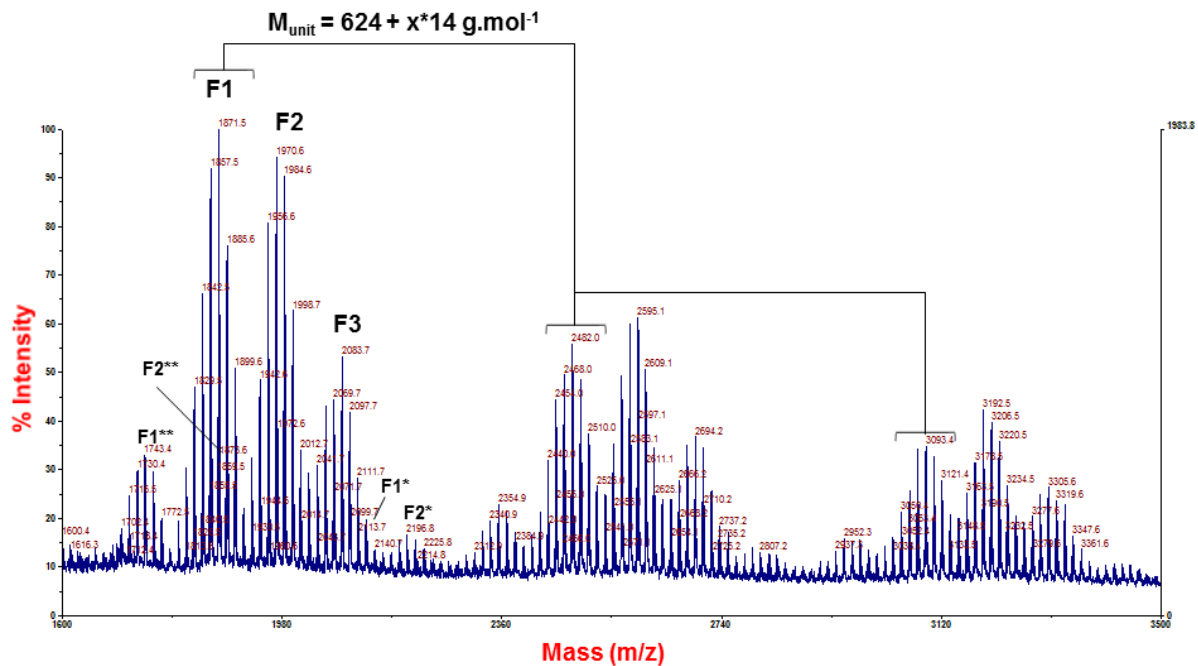


Figure II-3-19- MALDI-TOF MS analysis of PHU-2 between UndC20-b6CC and 12DA. (Matrix *trans*-3-indoleacrylic acid)

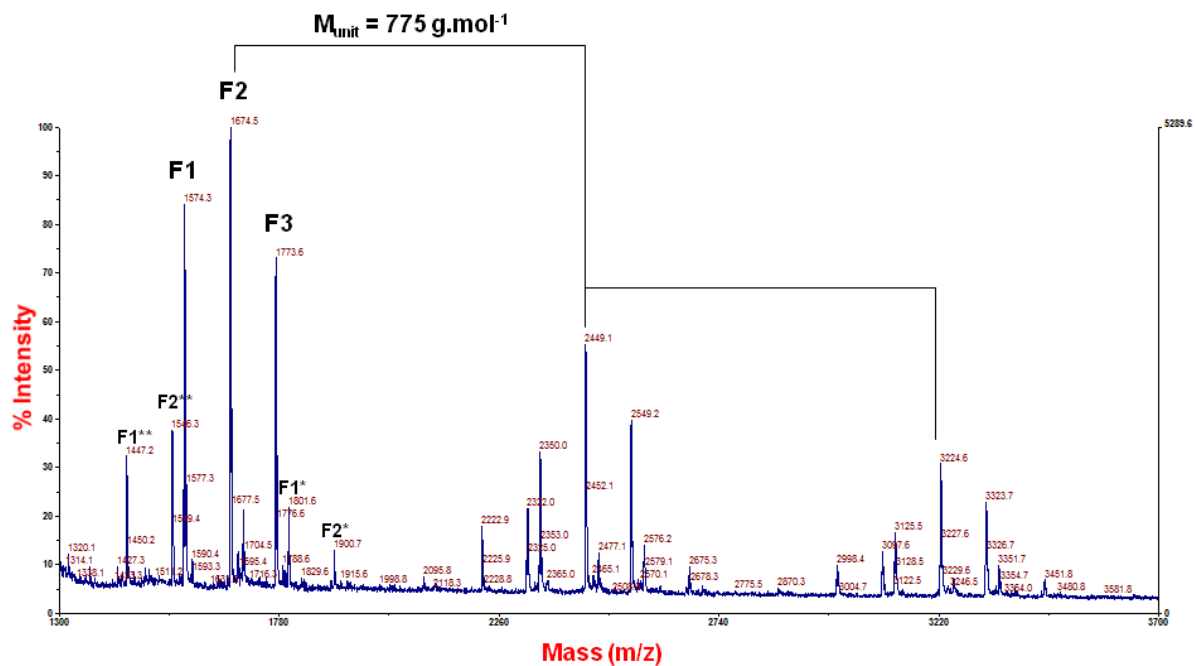
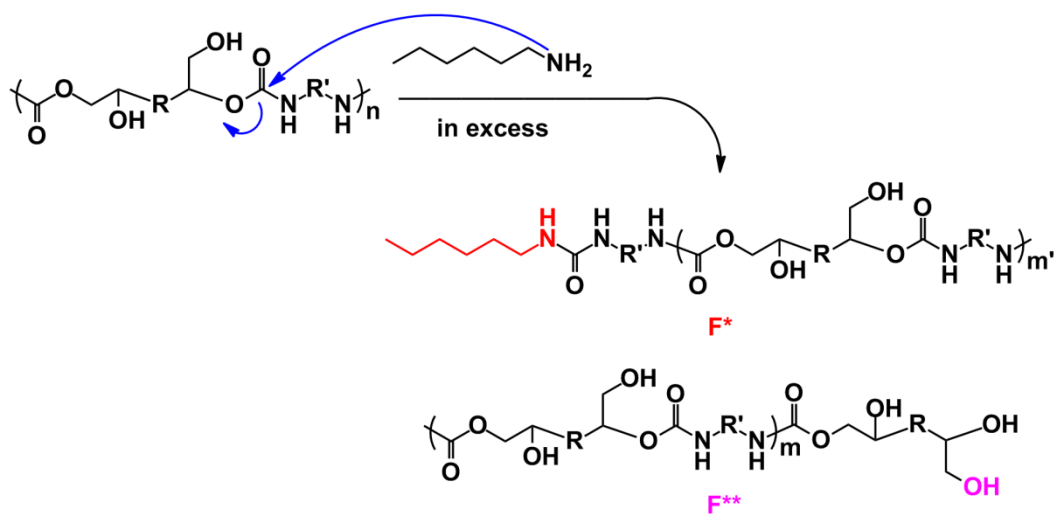


Figure II-3-20- MALDI-TOF MS analysis of the PHU-3 between UndS-b6CC and 12DA. (Matrix *trans*-3-indoleacrylic acid)

Table II-3-4- Different PHU families visible in MALDI-TOF MS.

PHU families	Description	For PHU-2	For PHU-3
		$(M_{\text{unit}} = 624 + x \cdot M_{\text{CH}_2} \cdot \text{g} \cdot \text{mol}^{-1})$	$(M_{\text{unit}} = 775 \text{ g} \cdot \text{mol}^{-1})$
F1	hex-C-(C _{n-1} -A _n)-C-hex	$n \cdot (M_{\text{unit}}) + M_{\text{UndC20-b6CC}} + 2 \cdot M_{\text{hex}} + M_{\text{Na}}$	$n \cdot (M_{\text{unit}}) + M_{\text{UndS-b6CC}} + 2 \cdot M_{\text{hex}} + M_{\text{Na}}$
F2	hex-C-(C _n -A _n)-A	$(n+1) \cdot (M_{\text{unit}}) + M_{\text{hex}} + M_{\text{Na}}$	$(n+1) \cdot (M_{\text{unit}}) + M_{\text{hex}} + M_{\text{Na}}$
F3	A-(C _{n+1} -A _n)-A	$(n+1) \cdot (M_{\text{unit}}) + M_{12\text{DA}} + M_{\text{Na}}$	$(n+1) \cdot (M_{\text{unit}}) + M_{12\text{DA}} + M_{\text{Na}}$
F1*	hex-C-(C _{n-1} -U ^A -A _n)-C-hex	$n \cdot (M_{\text{unit}}) + M_{\text{UndC20-b6CC}} + 2 \cdot M_{\text{hex}} + M_{\text{urea}} + M_{\text{Na}}$	$n \cdot (M_{\text{unit}}) + M_{\text{UndS-b6CC}} + 2 \cdot M_{\text{hex}} + M_{\text{urea}} + M_{\text{Na}}$
F2*	hex-C-(C _n -U ^A -A _n)-A	$(n+1) \cdot (M_{\text{unit}}) + M_{\text{hex}} + M_{\text{urea}} + M_{\text{Na}}$	$(n+1) \cdot (M_{\text{unit}}) + M_{\text{hex}} + M_{\text{urea}} + M_{\text{Na}}$
F1**	hex-C-(C _{n-1} -A _n)-C ^{OH}	$n \cdot (M_{\text{unit}}) + M_{\text{UndC20-6CC/OH}} + M_{\text{hex}} + M_{\text{Na}}$	$n \cdot (M_{\text{unit}}) + M_{\text{UndS-6CC/OH}} + M_{\text{hex}} + M_{\text{Na}}$
F2**	C ^{OH} -(C _n -A _n)-A	$n \cdot (M_{\text{unit}}) + M_{\text{UndC20-CC/OH}} + M_{12\text{DA}} + M_{\text{Na}}$	$n \cdot (M_{\text{unit}}) + M_{\text{UndS-6CC/OH}} + M_{12\text{DA}} + M_{\text{Na}}$

Abbreviations are as followed: hex=hexylamine with $M_{\text{hex}} = 101.12 \text{ g} \cdot \text{mol}^{-1}$; C=UndC20-b6CC or UndS-b6CC with $M_{\text{UndC20-b6CC}} = 424.51 + x \cdot 14 \text{ g} \cdot \text{mol}^{-1}$ and $M_{\text{UndS-b6CC}} = 774.57 \text{ g} \cdot \text{mol}^{-1}$; A=dodecane-1,12-diamine with $M_{12\text{DA}} = 200.23 \text{ g} \cdot \text{mol}^{-1}$; U^A=urea linkage on 12DA with $M_{\text{urea}} = M_{12\text{DA}} + M_{\text{CO}} - 2 \cdot M_{\text{H}} = 226.2 \text{ g} \cdot \text{mol}^{-1}$; C^{OH}=C-CO+H with $M_{\text{UndC20-6CC/OH}} = 424.51 + x \cdot 14 \cdot M_{\text{CO}} + M_{\text{H}} \text{ g} \cdot \text{mol}^{-1}$ and $M_{\text{UndS-6CC/OH}} = 774.57 - M_{\text{CO}} + M_{\text{H}} = 747.58 \text{ g} \cdot \text{mol}^{-1}$.



Scheme II-3-4- Generation of F* and F** from F2 PHU family during the quenching with an excess of hexylamine.

SEC data in Table II-3-5, indicate the formation of PHUs with molar masses in the range 9 000 to 23 000 $\text{g} \cdot \text{mol}^{-1}$ after one day in solvent. The molar mass dispersities were in the range of 1.2 to 1.7 after one day. As expected, higher molar masses were obtained at 50°C compared to room temperature, which is coherent with the different conversion. Besides, the reactivities of UndC20-b6CC and UndS-b6CC are similar as can be seen in the Table II-3-5 and Figure II-3-18. The evolution of the molar masses with time is consistent with the classical

evolution of the molar masses with time of step-growth polymerizations. (See Figure II-3-21) However, the dispersities were in the range 1-1.7 and in step-growth polymerization, the dispersity is supposed to reach 2. Thus by improving the reaction conditions, the molar masses could still be improved.

While comparing those results with the previous molar masses obtained with the 5-membered cyclic carbonates (See Part II - Chapter 2), one has to notice that the polymerization conditions are not the same. Indeed, in the case of the 6-membered cyclic carbonates, the polymerizations were carried out in DMF (1 mol.L⁻¹), which is well-known to lower the cyclic carbonate reactivity, and not in bulk. Moreover, really high polymerization temperatures (120°C/140°C) were used for the synthesis of the PHUs from the 5-membered cyclic carbonates.

Table II-3-5- Molar masses and dispersity of the PHUs from 6-membered cyclic carbonate polymerized in DMF (1mol.L⁻¹).

Sample	b6CC	Diamine	Temperature (°C)	Time	Conversion ¹ (%) ¹	\bar{M}_n (g.mol ⁻¹) ³	Dispersity
PHU-1	UndC20-b6CC	12DA	30	30min	0	3 400	1
				1h	0	3 400	1
				4h	1.3	6 700	1
				6h	3.3	9 600	1.1
				1d	43.4	8 900 ⁴	1.2
				2d	89.3	14 300 ⁴	1.4
PHU-2	UndC20-b6CC	12DA	50	30min	14.0	6 700	1
				1h	26.7	6 800	1
				4h	66.5	9 300 ⁴	1.2
				6h	76.6	11 500 ⁴	1.2
				8h	83.2	12 800 ⁴	1.4
				1d	90.3 ²	21 600	1.5
				2d	-	22 300	1.3
PHU-3	UndS-b6CC	12DA	50	30min	8.2	7 000	1
				1h	16.3	7 200	1
				4h	46.9	8 200 ⁴	1
				6h	63.3	6 500	1
				8h	73.5	11 100 ⁴	1.2
				1d	90.0 ²	22 600	1.7
				2d	-	20 000	1.4

(1) Calculated by ¹H NMR. (2) Calculated by FTIR-ATR. (3) SEC in DMF with 1wt% LiBr - calibration PS standards. (4) Multi modal molar masses.

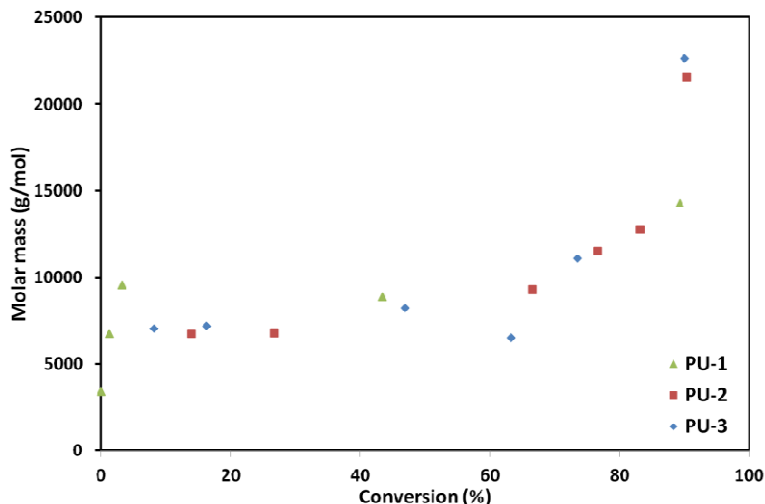


Figure II-3-21- Evolution of the molar masses with the conversion for PHU-1, PHU-2 and PHU-3.

3.2- Thermal stability and thermo-mechanical properties

Thermal stability of PHUs was investigated by TGA under a nitrogen stream at a heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ and the data are summarized in Table II-3-6. In this study, degradation temperatures after 5 wt% loss were obtained up to 313°C . The PHUs from UndC20-b6CC were less stable than the one from UndS-b6CC, probably due to the higher thermal degradation of the double bond.

The PHUs were further analyzed by DSC experiments. (See Table II-3-6) The reported DSC data are from non quenched samples due to the formation of urea in the quenched ones. The PHUs from UndC20-b6CC were amorphous and present glass transition temperatures around 0°C . The PHU from UndS-b6CC was amorphous as well, with a glass transition temperature of -20°C . This lower T_g can be explained by the presence of the sulfur atom, which is known to impart flexibility to the polymer chains.

Table II-3-6- Thermal stability and thermo-mechanical properties of the synthesized PHUs.

Sample	$T_g (^{\circ}\text{C})^1$	$T_{5\%} (^{\circ}\text{C})^2$
PHU-1	-0.3	254
PHU-2	-0.6	271
PHU-3	-20	313

(1) Determined by DSC at $10^{\circ}\text{C}\cdot\text{min}^{-1}$.

(2) Determined by TGA at $10^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen.

Conclusion

In conclusion, two bis 6-membered cyclic carbonates were synthesized from methyl undecenoate via malonate, 1,3-diol and monofunctional 6-membered cyclic carbonate intermediates. The latter was coupled by metathesis or thiol-ene reactions to produce two bis 6-membered cyclic carbonates, one with an internal double bond (UndC20-b6CC) or one with a sulfur atom (UndS-b6CC). The cyclization of the 6-membered cyclic carbonate Und-6CC could still be optimized using non phosgene cyclizations procedures.

The model reaction kinetics were performed to validate the higher reactivity of the 6-membered cyclic carbonate compared to the 5-membered ones. The effect of the substituent on the 5-membered cyclic carbonate was also demonstrated. The 6-membered cyclic carbonate was found to react faster than the 5-membered one, as the calculated reaction rate constants illustrate. For the reaction between the synthesized 6-membered cyclic carbonate Und-6CC and hexylamine, the activation energy was estimated to be 20.7 kJ.mol^{-1} . In some conditions, these model reactions revealed the presence of side reactions such as the ring opening of the cyclic carbonates with alcohols from, for example, the hydroxyurethane formed. Other catalysts could be further investigated to increase the selectivity of the reaction between 6-membered cyclic carbonate and amine as in the Part II - Chapter 2.

The synthesized bifunctional 6-membered cyclic carbonates were fully characterized and effectively used as building blocks for thermoplastic non isocyanate PHUs in combination with dodecane-1,12-diamine as comonomer. The PHUs formation was confirmed by FTIR-ATR, NMR and also MALDI-TOF MS analyses. The latter also revealed the occurrence of side reactions such as urea formation during the quenching. Molar masses up to $23\,000 \text{ g.mol}^{-1}$ (dispersity of 1.7) were obtained after only one day in DMF (1 mol.L^{-1}) at 50°C . Optimization of the polymerization reaction conditions could be performed to avoid the formation of gel. The thermo-mechanical properties of the so formed PHUs were investigated both by TGA and DSC respectively. Degradation temperature up to 313°C was obtained. Besides, the so-formed PHU were amorphous in nature with glass transition temperatures between -20°C and 0°C . The synthesized 6-membered cyclic carbonate Und-6CC could be an interesting precursor for polycarbonates and in self-assembled block copolymers as a highly hydrophobic block, in which the remaining instaurations could be further exploited.

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Experimental and supporting information

Experimental methods

6CC syntheses and characterizations

1- Malonate (Und-Malonate) synthesis

The optimizations were first performed on dimethyl sebacate varying the number of equivalents of DMC and the reaction times by using the same strategy. The methyl undecenoate (20 g, 100.9 mmol) was stirred with DMC (340 mL, 4.0 mol, 40 eq), NaH via a 60 wt% dispersion in mineral oil (6 g, 252.1 mmol, 2.5 eq) and DMF (7.8 mL, 109.9 mmol, 1 eq) at 60 °C. After 24 hours of reaction, 435 mL of diluted hydrochloric acid was slowly added to the reaction mixture. The organic phase was then washed twice with water, dried over anhydrous sodium sulfate, filtered and then the remaining DMC was removed on rotary evaporator. The compound **Und-malonate** was purified by flash chromatography using a mixture of cyclohexane and ethyl acetate and obtained as a viscous liquid. Yield=58%. ¹H NMR (CDCl₃, 25°C, 400 MHz) δ (ppm): 5.79 (m, 1H), 4.95 (m, 2H), 3.73 and 3.71 (s, 6H), 3.35 (t, 1H), 2.04 (m, 2H), 1.88 (m, 2H), 1.29 (m, 10H). ¹³C NMR (CDCl₃, 25°C, 100 MHz) δ (ppm): 170.12 (C=O), 139.28 (C=C), 114.32 (C=C), 52.57 (C=O), 51.87 (C-C=O), 33.89 (C-C=C), 29.27-27.46 (CH₂). IR (cm⁻¹): 2924, 2854, 1734.

2- Reduction of the malonate: 1,3-diol (Und-1,3-diol) synthesis

A solution of Und-malonate (10 g, 39.0 mmol) in THF (10 mL) was added to a solution of LiAlH₄ (6.1 g, 160.9 mmol, 4.1 eq.) in THF (80 mL) at 0°C. After the addition was completed, the reaction mixture was allowed to reach slowly room temperature and was refluxed at 80°C for 2 h. The reaction mixture was then cooled to 0°C, and distilled water followed by hydrochloric acid solution (2N) was added dropwise. The product was then extracted three times with ethyl acetate. The organic layer was washed twice with NaCl saturated solution and water, dried over anhydrous sodium sulfate, filtered and then the solvent was removed on rotary evaporator. The **Und-1,3-diol** was purified by flash chromatography using a

mixture of cyclohexane and ethyl acetate. Yield=66%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 5.81 (m, 1H), 4.93 (m, 2H), 3.78-3.63 (m, 4H), 2.96 (s, 2.OH), 2.02 (m, 2H), 1.75 (m, 1H), 1.36-1.22 (m, 12H). ^{13}C NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 139.42 ($\underline{\text{C}}\text{H}=\text{CH}_2$), 114.41 ($\text{CH}=\underline{\text{C}}\text{H}_2$), 67.02 ($\text{CH}-\underline{\text{C}}\text{H}_2\text{-OH}$), 42.18 ($\underline{\text{C}}\text{H}-\text{CH}_2\text{-OH}$), 34.02 ($\underline{\text{C}}\text{H}_2\text{-CH}=\text{CH}_2$), 30.05-27.44 (CH_2). IR (cm^{-1}): 3277, 2919, 2850.

3- Cyclization: 6-membered cyclic carbonate synthesis (Und-6CC)

The optimizations were first carried out on 1,3-propanediol varying the additive, carbonation agent and the concentration by using the same procedure. To a solution of triethylamine (10.1 g, 100 mmol, 2 eq.) in THF (400 mL), Und-1,3-diol (10 g, 50 mmol) was added. Then ethyl chloroformate (10.8 g, 100 mmol) was added to the mixture at 0°C . The reaction mixture was stirred at room temperature for 7 hours. Precipitated triethylamine hydrochloride was filtered off, and the filtrate was concentrated under vacuum. The **Und-6CC** was isolated from the reaction mixture by flash chromatography using a mixture of cyclohexane and ethyl acetate and obtained as a viscous liquid with 99.5% purity determined by GC-FID. Yield=75%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 5.81 (m, 1H), 4.96 (m, 2H), 4.40 (m, 2H), 4.09 (m, 2H), 2.21 (m, 1H), 2.05 (m, 2H), 1.35-1.30 (m, 12H). ^{13}C NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 148.72 (OCOO), 139.14 ($\underline{\text{C}}\text{H}=\text{CH}_2$), 114.42 ($\text{CH}=\underline{\text{C}}\text{H}_2$), 72.24 ($\underline{\text{C}}\text{H}_2\text{-OCOO}$), 33.84 ($\underline{\text{C}}\text{H}_2\text{-CH}=\text{CH}_2$), 31.39 ($\underline{\text{C}}\text{H}-\text{CH}_2\text{-OCOO}$), 29.53-26.69 (CH_2). IR (cm^{-1}): 2924, 2856, 1753.

4- Coupling reaction

4.1- Metathesis reaction: Bis 6-membered cyclic carbonate synthesis (UndC20-b6CC)

Into a round-bottom flask equipped with a mineral oil bubbler, the Und-6CC (4 g, 17.7 mmol) was charged with dried pentane (40mL) and 3rd generation Grubbs catalyst (78.2 mg, 0.088 mmol). The contents were vigorously stirred at room temperature for 4 hours. Afterwards, 3.8 mL of ethylvinyl ether was added to deactivate the Grubbs catalyst. The equilibrium was driven thanks to the precipitation of the formed product. The product was then purified with flash chromatography using a mixture of cyclohexane and ethyl acetate as eluent. **UndC20-b6CC** was obtained as a grey solid. Yield=51.5%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 5.37 (m, 2H), 4.41 (m, 4H), 4.09 (m, 4H), 2.20 (m, 2H), 1.97 (m, 4H), 1.35-1.28

(m, 22H). ^{13}C NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 148.71 (OCOO), 130.46 (CH=CH), 72.22 (CH- $\underline{\text{C}}\text{H}_2$ -OCO), 32.55 ($\underline{\text{C}}\text{H}_2$ -CH=CH), 31.32 ($\underline{\text{C}}\text{H}$ - CH_2 -OCO), 29.25-26.68 (CH_2). IR (cm^{-1}): 2918, 2850, 1726. $T_m=59^\circ\text{C}$.

4.2- Thiol-ene reaction: Bis 6-membered cyclic carbonate synthesis (UndS-b6CC)

The Und-6CC (4 g, 17.7 mmol) and 1,4-butanedithiol (2.38 g, 19.4 mmol, 1.1 eq.) were weighed into a flask. The reaction mixture was then UV-irradiated (254 nm) at room temperature. The reaction was monitored with ^1H NMR spectroscopy with the disappearance of the double bond. After completion of the reaction, **UndS-b6CC** was purified by recrystallization in a mixture of cyclohexane and ethyl acetate (70:30) and obtained as a white solid. Yield=37%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 4.40 (m, 4H), 4.09 (m, 4H), 2.52 (m, 8H), 2.20 (m, 2H), 1.68 (m, 4H), 1.57 (m, 4H), 1.35-1.28 (m, 28H). ^{13}C NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 148.71 (OCOO), 72.24 (CH- $\underline{\text{C}}\text{H}_2$ -OCO), 32.31 and 31.90 ($\underline{\text{C}}\text{H}_2$ -S- $\underline{\text{C}}\text{H}_2$), 31.42 ($\underline{\text{C}}\text{H}$ - CH_2 -OCO), 29.78 and 26.72 ($\underline{\text{C}}\text{H}_2$ - CH_2 -S- CH_2 - $\underline{\text{C}}\text{H}_2$), 29.60-26.72 (CH_2). IR (cm^{-1}): 2922, 2850, 1750, 1727. $T_m=82^\circ\text{C}$.

Kinetic experiments monitored by ^1H NMR

The kinetic experiments were performed in NMR tube at 50°C and $1 \text{ mol}\cdot\text{L}^{-1}$ in DMSO- d_6 and with a ratio 1:1 between cyclic carbonate and hexylamine. All reagents were dried before the reaction: on CaH_2 for hexylamine and on molecular sieves otherwise. For instance; a pre-solution of trimethyl carbonate (153 mg, 1.5 mmol, 3 eq.) and DMSO- d_6 1.5 mL) is first prepared. Then, one third of this solution and trichlorobenzene as internal reference (12.5 μL , 0.1 mmol, 0.2 eq.) were added into an NMR tube. The hexylamine (66 μL , 0.5 mmol, 1 eq.) was then added just before putting the tube in the NMR apparatus. The reaction mixture was then heated at the reaction temperature. The reaction was monitored with ^1H NMR spectroscopy with the disappearance of the cyclic carbonate protons. After 7 hours or 15 hours, if the reaction was not completed, the NMR tube was placed in an oil bath at the desired temperature and reanalyzed later. For some experiments, the concentration ($0.5 \text{ mol}\cdot\text{L}^{-1}$ and $5 \text{ mol}\cdot\text{L}^{-1}$), the temperature (30°C and 70°C) and the amine ratio (1:2 and 1:3) were modulated. Two tests were carried out with 7 mol% of additives such as triethylamine and acetic acid. ^1H NMR, ^{13}C NMR and IR detail are given below only for the reaction between Und-6CC+hexylamine.

Product of the reaction between Und-6CC+hexylamine: ^1H NMR (DMSO- d_6 , 70°C, 400 MHz) δ (ppm): 6.71 (NH), 5.79 (m, 1H), 4.97 (m, 2H), 3.94 (m, 2H), 3.41 (m, 2H), 2.98 (m, 2H), 2.02 (m, 2H), 1.66 (m, 1H), 1.29 (m, 20H), 0.88 (t, 3H). ^{13}C NMR (DMSO- d_6 , 70°C, 100 MHz) δ (ppm): 148.72 (OCOO), 139.14 ($\underline{\text{C}}\text{H}=\text{CH}_2$), 114.62 ($\text{CH}=\underline{\text{C}}\text{H}_2$), 64.62 ($\text{CH}-\underline{\text{C}}\text{H}_2\text{-OCONH}$), 61.80 ($\text{CH}-\underline{\text{C}}\text{H}_2\text{-OH}$), 41.83 ($\text{OH}-\text{CH}_2-\underline{\text{C}}\text{H}-\text{CH}_2\text{-OCONH}$), 40.8 ($\underline{\text{C}}\text{H}_2\text{-NHCOO}$), 33.50 ($\underline{\text{C}}\text{H}_2\text{-CH}=\text{CH}_2$), 33.65-22.40 (CH_2), 13.94 (CH_3). IR (cm^{-1}): 3384, 2924, 2858, 1705.

Synthesis of Dec-5CC: The commercially available 1,2-epoxy-9-decene (7g, 45.4 mmol) was first pre-mixed with the TBABr (0.21 g, 0.64 mmol, 3 wt%). Then the mixture was placed in a reactor and heated up at 80°C. Once the temperature got stabilized, CO_2 was slowly introduced into the reactor until 50 Bar. After 24 hours, the reactor was cooled down to RT and slowly depressurized to the atmospheric pressure. The ^1H NMR of the final mixture revealed a conversion of 94.5%. The Dec-5CC was purified by flash chromatography using a mixture of cyclohexane: ethyl acetate with 0% to 30% of ethyl acetate. Y=50%. **Dec-5CC:** ^1H NMR (CDCl_3 , 25°C, 400 MHz) δ (ppm): 5.77 (m, 1H), 4.96 (m, 2H), 4.71 (m, 1H), 4.51 (t, 1H), 4.03 (t, 1H), 2.04 (m, 2H), 1.77 (m, 1H), 1.68 (m, 1H), 1.45-1.33 (m, 8H). ^{13}C -NMR (CDCl_3 , 25°C, 100 MHz) δ (ppm): 155.18 (OCOO), 138.99 ($\underline{\text{C}}\text{H}=\text{CH}_2$), 114.54 ($\text{CH}=\underline{\text{C}}\text{H}_2$), 77.36 ($\underline{\text{C}}\text{H}-\text{OCOO}$), 69.51 ($\underline{\text{C}}\text{H}_2\text{-OCOO}$), 34.02 ($\underline{\text{C}}\text{H}_2\text{-CH-OCOO}$), 33.78 ($\underline{\text{C}}\text{H}_2\text{-CH}=\text{CH}_2$), 29.11-28.80 (CH_2), 24.48 ($\underline{\text{C}}\text{H}_2\text{-CH}_2\text{-CH-OCOO}$). IR (cm^{-1}): 2924, 2856, 1786.

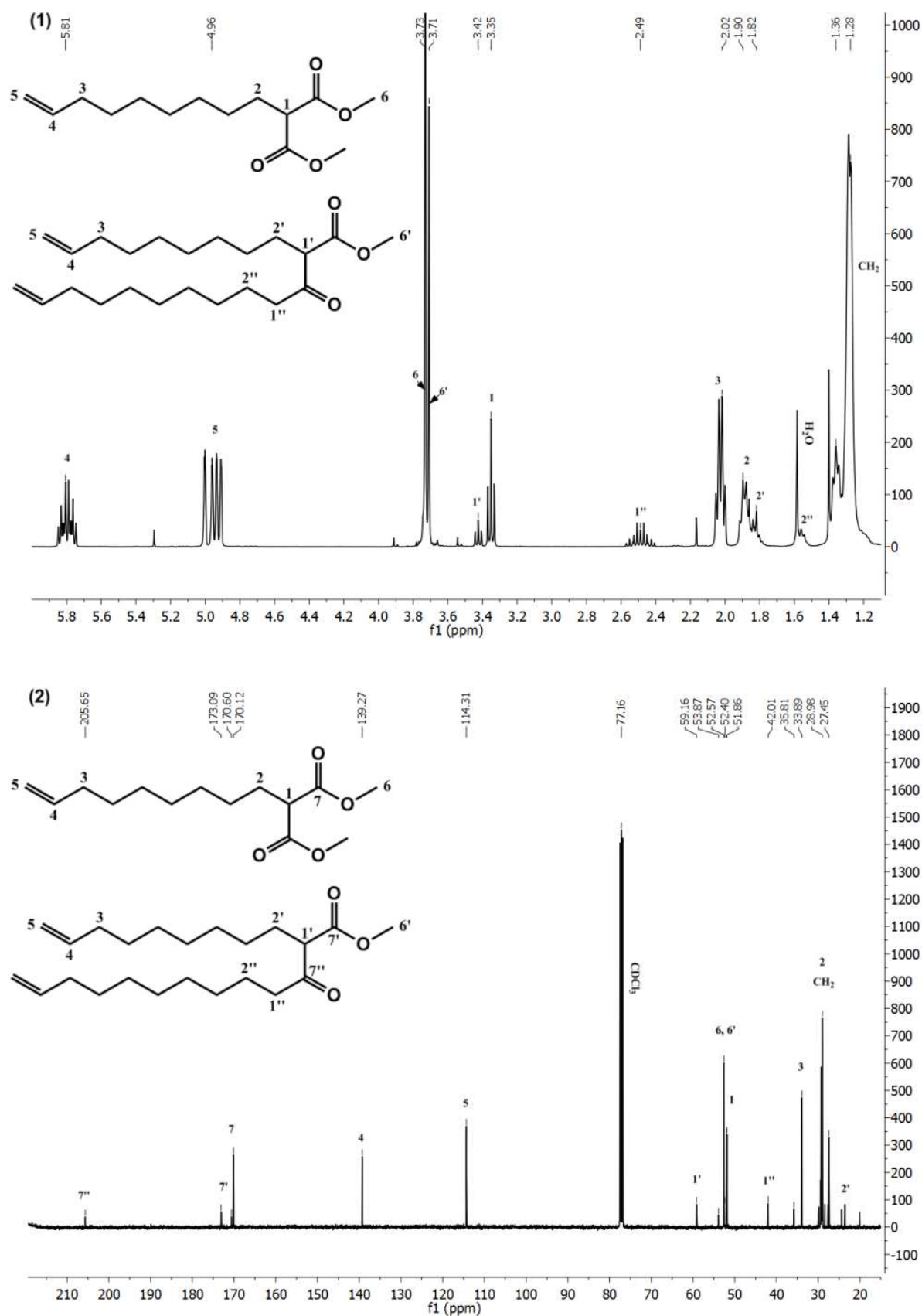
Polymer syntheses and characterizations

PHUs were prepared from the bis 6-membered cyclic carbonates (UndC20-b6CC and UndS-b6CC) and dodecane-1,12-diamine (12DA). PHU syntheses were performed in DMF at room temperature or at 50°C into a schlenk tube under magnetic stirring and nitrogen atmosphere for 2 days. TCB was used as a reference. No catalysts were added for the polymerization reactions.

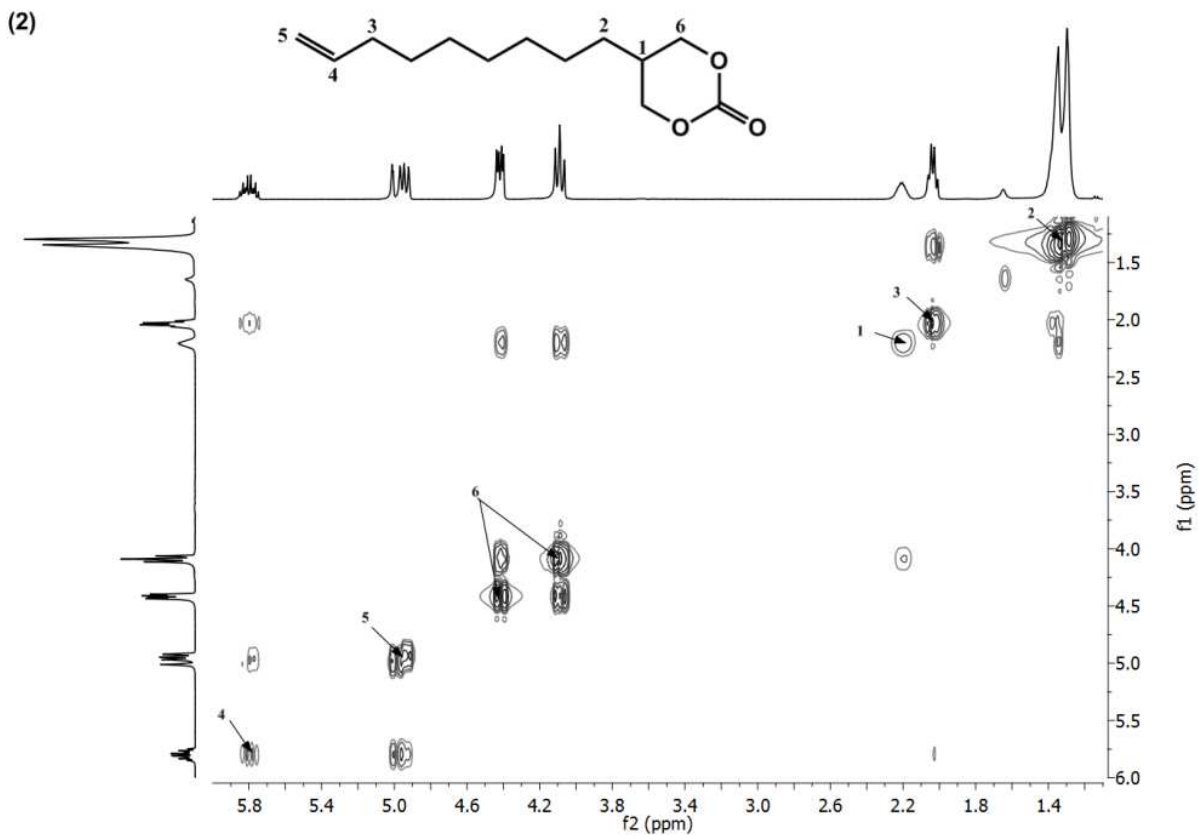
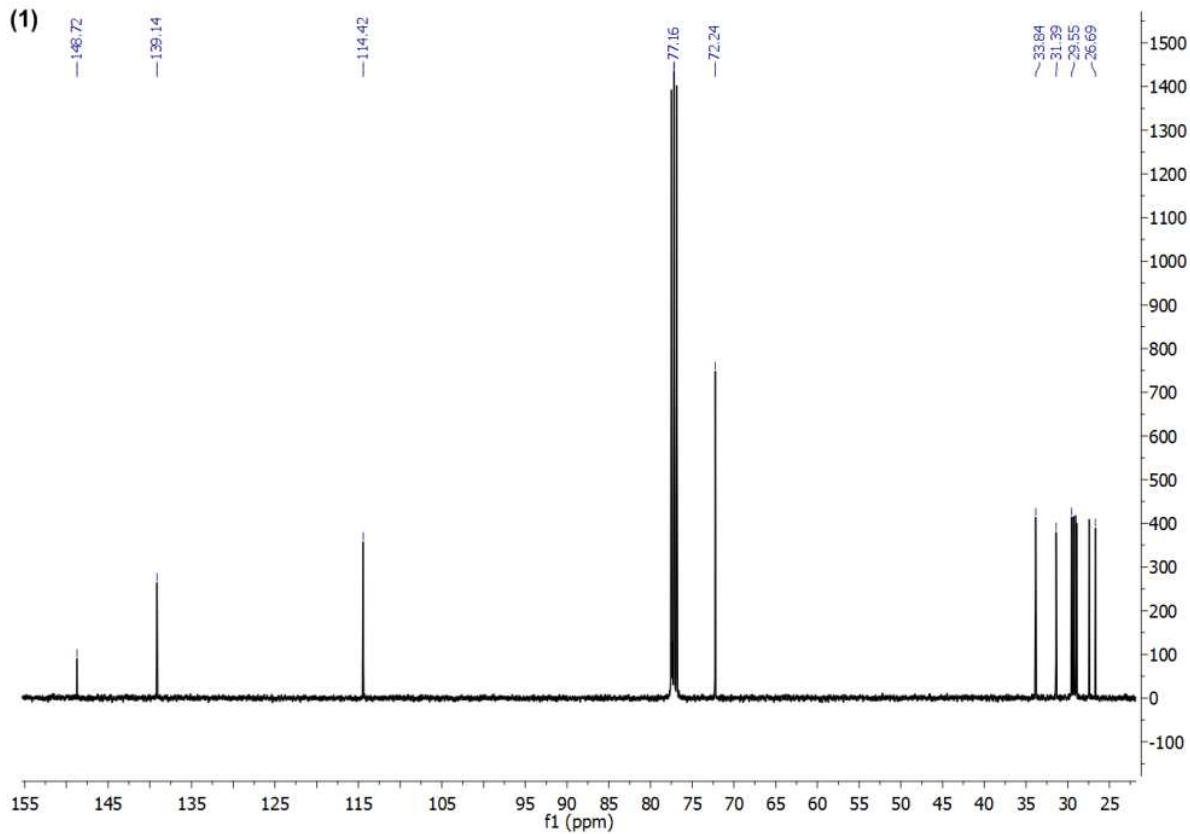
PU-2 [UndC20-b6CC+12DA]: ^1H NMR (TCE- d_2 , 25°C, 400 MHz) δ (ppm): 5.39 (s, 2H), 4.86 (s, 2.NH), 4.17-4.02 (m, 4H), 3.52-3.45 (m, 4H), 3.13 (m, 4H), 1.96 (m, 4H), 1.71 (m, 2H), 1.48-1.27 (m, CH_2). IR (cm^{-1}): 3620-3158, 2925, 2852, 1686, 1534.

PU-3 [UndS-b6CC+12DA]: ^1H NMR (TCE- d_2 , 25°C, 400 MHz) δ (ppm): 4.89 (s, 2.NH), 4.23-4.09 (m, 4H), 3.58-3.49 (m, 4H), 3.17 (m, 4H), 2.57 (m, 8H), 1.77-1.72 (m, 6H), 1.62 (m, 4H), 1.51-1.33 (m, CH_2). IR (cm^{-1}): 3620-3158, 2925, 2852, 1686, 1534.

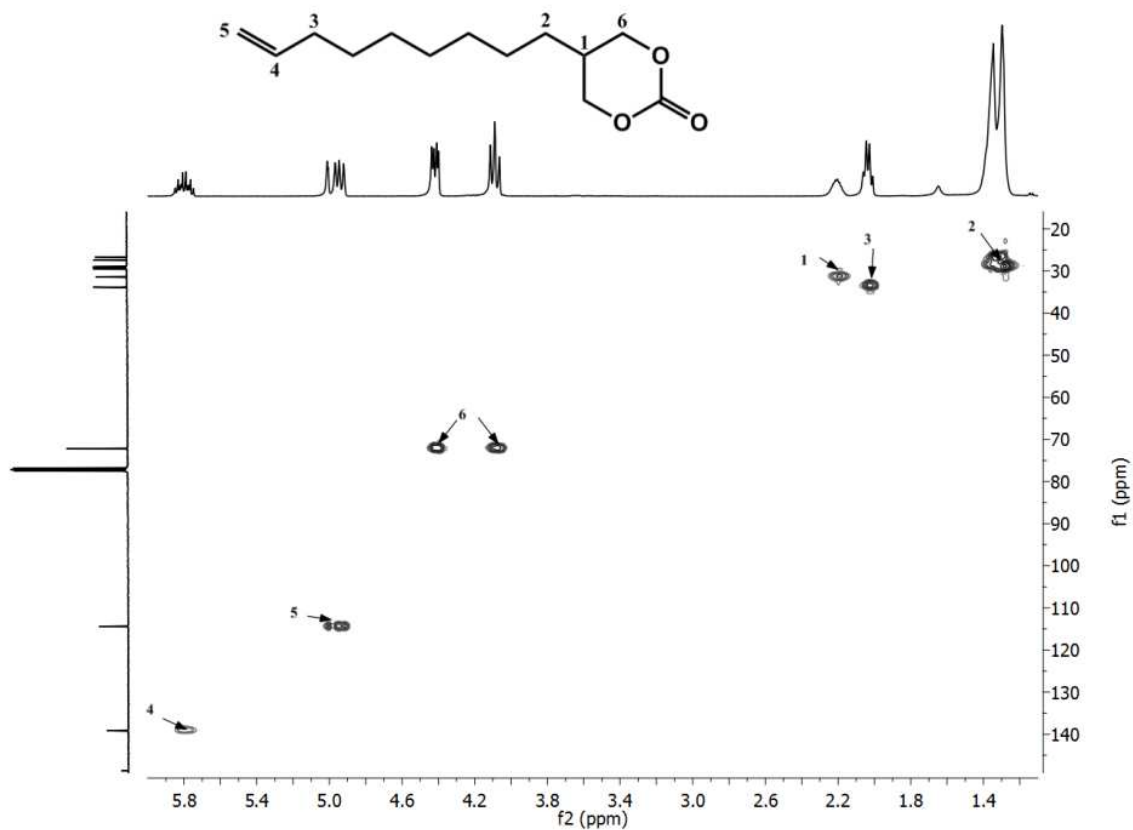
Supporting information



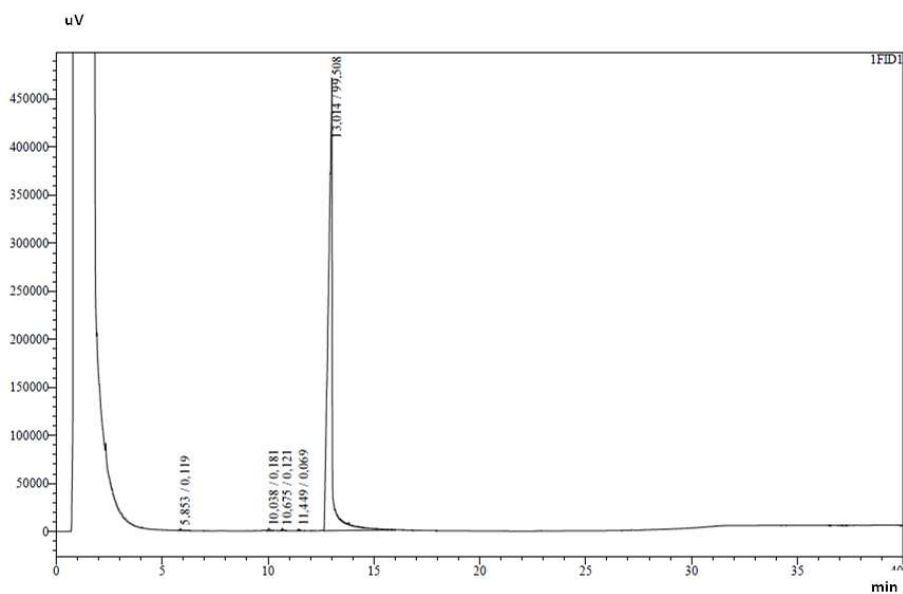
SI Figure II-3-1- Evidence of the formation of the Claisen-condensation product in a chromatography aliquot: (1) ^1H NMR and (2) ^{13}C NMR.



(3)



SI Figure II-3-2- NMR analyses of purified Und-6CC: (1) ^{13}C NMR, (2) ^1H - ^1H COSY 2D-NMR and (3) ^1H - ^{13}C HSQC-NMR.



SI Figure II-3-3- Gas chromatography of Und-6CC.

PART II - Chapter 4: Vegetable oils- based diamines toward fully bio- based and non-isocyanate PHUs

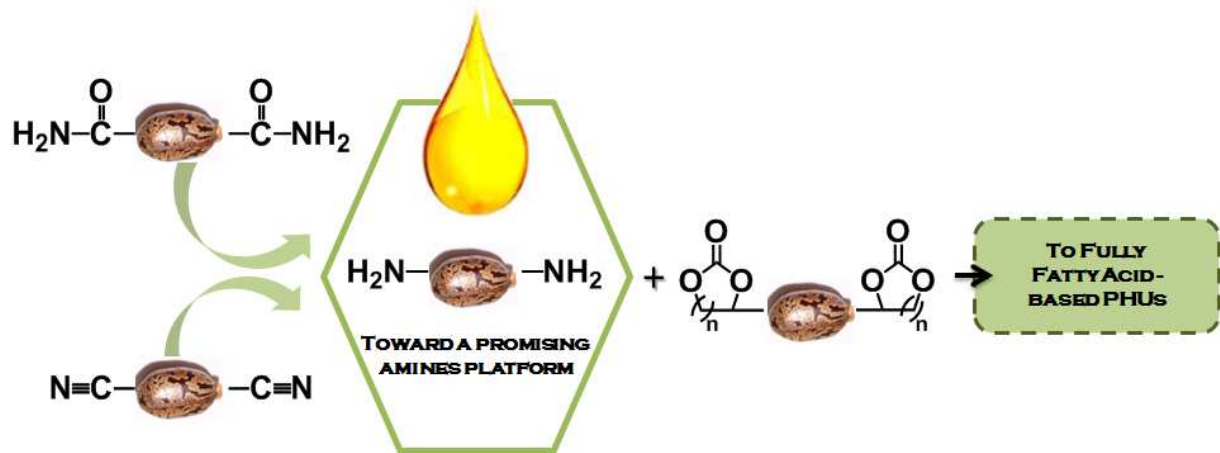


Table of contents

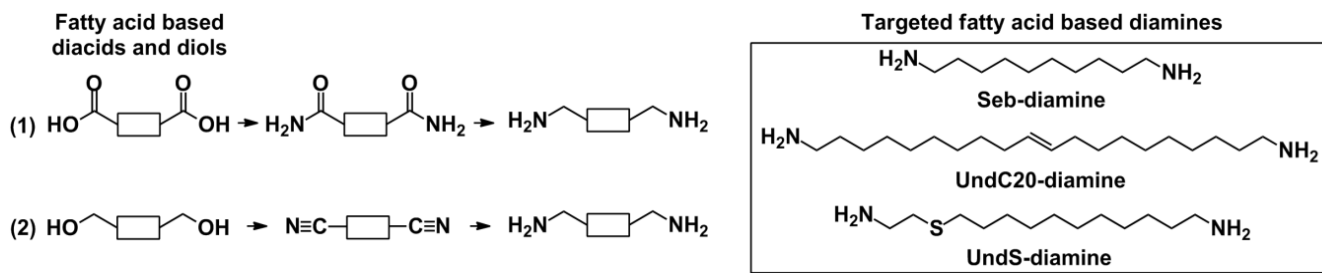
Introduction	220
1-Diamine synthesis	220
1.1- Route via amide intermediates	221
1.1.1- Diacid precursors	221
1.1.2- Diamide synthesis	223
1.2- Route via nitrile intermediates	226
1.2.1- Diol precursors	226
1.2.2- Dinitriles synthesis	227
1.3- Diamines synthesis and comparison of the two routes	232
1.3.1- Reduction of primary diamides and dinitriles	232
1.3.2- Comparison of the two routes	235
2- Polymerizations to fully fatty acid-based PHUs	236
3- Thermal stability and thermo-mechanical properties	238
Conclusion	239
References	240
Experimental and supporting information	241

Introduction

Nowadays, there is a lack of easy and green ways to bring amine functions directly onto vegetable oil derivatives. Substrates bearing acidic functions and primary alcohols can be easily obtained from vegetable oils, and therefore can be suitable candidates to prepare bio-based amines. To valorize those starting materials, two routes have been considered in this chapter to prepare vegetable oil-based diamines: (i) one via primary diamides and (ii) the second throughout dinitriles. The approach via primary diamides required the synthesis of acyl chloride intermediates to then prepare primary diamides in mild conditions with aqueous ammonia at room temperature. The preparation of diamines after the reduction of dinitriles from aqueous ammonia and O_2 as oxidant appeared as a really attractive and versatile route. The preparation of nitriles from primary alcohol has been carried out under mild conditions using cheap commercially available copper-based catalyst. Such promising strategy to nitriles, and thus to amines after reduction, was never valorized in the synthesis of diamines or vegetable oil-based amines. Finally, potentially fully bio-based non-isocyanate PHUs have been prepared with various fatty acid-based bis cyclic carbonate compounds. The various 5 and 6-membered cyclic carbonates used for the non-isocyanate PHU syntheses, under the same polymerization conditions, allowed their direct comparison in terms of reactivity.

1-Diamine synthesis

In order to obtain non-isocyanate and fully bio-based TPUs, the synthesis of vegetable oil-based diamines have been envisaged following two strategies: one via diamide intermediates and the second one throughout dinitriles (See Scheme II-4-1). The targeted diamines were completely aliphatic (Seb-diamine) or aliphatic with a double bond (UndC20-diamine) or a sulfur atom (UndS-diamine). The starting vegetable oil resources were the sebacic acid and the methyl undecenoate or undecenoic acid for the first route. The corresponding commercially available diols: 1,10-decanediol and 10-undecen-1-ol were used in the second approach. The methyl undecenoate, undecenoic acid and 10-undecen-1-ol were chosen due to the terminal double bond, which allowed efficient further metathesis and thiol-ene reaction to prepare bifunctional precursors.



Scheme II-4-1- The two approaches envisaged toward fatty acid-based diamines: (1) via diamides and (2) via dinitriles, as well as the targeted fatty acid-based diamines.

1.1- Route via amide intermediates

The route for the synthesis of diamines via primary diamides intermediates is illustrated in Scheme II-4-1-(1). The synthesis involved a first one pot preparation of diacyl chloride followed by diamide formation, and subsequent reduction of primary diamides.

1.1.1- Diacid precursors

Following the route via amide intermediates, diacid precursors are needed. Sebacic acid (Seb-diacid) was directly used, together with two diacids synthesized by self metathesis reaction or by thiol-ene reaction. The self-metathesis reaction was performed on undecenoic acid using Grubbs II catalyst (1/500) in dried pentane at room temperature overnight. As the reaction was running, the diacid (UndC20-diacid) got precipitated, which permits to drive the equilibrium toward the formation of products and limits as well isomerizations. The formation of the diacid was proved by ^1H NMR spectroscopy with the decrease of the signal for the terminal double bond protons (4.92-5.01 ppm and 5.76-5.86 ppm) and the appearance of a multiplet for the internal double bond protons (5.38 ppm). (See Figure II-4-1) A conversion of 44.8% and almost no isomerization were observed after one night by NMR. A purity of 97.0% was achieved after filtration and two recrystallizations in toluene ($Y=42\%$).

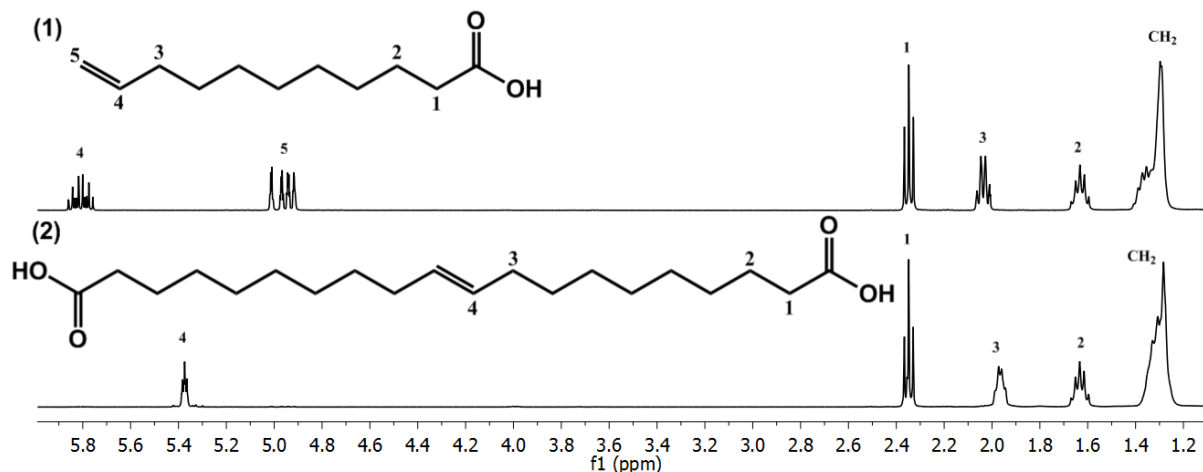


Figure II-4-1- Stacked ^1H NMR spectra of fatty acid precursor obtained by metathesis reaction. (1) Undecenoic acid (UndAc) and (2) the corresponding diacid (UndC20-diacid). (All analyses were performed in CDCl_3 .)

The thiol-ene reaction on methyl undecenoate with methyl thioglycolate leads to the formation of a diester bearing a thio linkage (UndS-diester). The thiol-ene reaction was performed using an excess of 3 eq. of methyl thioglycolate, at room temperature, under UV (256 nm) without photo-initiator. The progress of the reaction was monitored by the disappearance of the double bond protons (4.92-5.01 ppm and 5.76-5.86 ppm). After 3 hours the reaction was complete and the excess of methyl thioglycolate was removed by vacuum distillation. Then the formation of UndS-diester can also be confirmed in ^1H NMR spectroscopy with two singlets (3.66 ppm and 3.73 ppm) corresponding to the unequivalent ester linkage methyl protons. Besides, a singlet at 3.22 ppm corresponding to the methylene between the ester and the sulfur atom can be observed. The UndS-diester was obtained as a white powder ($Y=98.6\%$). The hydrolysis of the ester was carried out according to the literature to obtain the corresponding diacid (UndS-diacid).¹ The reaction was conducted in methanol with 4 eq. of KOH at 35°C for 1 hour. In ^1H NMR, the ester linkage methyl protons disappeared. Moreover in FTIR-ATR, a shift of the carbonyl band from 1734 cm^{-1} to 1686 cm^{-1} , assignable to the formation of the carboxyl function, was observed. A conversion of 97.3% was achieved and the remaining diester was removed by ethyl acetate washing. The UndS-diacid was finally recovered after acidification of the aqueous phase and extraction with ethyl acetate with a purity of 97.7% ($Y=97\%$). The Figure II-4-2 illustrates the synthesis of UndS-diacid from methyl undecenoate.

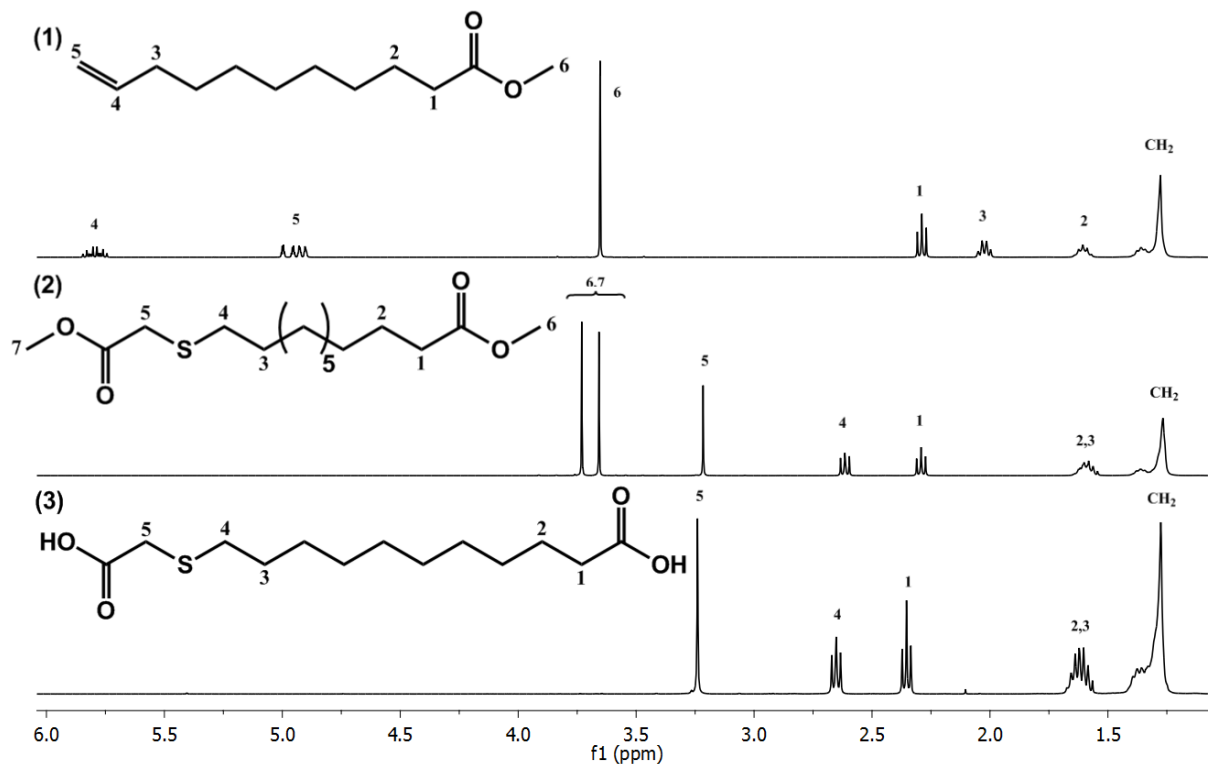
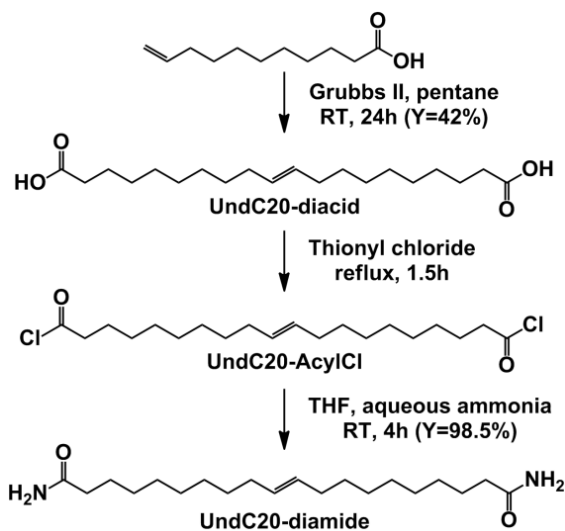


Figure II-4-2- Stacked ¹H NMR spectra of (1) Methyl undecenoate, (2) the corresponding diester obtained by thiol-ene reaction (UndS-diester) and (3) diacid after subsequent hydrolysis (UndS-diacid). (Analyses in CDCl₃.)

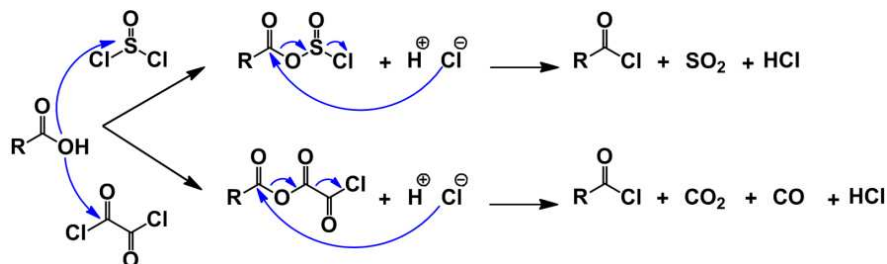
1.1.2- Diamide synthesis

The Scheme II-4-2 depicts the synthesis of UndC20-diamide from undecenoic acid. For the UndC20-diamide, the ¹H NMR and FTIR-ATR spectra of all steps of the reaction are presented in Figure II-4-3 and Figure II-4-4 respectively. In SI Figure II-4-1, ¹H-¹³C HSQC-NMR analysis is given for the purified UndC20-diamide, as an example. For Seb-diamide and UndS-diamide, ¹H NMR and FTIR-ATR spectra for all steps are given in SI. (SI Figures II-4-3 to II-4-6)



Scheme II-4-2- General synthetic route to UndC20-diamide.

The primary diamides were synthesized from the diacyl chlorides in one pot. Two chlorinated agents have been tested: thionyl chloride and oxalyl chloride. (See Scheme II-4-3) The latter one being more toxic, the thionyl chloride was preferred for the experiments.



Scheme II-4-3- Scheme for the acyl chloride formation from thionyl chloride and oxalyl chloride.

The diacyl chloride preparation was performed in bulk with 1.5 eq. of thionyl chloride under reflux. The generated SO_2 and HCl gases were quenched in a 0.1 mol.L^{-1} NaOH solution. A complete conversion was achieved after 1.5 hour. A downfield shift was observed for the methylene proton nearby the carbonyl moieties (from 2.35 ppm to 2.88 ppm). In the particular case of UndS-diacid, a downfield shift was also visible for the methylene protons between the acyl chloride function and the sulfur atom (from 3.24 ppm to 3.67 ppm). In FTIR-ATR, a shift can be observed between the diacid (1686 cm^{-1}) and the diacyl chloride (1790 cm^{-1}). The Figure II-4-3-(2) and Figure II-4-4-(2) present the ^1H NMR and FTIR-ATR respectively of the formation of diacyl chloride from Und20-diacid. (See SI for the FTIR-ATR of diacyl chlorides from sebacic acid and UndS-diacid - SI Figures II-4-3 and II-4-5)

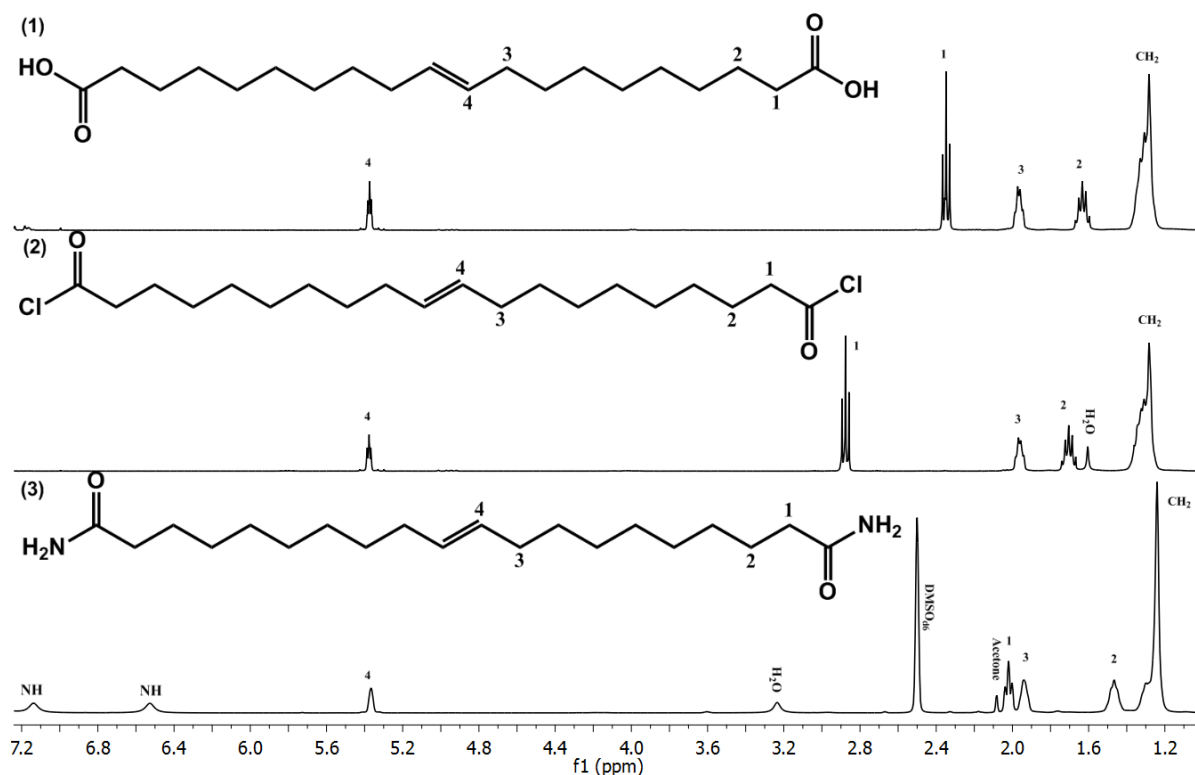


Figure II-4-3- All steps ^1H NMR for the UndC20-diamide synthesis. (1) UndC20-diacid (25°C in CDCl_3), (2) UndC20-AcylCl (25°C in CDCl_3) and (3) UndC20-diamide (50°C in DMSO-d_6).

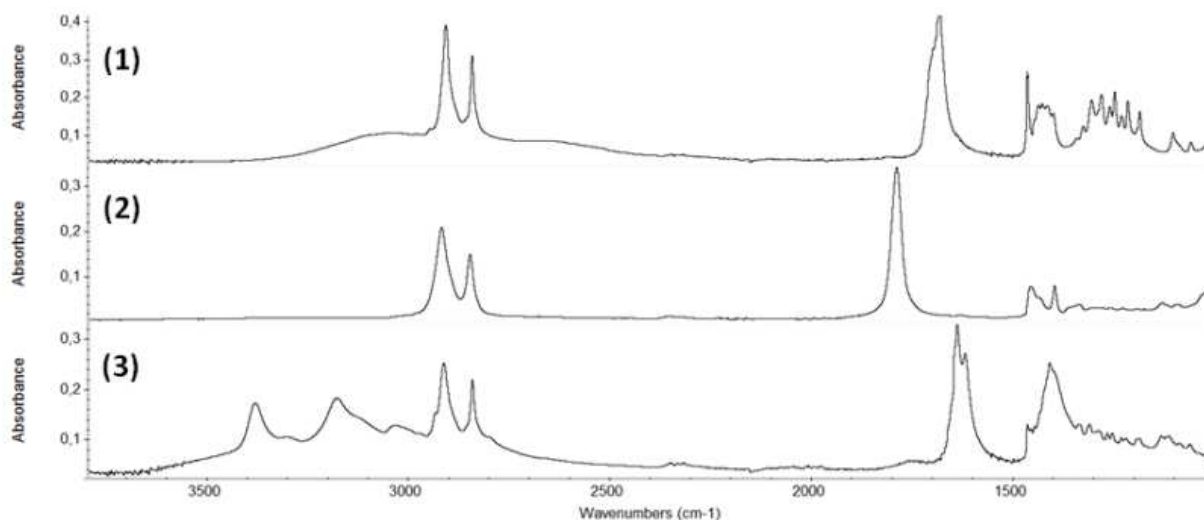


Figure II-4-4- All steps FTIR-ATR for the UndC20-diamide synthesis. (1) UndC20-diacid, (2) UndC20-AcylCl and (3) UndC20-diamide.

The primary diamides were formed *in situ* after thionyl chloride evaporation, by adding THF then aqueous ammonia solution dropwise. The Figure II-4-3-(3) and Figure II-4-4-(3) illustrate the formation of primary diamide UndC20-diamide. The obtained primary diamides were only soluble in DMSO upon heating. The reaction was confirmed by ^1H NMR with the appearance of the triplet corresponding to the methylene protons nearby the primary amide moieties at 2.01 ppm. (See SI Figures II-4-2 and II-4-4 for ^1H NMR spectra of the primary diamides from sebacic acid and UndS-diacid) ^{13}C NMR analysis attested the formation of amides with the carbon of the carbonyl at 174.12 ppm (in DMSO- d_6 due to solubility issues) compared to 180.2 ppm (diacid) and 173.8 ppm (diacyl chloride) (both in CDCl_3). In all cases, the diamide synthesis was also observed by means of FTIR-ATR with the shifting of the carbonyl band from 1795 cm^{-1} (diacyl chloride) to 1642 cm^{-1} (diamide). (See Figure II-4-4-(3)) Due to the presence of water in the selected procedure, the acyl chlorides get also transformed into acids in small amount (15.3% for Seb-acylCl, 3% for UndC20-acylCl and 4% for UndS-acylCl). The acid side products were removed by washing the insoluble primary diamides with DCM (Seb-diamide) or THF (UndC20-diamide and UndS-diamide). The primary diamides were obtained as white powders. ($Y_{\text{Seb-diamide}}=83\%$; $Y_{\text{UndC20-diamide}}=95.5\%$; $Y_{\text{UndS-diamide}}=95\%$)

1.2- Route via nitrile intermediates

1.2.1- Diol precursors

The second considered route involved the synthesis of nitrile intermediates. (See Scheme II-4-1-(2)) The starting precursors for this route are diols. As for the synthesis of diamines via nitrile intermediates, three diols were used: the commercially available 1,10-decanediol (Seb-diol) and the synthesized: UndC20-diol from self metathesis reaction of 10-undecen-1-ol as well as UndS-diol obtained by thiol-ene reaction.

The self metathesis reaction of 10-undecen-1-ol was performed using Grubbs II metathesis catalyst (1/100) in dried pentane at room temperature for 72 hours. As the reaction was going, the diol (UndC20-diol) got precipitated. The formation of the diol was proved by ^1H NMR spectroscopy with the peaks decrease of the terminal double bond protons (4.92-5.01 ppm and 5.76-5.86 ppm) and the appearance of a multiplet for the internal double bond protons (5.38 ppm). (See Figure II-4-5) The purification was performed by filtration and two recrystallizations in toluene and the final purity was 60.0% as determined by GC-FID. (Y=43%) However, a purity of 98.9% can be calculated with the peaks in GC-FID of the isomerized diols. Indeed, on the contrary to the synthesis of UndC20-diacid, important isomerizations were detected. This observation can be correlated to a lower precipitation of the diol.

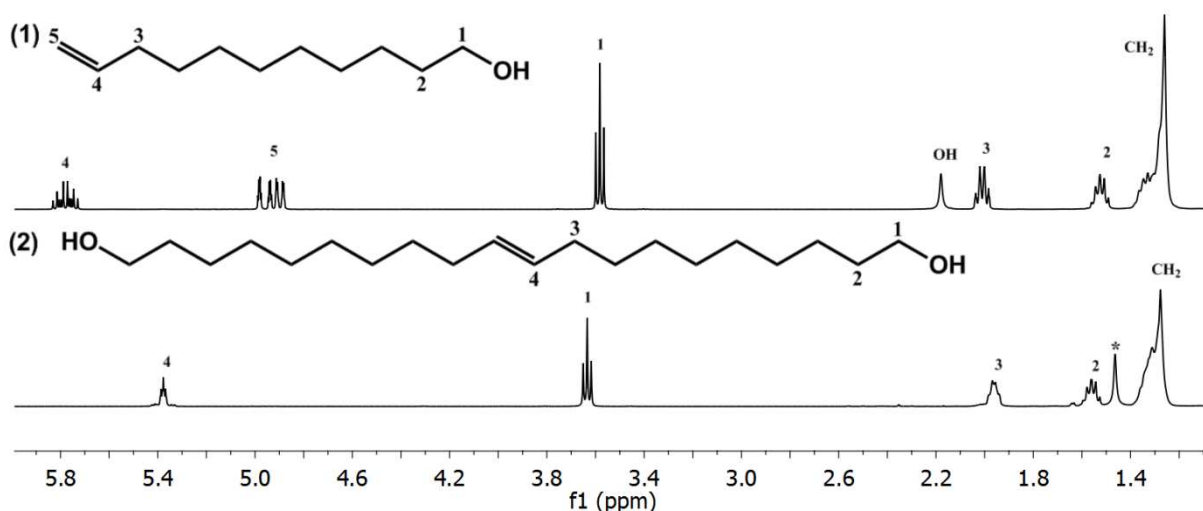


Figure II-4-5- Stacked ^1H NMR spectra of fatty acid precursors obtained by metathesis reaction. (1) 10-undecen-1-ol and (2) the corresponding diol (UndC20-diol). (All analyses were performed in CDCl_3) (*) Impurity.

The linear diol bearing a sulfur atom (UndS-diol) was obtained by thiol-ene reaction of 10-undecen-1-ol with 3 eq. of mercaptoethanol at room temperature, under UV (256 nm) without photo-initiator. The progress of the reaction was monitored by the disappearance of the double bond protons (4.92-5.01 ppm and 5.76-5.86 ppm). After 30 minutes of reaction, the conversion reached 99.8%. The formation of UndS-diol can also be confirmed in ^1H NMR spectroscopy by two triplets at 2.72 ppm and 2.51 ppm, corresponding to the nonequivalent methylene protons nearby the sulfur atom. (See protons H4 and H5 in Figure II-4-6) The UndS-diol was finally recovered with a purity of 98.1 % (Y=99.1%), after solubilization in DCM and several water washes to remove the excess of mercaptoethanol.

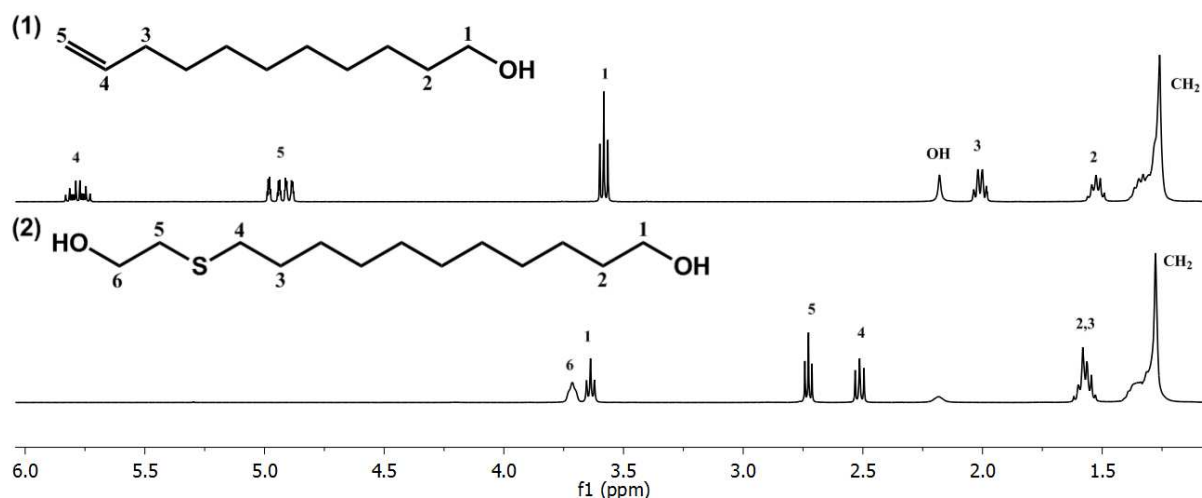
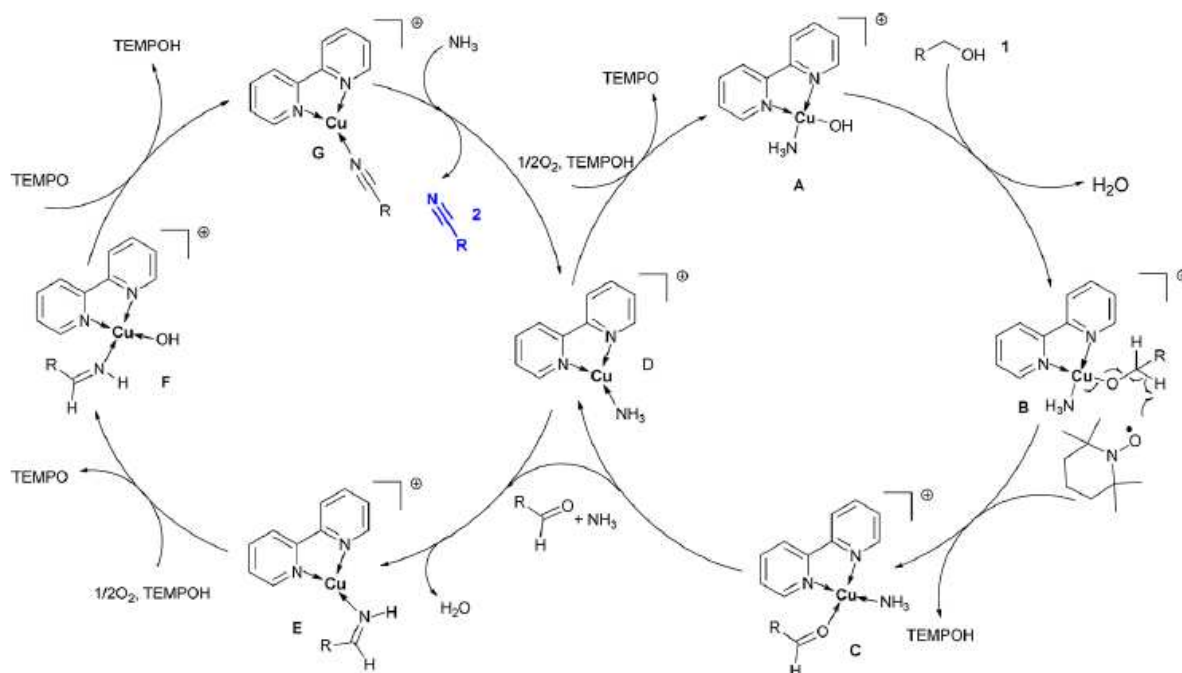


Figure II-4-6- Stacked ^1H NMR spectra of fatty acid precursor obtained by thiol-ene reaction. (1) 10-undecen-1-ol and (2) the corresponding diol (UndS-diol). (All analyses were performed in CDCl_3 .)

1.2.2- Dinitriles synthesis

Yin *et al.* have synthesized nitrile compounds by double aerobic dehydrogenation of alcohols under mild conditions using aqueous ammonia with a catalytic system composed of copper iodide, TEMPO and bipyridine (bpy).² The use of cheap available and low toxic copper catalyst makes this strategy attractive for industrial applications. Based on the mechanism of Stahl and coll.³, Yin *et al.* proposed a radical mechanism through the formation of aldehyde and imine intermediates. They demonstrated (i) that aqueous ammonia did not inhibit the initial aldehyde formation, (ii) that TEMPO was essential for the two steps (alcohol to aldehyde and aldehyde to nitrile), and (iii) that the chelating bpy ligand accelerate the aldehyde/imine formation.² In those conditions, no dead coordination complexes inhibit the reaction. Nevertheless, among the tested substrates, aliphatic alcohols are presented in a less extent with nitriles conversion from 0%⁴ to 90 %². They reported that the reaction was

very slow at room temperature for aliphatic alcohols. Moreover, no bifunctional molecules have been used as starting materials and no amines have been afterward prepared.



Scheme II-4-4- Proposed reaction mechanism for the synthesis of nitriles from primary alcohols as proposed by Yin et al. ²

Based on this recent developed strategy, fatty acid-based aliphatic dinitriles have been prepared under mild conditions using aqueous ammonia with a catalytic system composed of CuI, TEMPO and bpy. In the first step, the synthesis of dinitriles has been optimized on 1,10-decanediol. The reactions were conducted for 24 hours with an O₂ balloon with 1 eq. of NH₄OH. In ¹H NMR, the formation of nitrile from 1,10-decanediol was proved by the appearance of a triplet corresponding to the methylene protons nearby the nitrile at 2.34 ppm. (See Figure II-4-7)

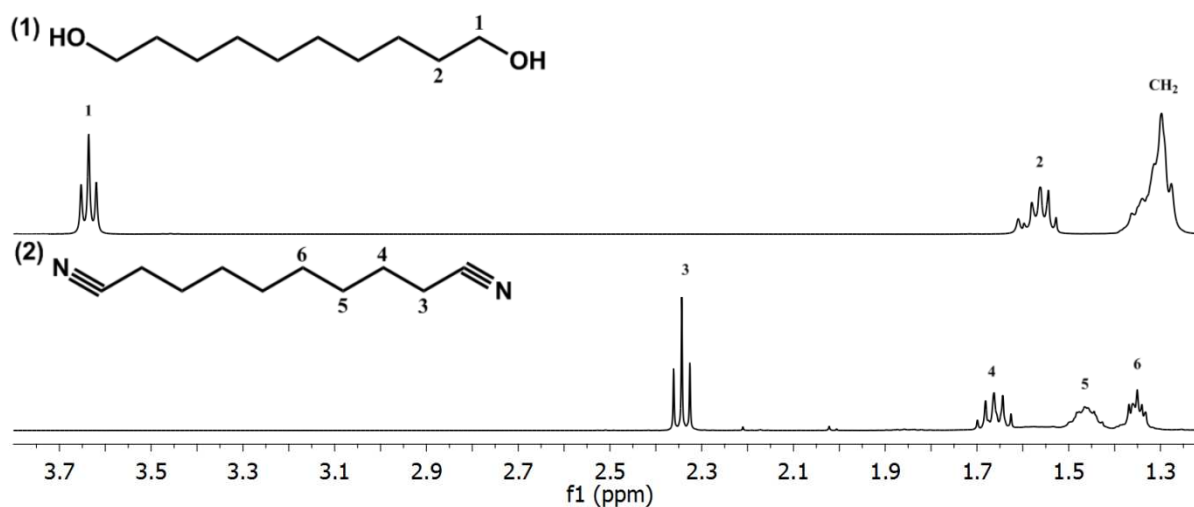


Figure II-4-7- Stacked ¹H NMR for (1) 1,10-decanediol (Seb-diol) and (2) the corresponding synthesized dinitrile (Seb-dinitrile). (Analyses were performed in CDCl₃.)

In FTIR-ATR, the formation of nitrile was also established by the disappearance of the two hydroxyl bands at 3360 cm^{-1} and 3400 cm^{-1} and by the appearance of a band at 2243 cm^{-1} corresponding to the nitrile vibration. The Figure II-4-8 exposed the FTIR-ATR spectra of Seb-diol and the corresponding synthesized dinitrile (Seb-dinitrile).

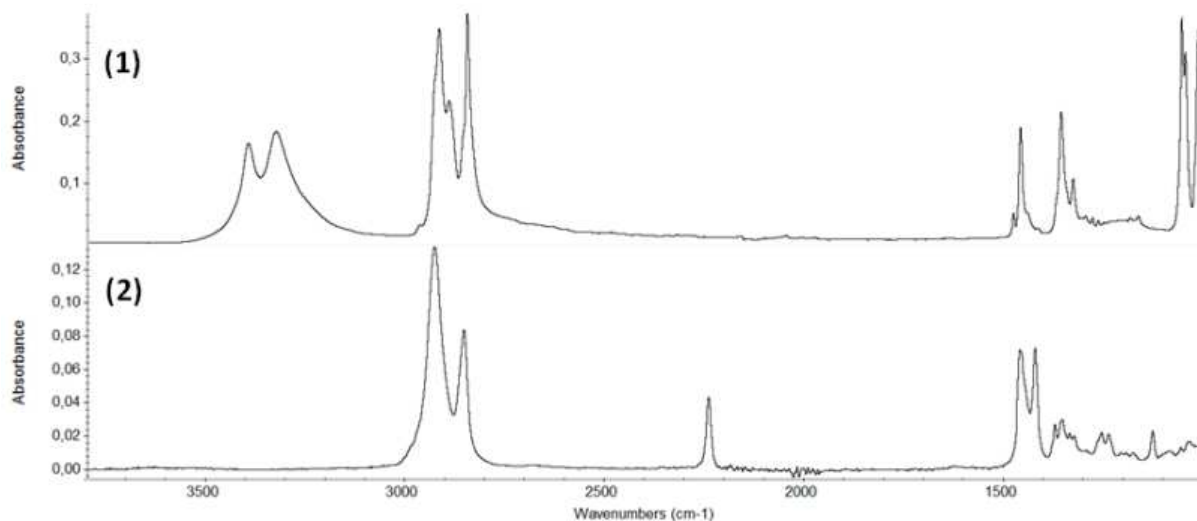


Figure II-4-8- Stacked FTIR-ATR for (1) 1,10-decanediol (Seb-diol) and (2) the corresponding synthesized dinitrile (Seb-dinitrile).

For the optimizations, tert-butanol has been tried as a solvent for the reaction due to the low solubility of 1,10-decanediol in acetonitrile (the used solvent for the aerobic oxidation with temperature). However, no nitrile was formed in tert-butanol, whereas in a non-homogenous mixture (1,10-decanediol in acetonitrile), the nitrile conversion was, under non-optimized conditions, 5.7% for 5 mol% catalysts per moles of 1,10-decanediol. Moreover, unpurified TEMPO and CuI have also been tested, but it has been demonstrated that their purification are highly necessary. Thus to obtain higher conversion, the TEMPO was sublimed and CuI was reprecipitated by dilution of a NaI aqueous solution containing soluble CuI. The TEMPO and CuI were obtained as a red and white powders respectively. Before the reaction, the saturation of the solvent with O_2 bubbling was also essential to reach high conversions. Under air, a nitrile conversion of 27% was achieved on 1,10-decanediol with 20 mol% of catalyst at 50°C after 24 hours. Afterwards, the influence of the catalysts quantity has been investigated, as illustrated in Figure II-4-9.

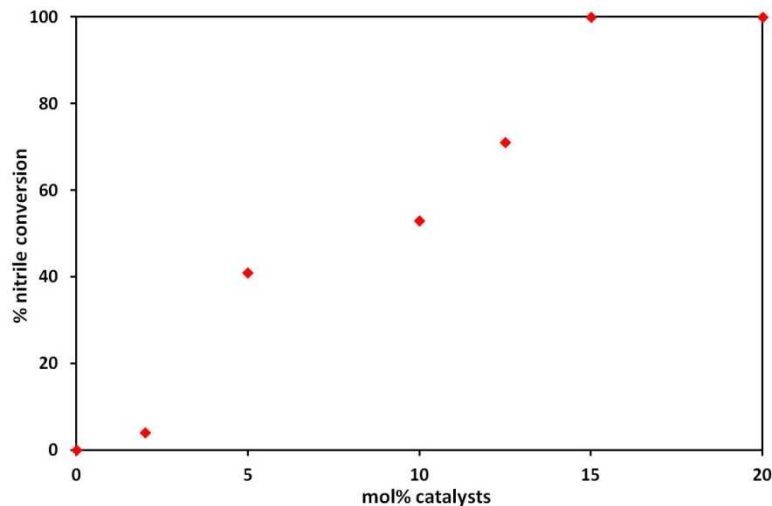


Figure II-4-9- Effect of the catalysts quantity on the nitriles conversion for 1,10-decanediol. (Optimized conditions, 24 hours and 50°C).

The nitrile conversion increased until a catalyst quantity of 15 mol% per mole of substrate. Besides under those conditions, no aldehyde was obtained at the end of the reaction. The optimized catalyst quantity was found to be between 12.5 mol% and 15 mol% per moles of substrate, which correspond to a range of 6.2-7.5 mol% per moles of hydroxyl functions. Subsequently, the effect of the temperature has been examined on 1,10-decanediol with 5 mol% of catalysts per moles of substrate. The Figure II-4-10 presents the results obtained for the variation of the temperature on the nitrile and aldehyde conversions.

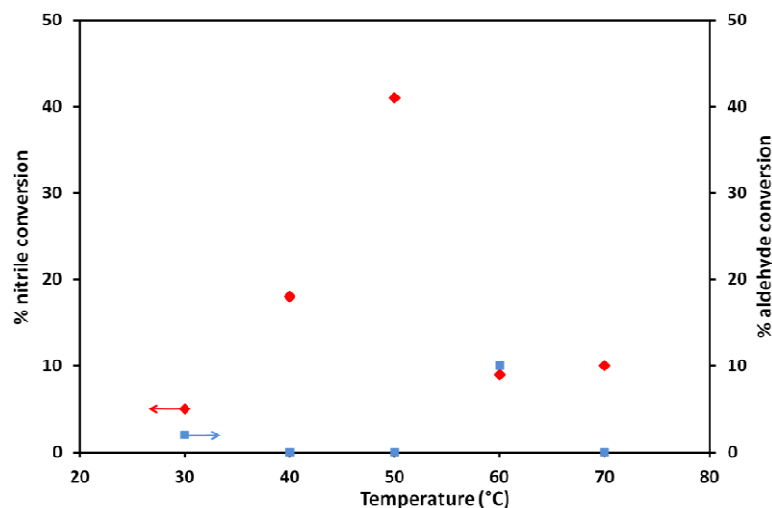


Figure II-4-10- Effect of the temperature on the nitrile and aldehyde conversions for 1,10-decanediol. (24 hours and 5 mol% catalysts)

As can be concluded from Figure II-4-10, the optimum of temperature is around 50°C. At higher temperature the percentage of nitrile conversion decreases drastically. This observation can be explained by the evaporation of ammonia from the solution.

The detection of aldehydes can be understood by the fact that the first dehydrogenation is faster than the second oxidation step. In some cases, the formation of aldehyde

intermediates was observed with a triplet at 2.41 ppm and a singlet at 9.75 ppm. For unoptimized reactions, the nitrile and aldehyde formation was confirmed in ^{13}C NMR with peaks at 119.80 ppm and 202.85 ppm respectively. Moreover, the carbon atoms nearby the nitrile or aldehyde groups presented expected shifts at 16.9 ppm and 43.7 ppm respectively. (See SI Figure II-4-6) A band at 1723 cm^{-1} was also observed in FTIR-ATR, which confirmed aldehyde formation. Moreover, no imine or hemi-aminal formation was detected. Yin *et al.* explained this feature by the better ligand behavior of imine, compared to aldehyde and nitrile, which form a favored Cu(I)-imine complex.² However, in all compounds used for the synthesis of nitriles, the formation of a very small triplet at 4.5-4.6 ppm has been detected in ^1H NMR and could be assigned to the hemi-acetal form.

After optimizations, the reaction was tested on the synthesized fatty acid diols (Seb-diol, UndC20-diol and UndS-diol) as well as on other bio-based resources. The procedure used was the following: the alcohol compound, 20 mol% per amount of substrate of CuI, 20 mol% per amount of substrate of bpy, and 20 mol% per amount of substrate of TEMPO were weighted. Then the schlenk was capped with a rubber septum, vacuumed and flushed with oxygen three times. Acetonitrile was added, followed by its saturation with oxygen by bubbling for 20 to 40 minutes depending on the scale. Aqueous ammonia (1 eq.) was subsequently added. The resulting orange-brown solution was stirred at 50°C for 24 hours under oxygen balloons. As the reaction is running the reaction mixture color is becoming light blue. For the fatty acid-based diol substrates: Seb-diol and UndC20-diol, full conversions were obtained with 20 mol% catalysts at 50°C after 24 hours. Nevertheless, for the sulfur atom-based fatty acid diol: UndS-diol, no reaction was observed. The sulfur atom is probably not tolerated as it can form complexes with the copper. In the literature, no aliphatic thio ether-based substrates have been already tested. Only, thiophene-based alcohols have been evaluated and nitrile conversions were in the range 60-95%, as determined by GC.^{4,5}

For UndC20-diol transformation, the nitrile products were also confirmed by ^1H NMR and FTIR-ATR. As for Seb-dinitrile, the formation of nitrile from UndC20-diol was proved in ^1H NMR by the appearance of a triplet corresponding to the methylene protons nearby the nitrile at 2.34 ppm. (See SI Figure II-4-7) The ^{13}C NMR of UndC20-dinitrile also revealed a peak at 119.94 ppm corresponding to the carbon of the nitrile group.

To explore the versatility of this nitrile platform; other bio-based substrates were subjected to nitrile syntheses, such as other vegetable oil derivatives (oleyl alcohol and undecenol), and terpenes (citronellol and phytol). Good to quantitative yields were achieved by ^1H NMR for the substrate scope of bio-based alcohols with a catalyst quantity of 20 mol% per moles

of substrates. The Figure II-4-11 shows the scope of the (di)nitriles synthesized from renewable resources. In the experimental section, the ^1H NMR data of all synthesized bio-based (di)nitriles are presented.

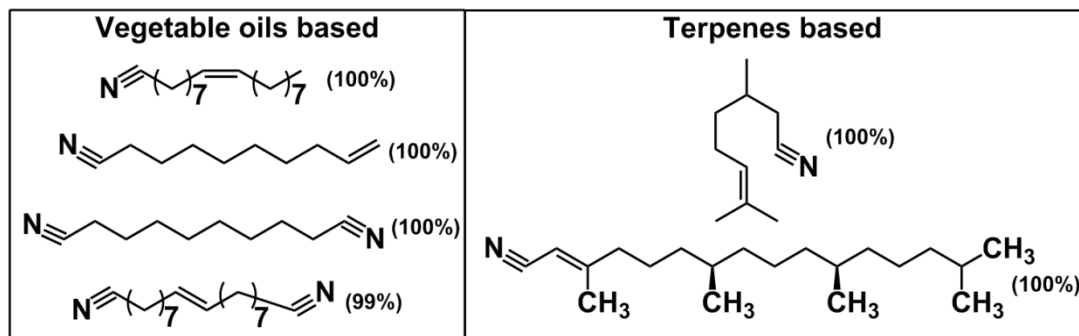


Figure II-4-11- Bio-based synthesized (di)nitriles. (24 hours, 50°C, 20 mol% per moles of substrates) (Conversion by ^1H NMR)

Reproducible conversions were achieved on 10 grams scale with 1,10-decanediol and 10-undecenol. This aerobic oxidation cascade reaction enables an easy one pot synthesis of (di)nitriles from primary alcohol-based compounds. This developed procedure appears to be highly efficient, green and economically accepted and industrially applicable. In the case of UndC20-diol, a lower conversion (62%) was achieved on 2.5 grams scale.

The isolation of pure nitrile compounds required to carry out a flash chromatography to separate the TEMPO. The yields were unexpectedly low ($Y=80\%$ for Seb-dinitrile and $Y=18\%$ for UndC20-dinitrile) and need to be further optimized. Indeed, the TEMPO was hard to remove and a classical alumina/celite filtration was not efficient. It should be mentioned that recently, the use of 4-hydroxy-TEMPO and 4-sulfonatoxy-TEMPO as co-catalyst were reported for the aerobic oxidation of primary alcohols. The authors claimed an easier removal from the product by aqueous extraction.⁵

1.3- Diamines synthesis and comparison of the two routes

1.3.1- Reduction of primary diamides and dinitriles

Different reduction conditions have been evaluated to reduce the fatty acid-based diamides. The reductions of the primary amides (UndC20-diamide and UndS-diamide) were first carried out in THF using 2.05 eq. then 4 eq. of LiAlH_4 per amide functions, as already reported in the literature.⁶ The reaction was conducted under reflux for 3 to 24 hours. Both acidic and basic works up have been tested. The diamines (UndC20-diamide and

UndS-diamide) were obtained in very small amount. The formation of diamines has been proved by FTIR-ATR and ^1H NMR. (See Figure II-4-12 and Figure II-4-13 for UndS-diamine) In FTIR-ATR, the band corresponding to the carbonyl of the primary amide at 1642 cm^{-1} disappeared. Besides, in the ^1H NMR of UndS-diamine, the singlet at 3.04 ppm between the amide function and the sulfur atom disappeared (See H5 protons in Figure II-4-13-(1)), together with the appearance of 4 triplets in the range 2.49-2.86 ppm. They were assigned to the protons nearby the amines and sulfur atom. Alcohols were also observed as the result of the hydrogenation of the remaining carboxyl functions in the UndS-diamide. The low yields (<2%) obtained were probably due to solubility issue of the primary diamides during the reaction. Thus, in order to increase the yields, reduction in DMSO at room temperature and 50°C has been tested using 3 eq. of NaBH_4 per amide functions and methanesulfonic acid.⁷ However, even under those conditions low conversions were also observed.

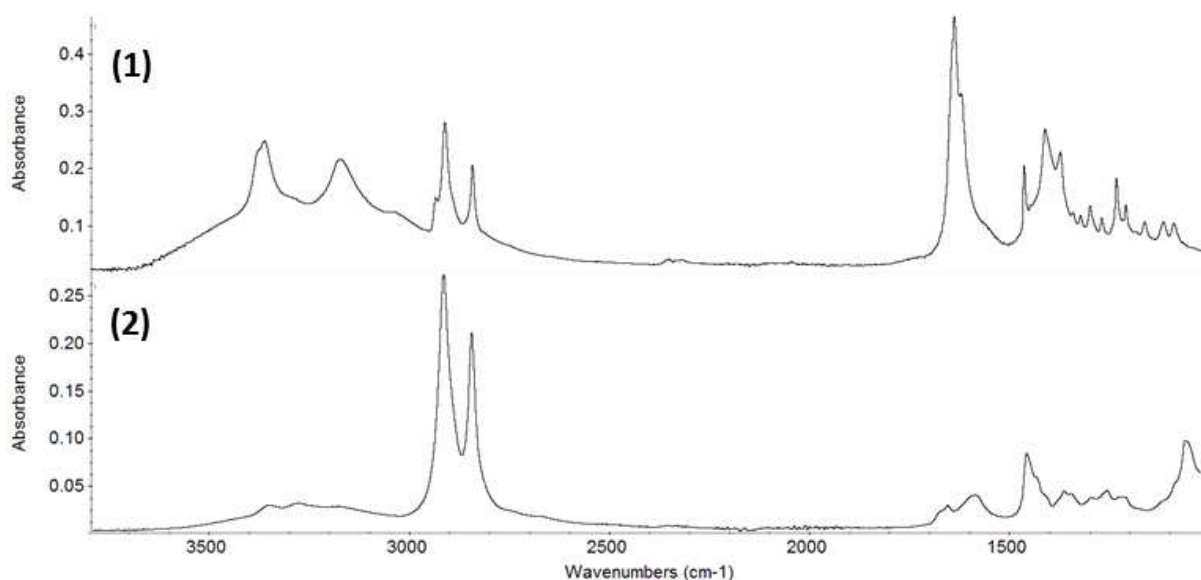


Figure II-4-12- Stacked FTIR-ATR spectra of fatty acid UndS-diamide and UndS-diamine.

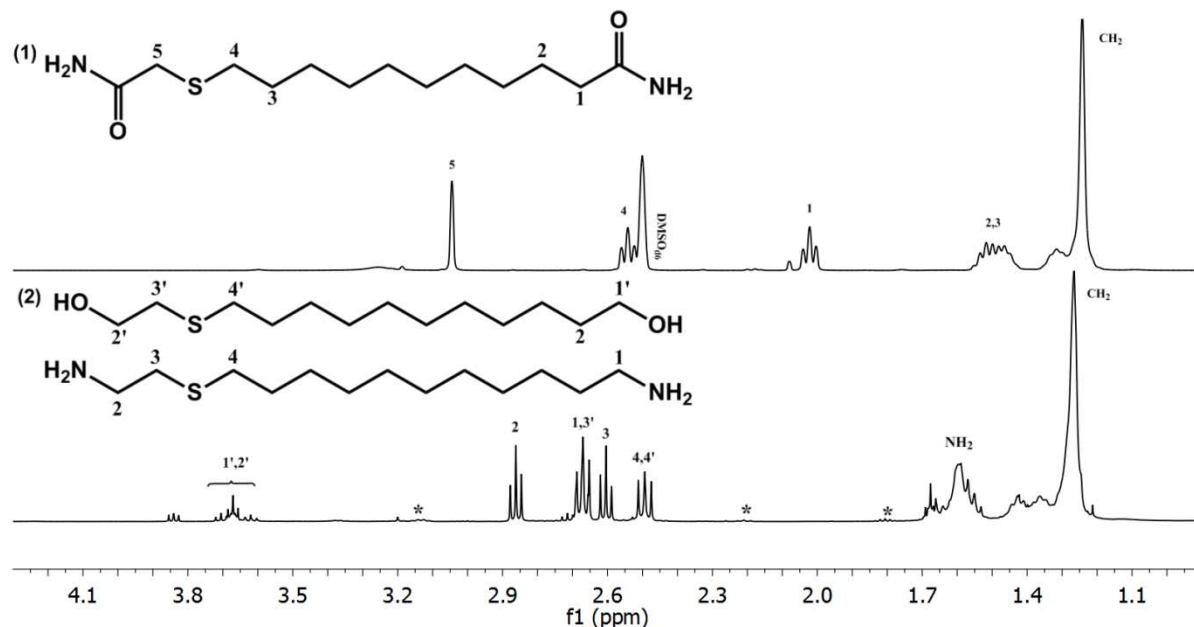


Figure II-4-13- Stacked ¹H NMR spectra of fatty acid UndS-diamide (in DMSO-d₆) and UndS-diamine with alcohol (in CDCl₃). (*) Impurities.

Due to these solubility concerns, the route via nitriles has been preferred to prepare Seb-diamine and UndC20-diamine. The reduction of Seb-dinitrile was first performed in ethanol using 10 wt% of Pd/C. The reaction was conducted under 30 Bar of H₂ at 50-60°C overnight. No amine was detected at the end of the reaction. Thus Raney nickel has been tested as a known nitrile hydrogenation catalyst. Using 1 mL of Raney nickel slurry in water (Ni>89%), with 10 Bar of H₂ at 70°C overnight. Seb-diamine has been obtained in ethanol with a conversion of 93%. The corresponding diamines have been then obtained after evaporation of the ethanol, solubilization in ethyl acetate and filtration. While the hydrogenation of UndC20-dinitrile, the double bonds have been hydrogenated with a conversion of 82.5%. The formation of Seb-diamine and UndC20-diamine has been proved by FTIR-ATR and ¹H NMR. In FTIR-ATR, the band corresponding to the nitrile at 2244 cm⁻¹ disappeared and three peaks in the range 3 000-3 500 cm⁻¹ appeared. The latter are not well distinct probably because of the presence of impurities and the fact that the diamine was not dried enough. Moreover in ¹H NMR, the disappearance of the triplet at 2.34 ppm corresponding to the methylene protons nearby the nitriles, as well as the appearance of a triplet at 2.67 ppm which can be attributed to the methylene protons nearby the amine functions, confirmed the synthesis of the diamines. The impurities observable in the diamine NMR spectra could be the result of the formation of salt while the reaction of the amine with CO₂.⁸ Further purifications under inert atmosphere would be required to purify the synthesized diamines. The higher solubility of nitriles compared to primary amides allows the synthesis of the diamines in larger quantity with easier work up.

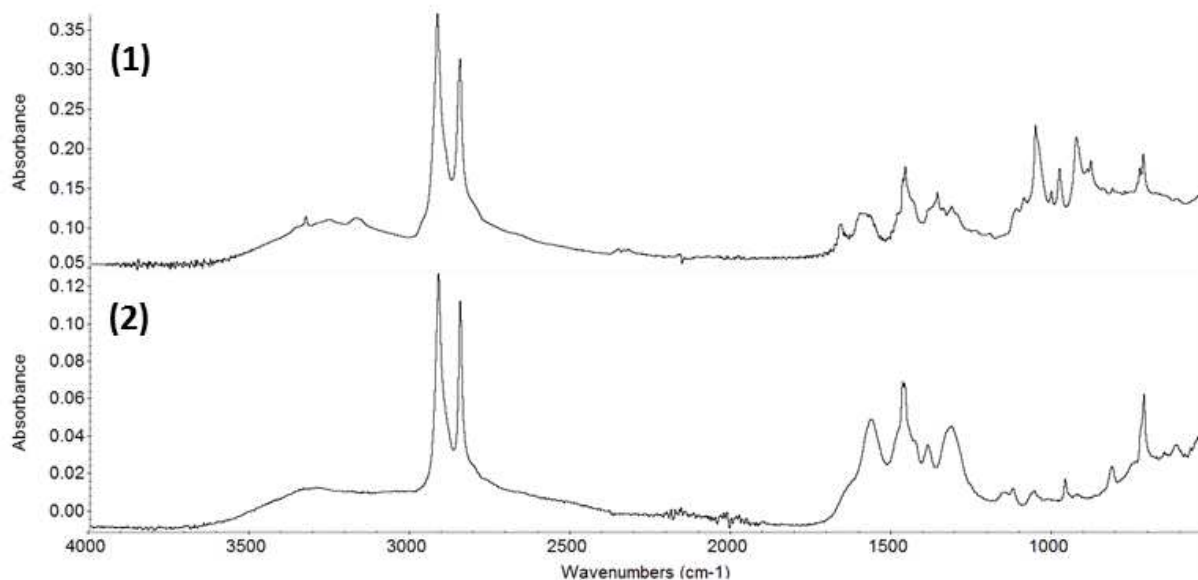


Figure II-4-14- Stacked FTIR-ATR spectra of fatty acid Seb-diamine and UndC20-diamine.

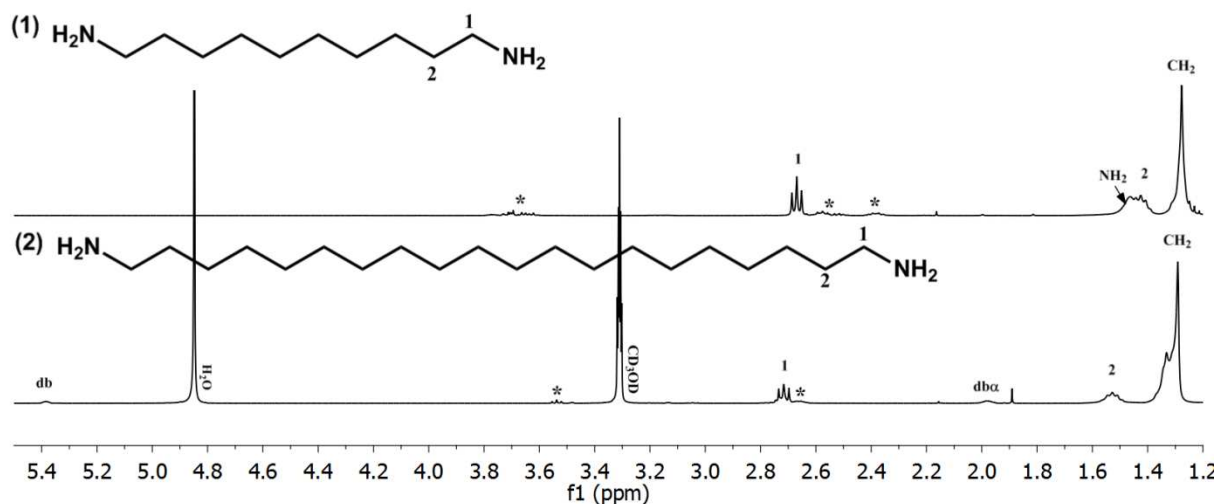


Figure II-4-15- Stacked ^1H NMR spectra of fatty acid Seb-diamine (CDCl_3) and UndC20-diamine (CD_3OD). (*) Impurities. db stands for double bond protons and db α for the protons in α of the double bond.

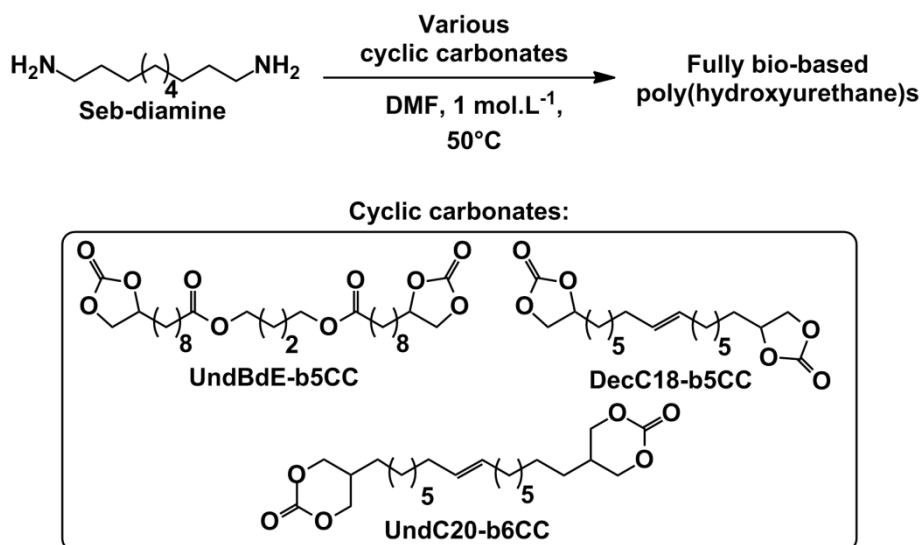
1.3.2- Comparison of the two routes

The two routes to diamines from usual vegetable oil derivatives need to be balanced, taking into account the number of steps, the conversions and yields, the elsewhere valorization of the intermediates and the work up of intermediates and amines. The method involving nitriles appears to be more attractive overall: cheap available catalysts, high atom efficiency, low toxicity of the reactants, mild reaction conditions, high conversions... Concerning the number of steps and the work up, the two routes are hardly comparable as it mainly depends on the chemical structure of the substrates. Concerning the valorization, nitriles can be valorized as intermediates in pharmaceuticals, agricultural and fine chemicals synthesis. Regarding the Seb-diamine and UndC20-diamine, the preferred route was the approach via

nitrile intermediates due to the high efficiency of the nitrile formation and the solubility issues of the corresponding primary diamides. However, in the case of UndC20-diamine, the initial diol formation needs to be optimized in order to reduce the isomerization. For UndS-diamine, as for other potentially fatty acid-based sulfur-containing substrates, the first method via amides was favored. Nevertheless, the reduction of the primary amides still need to be optimized in order to obtain higher conversions and thus yields.

2- Polymerizations to fully fatty acid-based PHUs

In order to prepare a wide range of PHUs and to evaluate the potential of possible fatty acid-based diamine, the commercially available Seb-diamine was used in polyaddition with various bis cyclic carbonates: 5-membered ones (UndBdE-b5CC and DecC18-b5CC) and 6-membered one (UndC20-b6CC). (Scheme II-4-5) The DecC18-b5CC was used with the aim to compare its reactivity in polyaddition and final PHU properties with the corresponding bis 6-membered cyclic carbonate: UndC20-b6CC. The polymerizations were performed in DMF at 1 mol.L^{-1} and 50°C , except for PHU-4 that have been prepared in bulk.



Scheme II-4-5- Poly(hydroxyurethane)s synthesis from the synthesized diamines.

The PHUs formation was confirmed by FTIR-ATR with the disappearance of the carbonyl band corresponding to the cyclic carbonate. Besides, the appearance of the characteristic bands for the urethane functions at 1692 cm^{-1} and 1530 cm^{-1} confirmed the formation of PHUs. The large band in the range 3114 cm^{-1} and 3594 cm^{-1} , which correspond to the vibrations of both NH and OH, was also visible. The FTIR-ATR spectra of the PHUs after 5 hours of polymerization are given in Figure II-4-16.

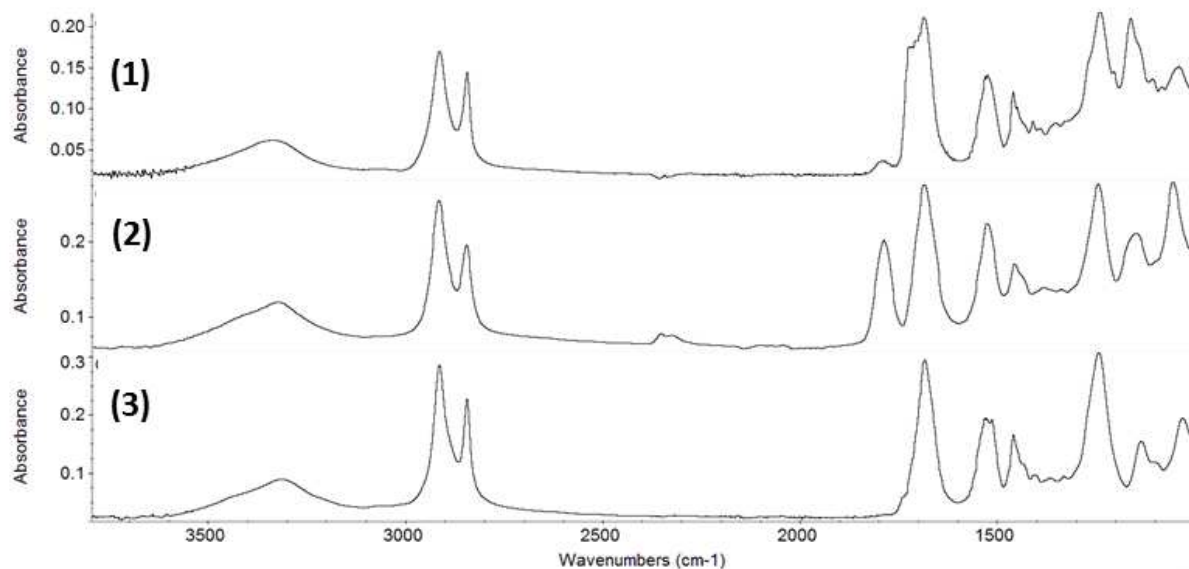


Figure II-4-16- Stacked FTIR-ATR spectra of (1) PHU-4, (2) PHU-5 and (3) PHU-6.

While comparing the FTIR-ATR spectra of PHU-4 and PHU-5, both based on bis 5-membered cyclic carbonates, one can notice a higher conversion for PHU-4 after 5 hours. This difference is explained by the bulk polymerization of this PHU. Besides, the difference in reactivity between 5- and 6-membered cyclic carbonates is clearly visible from the FTIR-ATR of PHU-5 and PHU-6. (See Figure II-4-16-(2) and Figure II-4-16-(3))

The chemical structures of the synthesized PHUs were also supported by ^1H NMR analyses, as presented in the Figure II-4-17 for PHU-6. The signals for the protons corresponding to the cyclic carbonates disappeared. Moreover, the appearance of a signal at 3.12 ppm confirmed the urethane formation. (See protons H7' in Figure II-4-17)

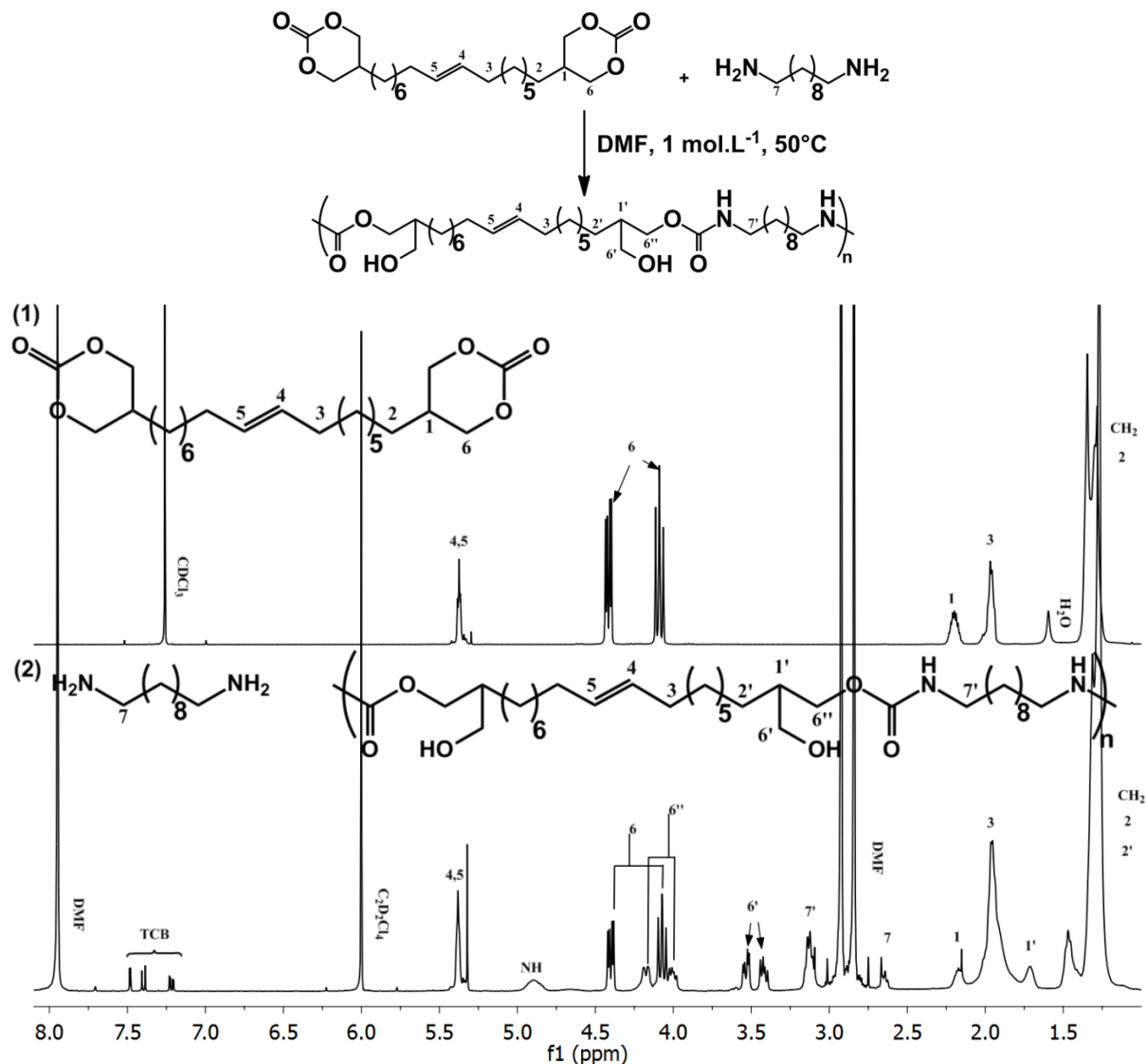


Figure II-4-17- Stacked ¹H NMR spectra of (1) UndC20-b6CC (CDCl₃) and (2) PHU-6 from UndC20-b6CC and Seb-diamine (25.3% cyclic carbonate conversion) (TCE with TCB as internal reference).

3- Thermal stability and thermo-mechanical properties

The thermal stability of the synthesized PHUs was evaluated by TGA under a nitrogen stream at a heating rate of 10°C.min⁻¹ and the data are summarized in Table II-4-1. In this study, degradation temperatures after 5 wt% loss up to 276°C were achieved.

The PHUs were further analyzed by DSC experiments. (See Table II-4-1) The PHU from UndC20-b6CC was amorphous and present a glass transition temperature of -3°C, which is consistent with results presented in the previous chapter. In comparison, the lower glass transition temperature obtained with DecC18-b5CC as comonomer could be explained by its lower molar mass. The molar masses and dispersities were not determined due to solubility

issues. A semi-crystalline PHU (PHU-4) have been achieved by polyaddition of Seb-diamine and UndBdE-b5CC. This feature is explained by the presence of ester functions in the cyclic carbonate, which are known to facilitate polymer chains packing and thus crystallinity.

Table II-4-1- Thermal stability and thermo-mechanical properties of the synthesized PHUs.

Sample	bCC	Diamine	T _g (°C) ¹	T _m (°C) ¹	T _{5%} (°C) ²
PHU-4	UndBdE-b5CC	Seb-diamine	-15	46	276
PHU-5	DecC18-b5CC	Seb-diamine	-50	-	236
PHU-6	UndC20-b6CC	Seb-diamine	1	-	266

(1) Determined by DSC at 10°C.min⁻¹. (2) Determined by TGA at 10°C.min⁻¹ under nitrogen. nd= not determined.

Conclusion

In conclusion, 3 diamines have been synthesized from castor oil derivatives such as sebacic acid and undecenoic acid. Two routes have been envisaged. The first approach was based on the synthesis of diacyl chloride and primary diamide intermediates from fatty acids. The second route was the preparation of dinitriles from diols using mild condition procedure with a copper catalytic system, oxygen as oxidant and aqueous ammonia as a nitrogen source. Reductions of the so formed primary diamides and dinitriles led to fatty acid-based diamines. The route via dinitriles turned out to be much more promising due to high efficiency and solubility issue with the primary diamides. The promising results of this chapter on the synthesis of fatty acid-based diamines need to be further developed in order to reach higher conversion and yield. In addition, a perspective for the dinitrile synthesis could be the optimization of the reaction under air.^{5,9} Afterwards, fully bio-based and non-isocyanate PHUs have been synthesized using both bis 5- and 6-membered cyclic carbonates in comparable polymerization conditions. The higher reactivity of the bis 6-membered cyclic carbonates in comparison to the bis 5-membered ones was then observed in polyaddition with a diamine, by the means of FTIR-ATR and ¹H NMR data. Moreover, the polymerization kinetics were faster in bulk than in solvent. Both amorphous and semi-crystalline PHUs were achieved depending on the chemical structure of the monomers used. Glass transition temperatures from -50°C to -3°C were obtained. Degradation temperatures after 5 wt% loss up to 276°C were observed for the synthesized PHUs.

The fatty acid-based diamines presented in this chapter are also potential monomers for PA and epoxy resins. Besides, the routes tested allow us to transform the existing platform of fatty acid based-diols and diacids to a new diamine platform.

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Experimental and supporting information

Experimental methods

Diamine synthesis and characterizations

1- Metathesis reactions

The self metathesis reactions were performed under inert atmosphere, using Grubbs II metathesis catalyst (1/500 for UndAc and 1/100 for Undol in pentane dried on CaH₂ at room temperature for 24 hours (UndC20-diacid) or 72 hours (UndC20-diacid). As the reaction was running, the product got precipitated, which allows the shift of the equilibrium toward the formation of products and limits as well isomerizations. Afterwards, ethyl vinyl ether was added to deactivate the Grubbs catalyst and then the reaction mixture was filtered and the recovered solid was recrystallized two times in toluene.

UndC20-diacid: Undecenoic acid (20 g, 109 mmol), Grubbs II catalyst (0.46 g, 0.54 mmol) and pentane (100 mL). UndC20-diacid was obtained as a white powder with a purity of 97.0% (determined by GC-FID). Yield = 42%. ¹H NMR (CDCl₃, 25 °C, 400 MHz) δ (ppm): 5.37 (m, 2H), 2.35 (t, 4H), 1.97 (m, 4H), 1.63 (m, 4H), 1.28 (m, 20H). ¹³C NMR (CDCl₃, 25 °C, 100 MHz) δ (ppm): 180.23 (C=OOH), 130.50 (CH=CH), 34.17 (CH₂-C=OOH), 32.66 (CH₂-CH=CH), 29.66-29.03 (CH₂), 24.79 (CH₂-CH₂-C=OOH). IR (cm⁻¹): 2912, 2849, 1687.

UndC20-diol: 10-undecen-1-ol (20 g, 117 mmol), Grubbs II catalyst (0.99 g, 1.17 mmol) and pentane (100 mL). UndC20-diol was obtained as a white powder with a purity of 60.0% (determined by GC-FID, due to isomers) Yield = 43%. ¹H NMR (CDCl₃, 25 °C, 400 MHz) δ (ppm): 5.38 (m, 2H), 3.63 (t, 4H), 1.97 (m, 4H), 1.56 (m, 4H), 1.28 (m, 24H). ¹³C NMR (CDCl₃, 25 °C, 100 MHz) δ (ppm): 130.51 (CH=CH), 63.23 (CH₂-OH), 32.93 (CH₂-CH₂-OH), 32.71 (CH₂-CH=CH), 29.75-25.89 (CH₂). IR (cm⁻¹): 3360, 2912, 2849.

2- Thiol-ene reactions

UndS-diester: Methyl undecenoate (40 g, 201.7 mmol) and methyl thioglycolate (64 g, 603.0 mmol) (3 eq. / double bond) were stirred at room temperature under UV irradiation (254 nm). After the disappearance of double bond protons (monitored by ¹H NMR spectroscopy), the excess methyl thioglycolate was removed from the reaction mixture by distillation under vacuum. The UndS-diester was obtained as a white powder. Yield = 98.6%. ¹H NMR (CDCl₃,

25 °C, 400 MHz) δ (ppm): 3.73 (s, 3H), 3.66 (s, 3H), 3.22 (s, 2H), 2.61 (t, 2H), 2.29 (t, 2H), 1.60 (m, 4H), 1.27 (m, 12H). ^{13}C NMR (CDCl_3 , 25 °C, 100 MHz) δ (ppm): 174.30 and 171.08 ($\text{C}=\text{OOCH}_3$), 52.34 and 51.35 ($\text{C}=\text{OOCH}_3$), 34.13 ($\text{CH}_2\text{-C}=\text{OOCH}_3$), 33.53 ($\text{S-CH}_2\text{-C}=\text{OOCH}_3$), 32.79 ($\text{CH}_2\text{-S}$), 29.43-24.98 (CH_2). IR (cm^{-1}): 2927, 2856, 1735.

UndS-diol: 10-undecen-1-ol (20 g, 117.4 mmol) and mercaptoethanol (27.5 g, 352.0 mmol) (3 eq. / double bond) were stirred at room temperature under UV irradiation (254 nm). After the disappearance of double bond protons (monitored by ^1H NMR spectroscopy), the reaction mixture was taken into dichloromethane (DCM) and thoroughly washed with water (5 times). The DCM solution was dried over anhydrous sodium sulfate, filtered and solvent was removed on rotary evaporator to obtain UndS-diol as white powder with a purity of 98.1% (determined by GC-FID). Yield = 99%. ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 3.71 (t, 2H), 3.67 (t, 2H), 2.73 (t, 2H), 2.51 (t, 2H), 1.58 (m, 4H), 1.28 (m, 14H). ^{13}C NMR (CDCl_3 , 25 °C, 100 MHz) δ (ppm): 63.18 and 60.44 ($\text{CH}_2\text{-OH}$), 32.89-25.84 (CH_2). IR (cm^{-1}): 3360, 2925, 2853.

3- Hydrolysis of UndS-diester

UndS-diester (1 g, 3 mmol) was placed with methanol (3 mL) in a round-bottomed flask and maintained at 35°C. Then KOH (0.74 g, 13 mmol, 4 eq.) were added and the reaction mixture was stirred for 1 hour at 35°C. Afterwards, water was added to quench the reaction. The remaining UndS-diester was removed by ethyl acetate extraction. Then the UndS-diacid was recovered after acidification of the aqueous phase with HCl, and extraction with ethyl acetate (3 times). The combined extracts phases were dried over anhydrous sodium sulfate and concentrated on rotary evaporator.

UndS-diacid was obtained after vacuum drying as a white powder with a purity of 97.7% (determined by GC-FID). Yield = 97%. ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 3.24 (s, 2H), 2.65 (t, 2H), 2.35 (t, 2H), 1.62 (m, 4H), 1.28 (m, 12H). ^{13}C NMR (CDCl_3 , 25 °C, 100 MHz) δ (ppm): 180.43 and 176.84 ($\text{C}=\text{OOH}$), 34.15 ($\text{CH}_2\text{-C}=\text{OOH}$), 33.91 ($\text{S-CH}_2\text{-C}=\text{OOH}$), 32.94 ($\text{CH}_2\text{-S}$), 29.09-24.68 (CH_2). IR (cm^{-1}): 2916, 2847, 1685.

4- Synthesis of diamines via primary amide intermediates

4.1- Acyl chlorides synthesis

The diacid was placed in a round-bottomed flask equipped with a condenser connected to gases trapping system filled with NaOH solution (0.1M). Then thionyl chloride or oxalyl chloride (1.5 eq. / acid function) was slowly added at RT. After 1.5 hours at reflux, the excess

of chlorating agent was evaporated under vacuum. Quantitative yields were obtained in all cases.

Seb-AcylCl: Sebacic acid (1 g, 5 mmol) and thionyl chloride (1.88 g, 15 mmol, 3 eq.). ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 2.87 (t, 4H), 1.69 (m, 4H), 1.31 (m, 8H). IR (cm^{-1}): 2930, 2859, 1789.

UndC20-AcylCl: UndC20-diacid (1 g, 3 mmol) and thionyl chloride (1.05 g, 9 mmol). ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 5.38 (m, 2H), 2.88 (t, 4H), 1.97 (m, 4H), 1.70 (m, 4H), 1.28 (m, 20H). IR (cm^{-1}): 2924, 2853, 1795.

UndS-AcylCl: UndS-diacid (1 g, 4 mmol) and thionyl chloride (1.26 g, 11 mmol). ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 3.67 (s, 2H), 2.88 (t, 2H), 2.63 (t, 2H), 1.71-1.60 (m, 4H), 1.28 (m, 12H). IR (cm^{-1}): 2916, 2847, 1790.

4.2- Synthesis of primary diamides

To the diacyl chloride synthesized in the previous part, dry THF was added and the mixture was cooled at 0°C. Then aqueous ammonia was added dropwise and the reaction mixture was then stirred at RT for 4 hours. Afterwards, the resulting solid was filtered and washed with THF, and then dried under vacuum.

Seb-diamide: Seb-AcylCl (1.17 g, 4.9 mmol), THF (20 mL) and aqueous ammonia (1.9 mL, 49 mmol, 10 eq.). Seb-diamide was obtained as a white powder. Yield = 87%. ^1H NMR (DMSO-d_6 , 50°C, 400 MHz) δ (ppm): 7.25 (s, NH_2), 6.65 (s, NH_2), 2.01 (t, 4H), 1.45 (m, 4H), 1.23 (m, 8H). ^{13}C NMR (DMSO-d_6 , 50°C, 100 MHz) δ (ppm): 174.10 (C=ONH_2), 34.96 ($\text{CH}_2\text{-C=ONH}_2$), 28.50 (CH_2), 24.89 ($\text{CH}_2\text{-CH}_2\text{-C=ONH}_2$). IR (cm^{-1}): 3370, 3178, 2923, 2849, 1644.

UndC20-diamide: UndC20-AcylCl (1.13 g, 3 mmol), THF (20 mL) and aqueous ammonia (1.2 mL, 29 mmol). UndC20-diamide was obtained as a white powder. Yield = 98.5%. ^1H NMR (DMSO-d_6 , 50 °C, 400 MHz) δ (ppm): 7.26 (s, NH_2), 6.65 (s, NH_2), 5.36 (m, 2H), 2.01 (t, 4H), 1.93 (m, 4H), 1.45 (m, 4H), 1.23 (m, 20H). ^{13}C NMR (DMSO-d_6 , 50 °C, 100 MHz) δ (ppm): 174.12 (C=ONH_2), 129.87 (CH=CH), 34.97 ($\text{CH}_2\text{-C=ONH}_2$), 31.71 ($\text{CH}_2\text{-CH=CH}$), 28.81-28.26 (CH_2), 24.85 ($\text{CH}_2\text{-CH}_2\text{-C=ONH}_2$). IR (cm^{-1}): 3387, 3184, 2918, 2849, 1645.

UndS-diamide: UndS-AcylCl (1.25 g, 4 mmol), THF (25 mL) and aqueous ammonia (1.4 mL). UndS-diamide was obtained as a white powder. Yield = 95%. ^1H NMR (DMSO-d_6 , 50 °C, 400 MHz) δ (ppm): 7.41-6.53 (2. NH_2), 3.04 (s, 2H), 2.54 (t, 2H), 2.02 (t, 2H), 1.52 (m, 4H), 1.32 (m, 2H), 1.24 (m, 10H). ^{13}C NMR (DMSO-d_6 , 50 °C, 100 MHz) δ (ppm): 174.18 and 170.93 (C=ONH_2), 34.97 ($\text{CH}_2\text{-C=ONH}_2$), 34.48 ($\text{S-CH}_2\text{-C=ONH}_2$), 31.65 ($\text{CH}_2\text{-S}$), 28.68-24.92 (CH_2). IR (cm^{-1}): 3366, 3178, 2917, 2848, 1645.

4.3- Reduction of UndS-diamide

To a suspension of LiAlH_4 (1.1 g, 29 mmol, 8 eq.) in THF (45 mL), UndS-diamide (1 g, 3.6 mmol) was slowly added under magnetic stirring at 0°C . After the total addition, the mixture was heated and allowed to reflux overnight. Next, the reaction mixture was cooled to RT and excess LiAlH_4 was quenched with NaOH solution (4N) (2mL) and water (2 mL). After filtration, the filtrate was dried over anhydrous sodium sulfate and the solvent was removed under vacuum. **UndS-diamine:** UndS-diamine was obtained as a white/yellow powder. Yield < 2%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 2.86 (t, 2H), 2.67 (t, 2H), 2.60 (t, 2H), 2.49 (t, 2H), 1.60 (m, 2.NH₂), 1.57-1.27 (4.m, 18H). ^{13}C NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 42.32 and 41.26 ($\text{CH}_2\text{-NH}_2$), 36.49 ($\text{S-CH}_2\text{-CH}_2\text{-NH}_2$), 32.02 (S-CH_2), 33.90-27.03 (CH_2). IR (cm^{-1}): 3359, 3285, 3174, 2922, 2851.

5- Synthesis of diamines via nitrile intermediates

5.1- General procedure for (di)nitriles synthesis

In a schlenk tube, the substrat, CuI (20 mol% per amount of substrate), bpy (20 mol% per amount of substrate) and TEMPO (20 mol% per amount of substrate) were weighted. Then the schlenk was capped with a rubber septum, vacuumed and flushed with oxygen three times. Acetonitrile was added, followed by its saturation with oxygen by bubbling for 20 minutes (for 0.5 g scale). Aqueous ammonia (25-28% w/w, 0.11 mL, 3 mmol, 1 eq.) were subsequently added. The resulting orange-brown solution was stirred at 50°C for 24 hours under oxygen balloons. As the reaction is running the reaction mixture color is becoming light blue. The crude reaction mixture was analyzed by ^1H NMR and ^{13}C NMR in some cases. When purification was needed, the solvent was removed under vacuum and the residue was purified by flash chromatography.

Seb-dinitrile: 1,10-decenediol (0.5 g, 2.9 mmol), CuI (110 mg, 0.58 mol, 20 mol%), bpy (90 mg, 0.58 mmol, 20 mol%), TEMPO (90 mg, 0.58 mmol, 20 mol%), acetonitrile (5 mL) and aqueous ammonia (0.44 mL). Seb-dinitrile was obtained as a transparent liquid after flash chromatography (eluent: cyclohexane–ethyl acetate 90/10 to 43/57). Yield = 90%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 2.34 (t, 4H), 1.66 (m, 4H), 1.46 (m, 4H), 1.35 (m, 4H). ^{13}C NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 119.82 (CN), 28.60 (CH_2), 25.40 ($\text{CH}_2\text{-CH}_2\text{-CN}$), 17.23 ($\text{CH}_2\text{-CN}$). IR (cm^{-1}): 2932, 2859, 2244, 1464, 1427.

UndC20-dinitrile: UndC20-diol (0.5 g, 1.6 mol), CuI (61 mg, 0.32 mmol, 20 mol%), bpy (0.5 mg, 0.32 mmol, 20 mol%), TEMPO (0.5 mg, 0.32 mmol, 20 mol%), acetonitrile (5 mL) and aqueous ammonia (0.25 mL). UndC20-dinitrile was obtained as a viscous transparent liquid

after flash chromatography (eluent: cyclohexane–ethyl acetate 100/0 to 80/20). Yield = 18%. ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 5.38 (m, 2H), 2.33 (t, 4H), 1.96 (m, 4H), 1.66 (m, 4H), 1.45 (m, 4H), 1.30 (m, 16H). ^{13}C NMR (CDCl_3 , 25 °C, 100 MHz) δ (ppm): 119.94 (CN), 130.42 (CH=CH), 32.62 ($\text{CH}_2\text{-CH=CH}$), 29.63-28.74 (CH_2), 25.41 ($\text{CH}_2\text{-CH}_2\text{-CN}$), 17.22 ($\text{CH}_2\text{-CN}$). IR (cm^{-1}): 2924, 2855, 2244.

From undecenol: Undecenol (0.5 g, 2.9 mmol), CuI (112 mg, 0.59 mmol, 20 mol%), bpy (92 mg, 0.59 mmol, 20 mol%), TEMPO (92 mg, 0.59 mmol, 20 mol%), acetonitrile (5 mL) and aqueous ammonia (0.45 mL). **Und-nitrile** was obtained as a viscous transparent liquid after flash chromatography (eluent: cyclohexane–ethyl acetate 100/0 to 93/7). Yield = 26%. ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 5.83 (m, 1H), 5.02 (m, 2H), 2.38 (t, 2H), 2.10 (m, 2H), 1.71 (m, 2H), 1.50-1.36 (m, 10H).

From oleyl alcohol: Oleyl alcohol (0.5 g, 1.9 mol), CuI (71 mg, 0.37 mmol, 20 mol%), bpy (58 mg, 0.37 mol, 20 mol%), TEMPO (58 mg, 0.37 mmol, 20 mol%), acetonitrile (5 mL) and aqueous ammonia (0.29 mL). ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 5.38 (m, 2H), 2.35 (t, 2H), 2.04 (m, 4H), 1.68 (m, 2H), 1.47-1.29 (m, 22H), 0.91 (t, 3H).

From citronellol: Citronellol (0.5 g, 3.2 mmol), CuI (122 mg, 0.64 mmol, 20 mol%), bpy (100 mg, 0.64 mmol, 20 mol%), TEMPO (100 mg, 0.64 mmol, 20 mol%), acetonitrile (5 mL) and aqueous ammonia (0.5 mL). ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 5.09 (t, 1H), 2.32 (m, 2H), 2.02 (m, 2H), 1.89 (m, 1H), 1.71 (s, 3H), 1.63 (s, 3H), 1.47-1.39 (m, 2H), 1.10 (d, 3H).

From phytol: Phytol (0.5 g, 1.7 mmol), CuI (64 mg, 0.34 mmol, 20 mol%), bpy (53 mg, 0.34 mmol, 20 mol%), TEMPO (53 mg, 0.34 mmol, 20 mol%), acetonitrile (5 mL) and aqueous ammonia (0.26 mL). ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 5.12 (s, 1H), 2.40 and 2.17 (2.t, 2H), 2.06 and 1.92 (2.s, 3H), 1.52-1.09 (m, 19H), 0.89 (m, 12H).

5.2- Reduction of Seb-dinitrile

In a reactor, Seb-dinitrile (0.5 g, 3 mmol), Raney Nickel slurry in water (1 mL) and 15 mL of ethanol were successively added. The reaction was stirred under 10 Bar of H_2 , at 70°C overnight. After, the reactor was cooled down and slowly depressurized. The reaction media was then filtered over celite to remove the Raney nickel catalyst. The ethanol was evaporated and the obtained white powder was washed with ethyl acetate to remove the unreacted nitrile.

Seb-diamine: Seb-diamine was obtained as a white powder. conversion = 93%. Y=43%. ^1H NMR (CDCl_3 , 25 °C, 400 MHz) δ (ppm): 2.64 (t, 4H), 1.40 (m, 4H and 2.NH₂), 1.25 (m, 12H). ^{13}C NMR (CDCl_3 , 25 °C, 100 MHz) δ (ppm): 42.30 ($\text{CH}_2\text{-NH}_2$), 29.72-27.04 (CH_2). IR (cm^{-1}): 3330, 3257, 3163, 2919, 2848.

UndC20-diamine: UndC20-diamine was obtained as a white/yellow powder. Y=71%. ^1H NMR (CD_3OD , 25 °C, 400 MHz) δ (ppm): 2.72 (t, 4H), 1.53 (m, 4H), 1.29 (m, 32H). ^{13}C NMR (CD_3OD , 25 °C, 100 MHz) δ (ppm): 41.96 ($\text{CH}_2\text{-NH}_2$), 32.06-27.86 (CH_2). IR (cm^{-1}): 3299, 2916, 2850.

Polymers synthesis and characterizations

1- Synthesis of the bis 5-membered cyclic carbonates

From Dec-5CC

Into a round-bottom flask equipped with a mineral oil bubbler, the Dec-5CC (1 g, 5.0 mmol) was charged with dried DCM (40 mL) and 3rd generation Grubbs catalyst (22.3 mg, 0.03 mmol, 1/200). The contents were vigorously stirred at RT for 72 hours. Afterwards, 1.1 mL of ethylvinyl ether was added to deactivate the Grubbs catalyst. The product was then purified with flash chromatography using a mixture of cyclohexane and ethyl acetate as eluent.

DecC18-b5CC was obtained as a grey solid. Yield=65%. **DecC18-b5CC:** ^1H NMR (CDCl_3 , 25°C, 400 MHz) δ (ppm): 5.36 (m, 2H), 4.69 (m, 2H), 4.51 (t, 2H), 4.05 (t, 2H), 1.97 (m, 4H), 1.79 (m, 2H), 1.68 (m, 2H), 1.46-1.34 (m, 16H). ^{13}C -NMR (CDCl_3 , 25°C, 100 MHz) δ (ppm): 155.20 (OCOO), 130.60 (CH=CH), 76.84 ($\underline{\text{C}}\text{H-OCOO}$), 69.51 ($\underline{\text{C}}\text{H}_2\text{-OCOO}$), 34.03 ($\underline{\text{C}}\text{H}_2\text{-CH-OCOO}$), 32.56 ($\underline{\text{C}}\text{H}_2\text{-CH=CH}$), 29.40-28.69 (CH_2), 24.48 ($\underline{\text{C}}\text{H}_2\text{-CH}_2\text{-CH-OCOO}$). IR (cm^{-1}): 2924, 2856, 1786.

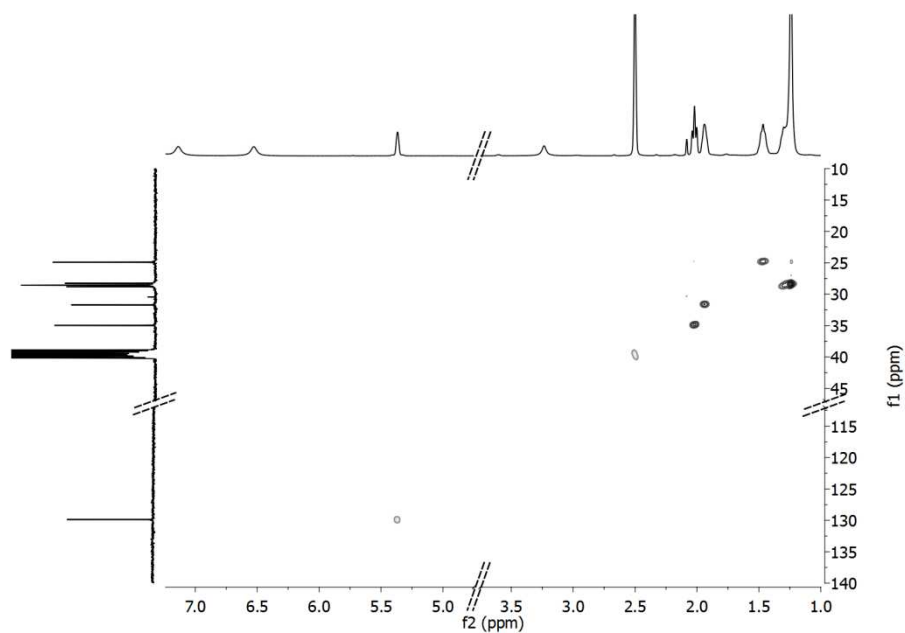
UndBdE-b5CC synthesis

The UndBdE-b5CC was synthesized by the same strategy as the one used for the preparation of UndPdE-b5CC in Part II - Chapter 2.

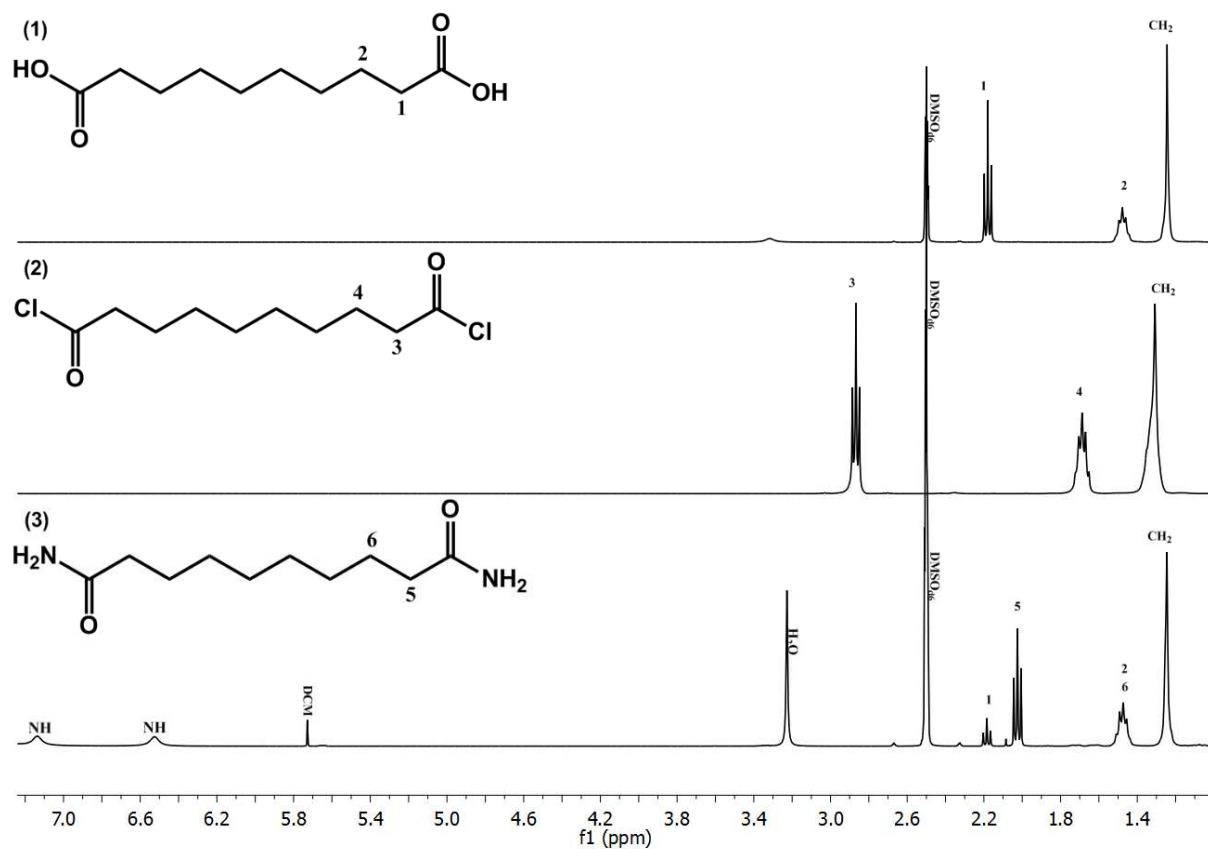
2- General procedure for the poly(hydroxyurethane)s synthesis

PHUs were prepared from the bis 5- and 6-membered cyclic carbonates and the commercially available 1,10-decane diamine (Seb-diamine) in order to save time. Poly(hydroxyurethane) syntheses were performed in DMF at 50°C into a schlenk tube under magnetic stirring and nitrogen atmosphere for 2 days. TCB was used as a reference, and no catalysts were added for the polymerization reactions.

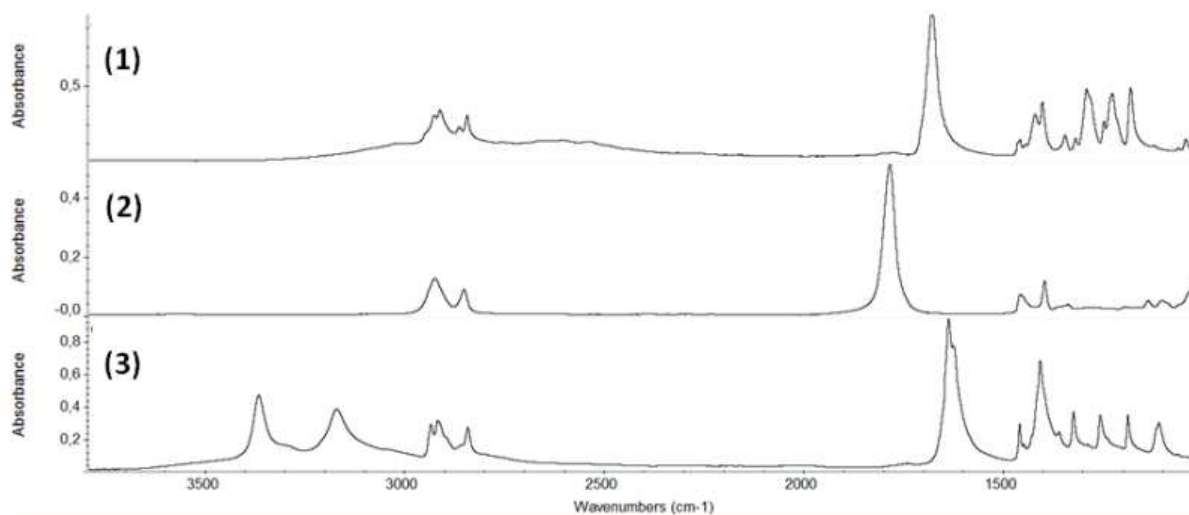
Supporting information



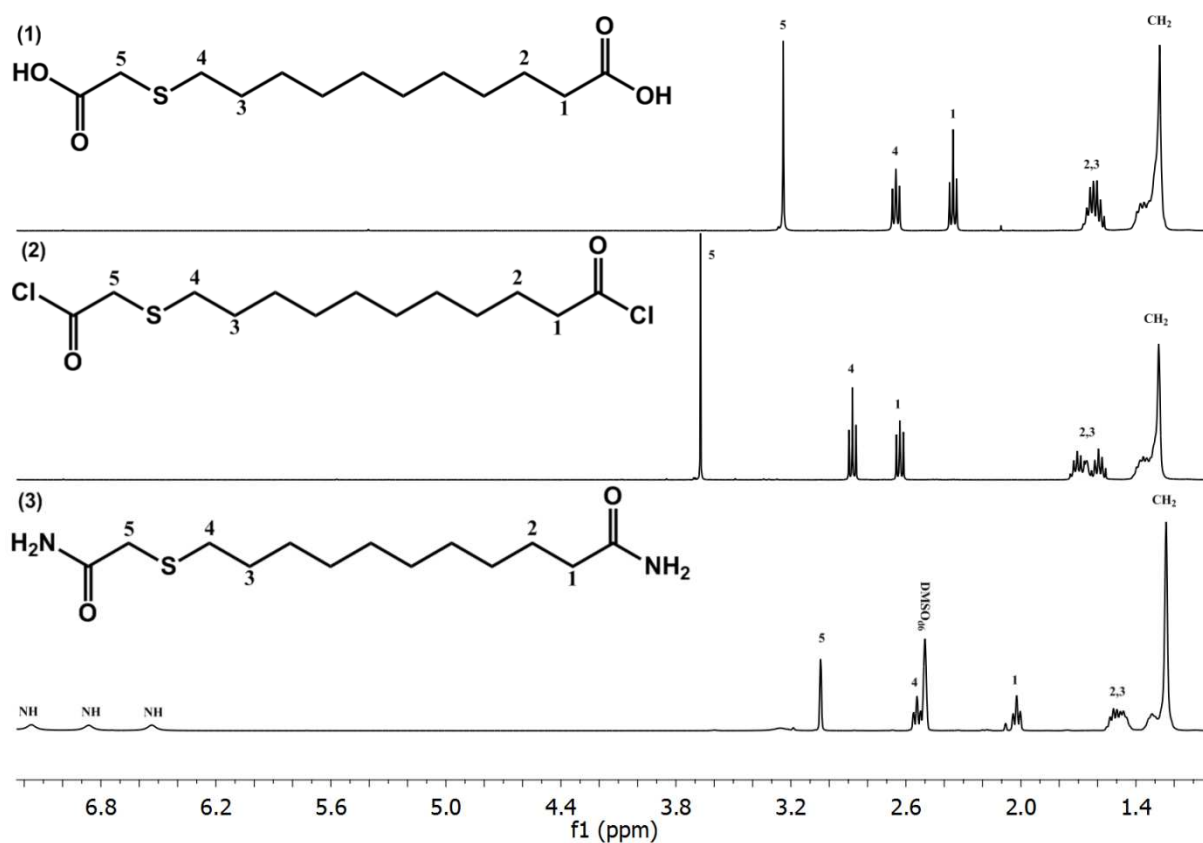
SI Figure II-4-1- ^1H - ^{13}C HSQC-NMR for UndC20-diamide (50°C in DMSO- d_6).



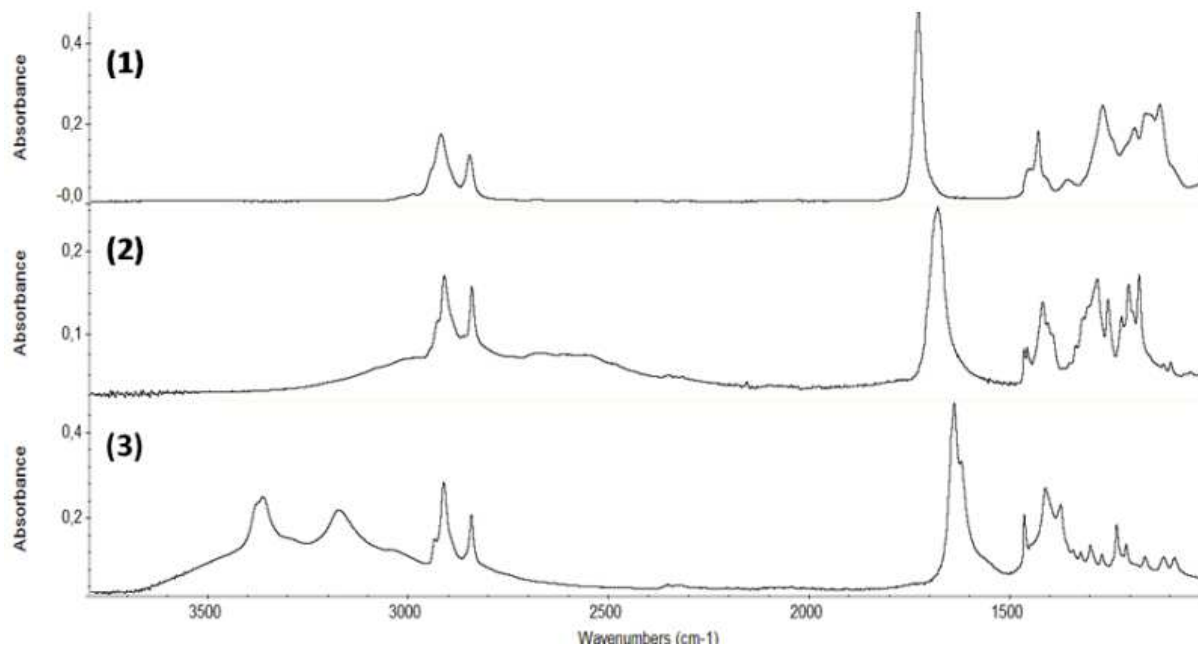
SI Figure II-4-2- All steps ^1H NMR for the Seb-diamide synthesis. (1) Seb-diacid (25°C in DMSO- d_6), (2) Seb-AcylCl (25°C in CDCl_3) and (3) unpurified Seb-diamide (50°C in DMSO- d_6).



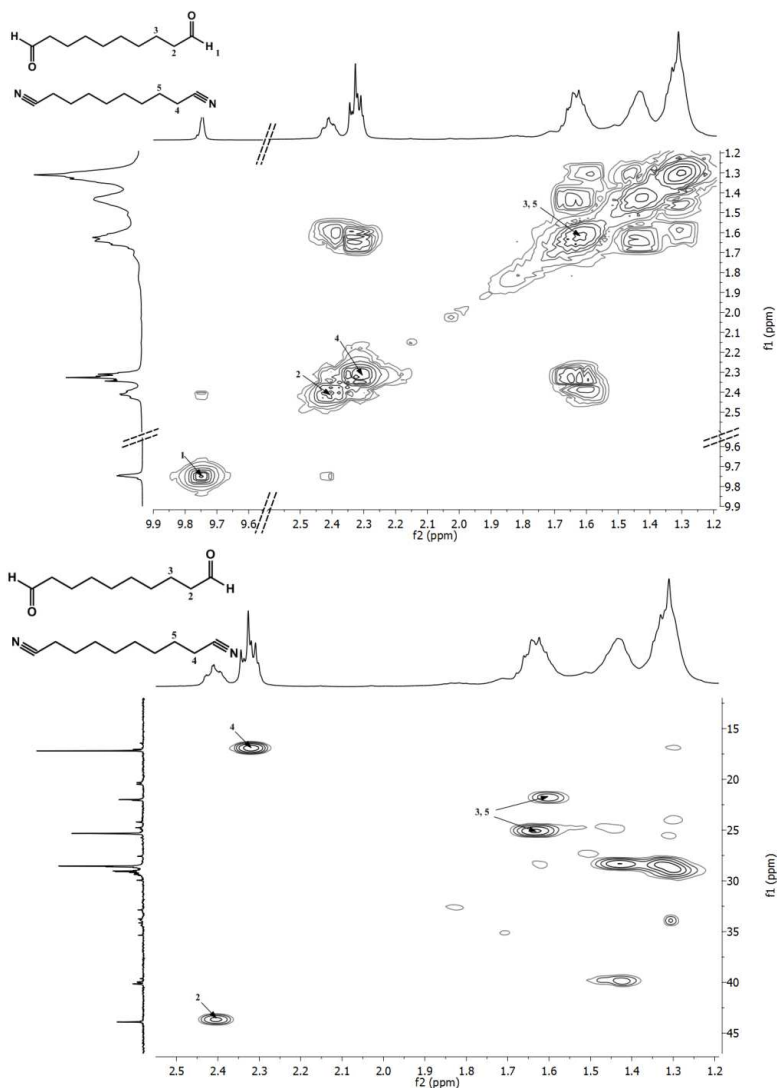
SI Figure II-4-3- All steps FTIR-ATR for the Seb-diamide synthesis. (1) Seb-diacid, (2) Seb-AcylCl and (3) Seb-diamide.



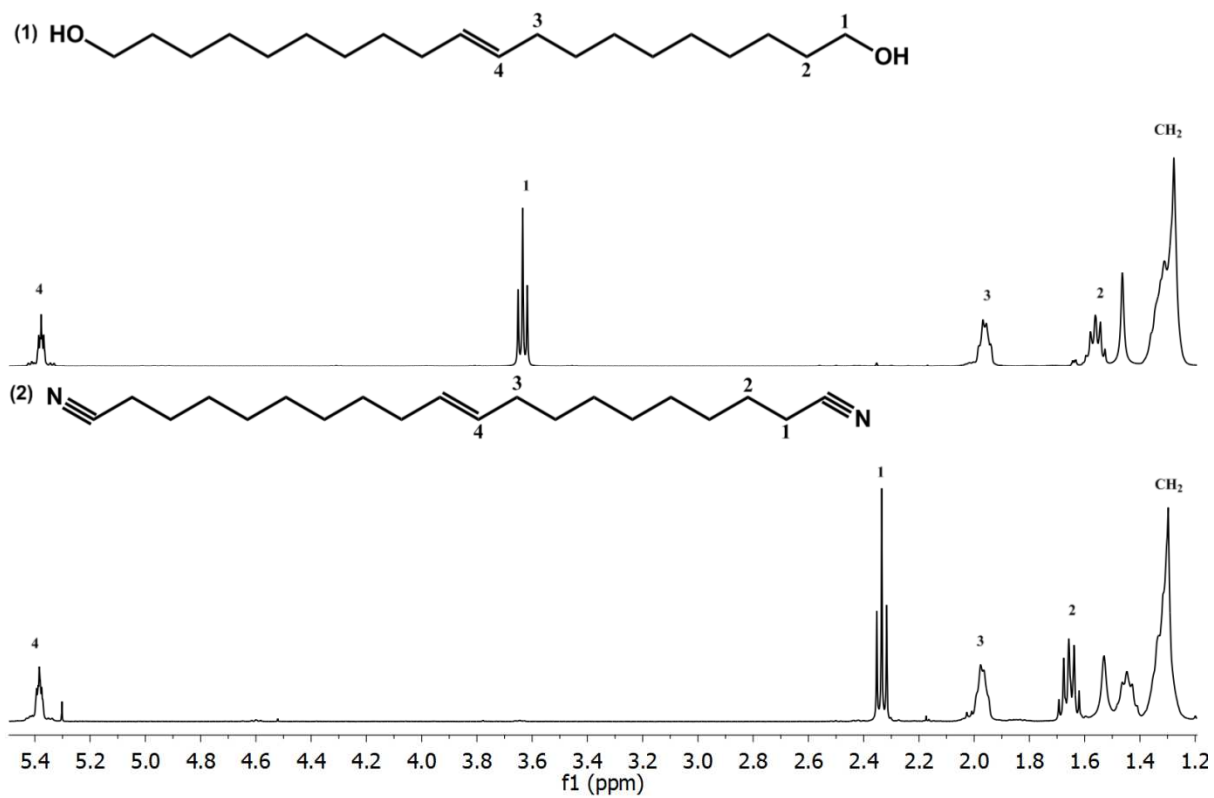
SI Figure II-4-4- All steps ^1H NMR for the UndS-diamide synthesis. (1) UndS-diacid (25°C in CDCl_3), (2) UndS-AcylCl (25°C in CDCl_3) and (3) purified UndS-diamide (50°C in DMSO-d_6).



SI Figure II-4-5- All steps FTIR-ATR for the UndS-diamide synthesis. (1) UndS-diester, (2) UndS-diacid and (3) UndS-diamide.



SI Figure II-4-6 - Presence of aldehyde and nitrile confirmed by ^{13}C - ^{13}C COSY and ^1H - ^{13}C HSQC for the synthesis of nitrile from 1,10-decenediol, under non optimized conditions. (Analyses in CDCl_3)



SI Figure II-4-7- Stacked ^1H NMR of (1) UndC20-diol and (2) UndC20-dinitrile. (Analyses in CDCl_3)

Conclusions and perspectives

As stated in the introduction, the aim of this thesis was the use of vegetable oils as a platform for the design of sustainable and non-isocyanate thermoplastic PUs. Indeed, as a next generation of PUs, some requirements such as bio-based origin and non-isocyanate and non-phosgene synthetic routes may be pointed out from the literature. Castor oil and sunflower oil have been used as unique resources to PU precursors via methyl undecenoate and methyl oleate derivatives. Besides, during this thesis, we fulfill in preparing more sustainable thermoplastic PUs via the synthesis of diols, bis 5- and 6-membered cyclic carbonates and diamines from these fatty acids derivatives. (See Figure C-1)

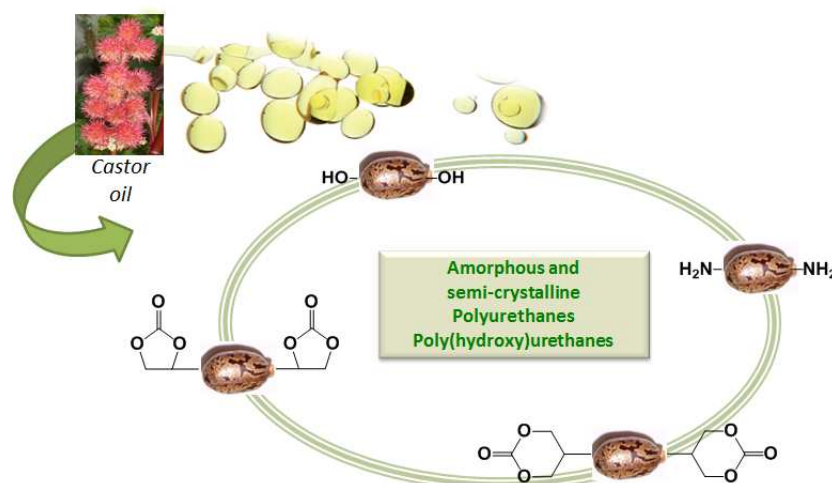


Figure C-1- More sustainable thermoplastic PUs via the synthesis of diols, bis 5- and 6-membered cyclic carbonates and diamines from fatty acids.

In the first part of this manuscript, fatty acid-based diols have been synthesized from methyl undecenoate and methyl oleate by transesterification and/or amidation followed by thiol-ene addition. With the idea of reaching high T_g amorphous to semi-crystalline PUs, amide linkages, which are highly cohesive by hydrogen bonds, have been incorporated. The obtained PUs, by polyaddition of these diols with two diisocyanates (the isophorone diisocyanate (IPDI) and the 4,4'-methylene diphenyl diisocyanate (MDI)), presented a large range of thermo-mechanical properties. The PUs were amorphous to semi-crystalline depending on the chemical structure of the diol and the diisocyanate used. Glass transition temperatures from -27 °C to 63 °C were achieved as well as melting points up to 183°C. Some of the synthesized semi-crystalline PUs presented metastable phases as observed by modulated DSC, AFM and WAXS experiments. Thanks to the amide linkages, a significant

improvement of the Young modulus from 287 MPa to 775 MPa has been carried out. Besides, the organocatalysis of the polyaddition between a fatty acid-based diol and a diisocyanate have been investigated. This study has demonstrated that guanidines such as MTBD enable the preparation of PUs with high molar masses.

However, a major issue in PU chemistry is the high toxicity of its precursors namely the diisocyanate. Thus in the second part of this work, the cyclic carbonate-amine approach has been studied from vegetable oils as a way to solve these toxicity problems. A set of bis 5-membered cyclic carbonates bearing ester and amide moieties has been developed from methyl undecenoate by transesterification or amidation followed by epoxidation and carbonation of the double bonds with CO₂. The use of stable amide groups, rather than ester ones present the interest of limiting the secondary reactions of amidification, reported in the literature while the polyaddition of some bis cyclic carbonates and diamines. Non-isocyanate PHUs have then been synthesized by polyaddition of the prepared bis 5-membered cyclic carbonates and various diamines (isophorone diamine (IPDA), butane-1,4-diamine (4DA), CRODA diamine and Jeffamine 400). Molar masses in the range 11 000 g.mol⁻¹ - 31 000 g.mol⁻¹ have been achieved. The PHUs were amorphous to semi-crystalline with glass transition temperatures and melting points up to 55°C and 115°C respectively. Nevertheless, high temperatures and long polymerization times, as well as bulk conditions, were necessary to reach high conversions.

The low reactivity of the fatty acid-based bis 5-membered cyclic carbonates can be explained by the electron releasing effect of the cyclic carbonate substituents which are in this case alkyl chains. Two of the keys to improve the kinetics of the polyaddition are the catalysis of the cyclic carbonate-amine reaction and the design of more reactive cyclic carbonates such as 6-membered ones. The catalysis of the reaction between propylene carbonate and hexylamine has been investigated. It has demonstrated the efficiency of the bidentate hydrogen bonding Schreiner catalyst at the beginning of the reaction. However, this catalyst doesn't seem active anymore after a certain time, maybe due to the increasing hydrogen bonds density in the reaction medium, which scavenges the hydrogen donor catalyst.

Up to now, the polyaddition rate of cyclic carbonates and amines has been shown to be quite slow compared to the direct isocyanate-alcohol reaction. To circumvent the lack of reactivity of fatty acid bis 5-membered cyclic carbonates, bis 6-membered cyclic carbonates have been synthesized for the first time from vegetable oil derivatives. Firstly a 6-membered cyclic carbonate has been prepared from methyl undecenoate via malonate and 1,3-diol

intermediates. Afterwards, mild condition metathesis reaction and thiol-ene addition were successfully used to couple the 6-membered cyclic carbonate into a bifunctional monomer. The reactivity of the fatty acid-based 6-membered cyclic carbonates has been analyzed in model reaction by comparison with cyclic carbonates displaying different chemical structures. Second order equations permitted a fine correlation with experimental data. The 6-membered cyclic carbonates drew additional interest in terms of reactivity compared to 5-membered ones. For instance reaction rate constants of $1.42 \text{ L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ and $0.55 \text{ L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ for the reaction of hexylamine with trimethylene carbonate and ethylene carbonate respectively were obtained. The presence of side reactions between 6-membered cyclic carbonates and primary alcohols have been evidenced with ESI-TOF MS analyses in certain conditions. Besides, from model reactions at different temperatures, the activation energy of the prepared fatty acid-based 6-membered cyclic carbonate has been estimated to be $20.7 \text{ kJ}\cdot\text{mol}^{-1}$. Afterwards, the bis 6-membered cyclic carbonates have been polymerized with dodecane-1,12-diamine (12DA). Working with less stable 6-membered cyclic carbonates allowed us to obtain non-isocyanate PHUs with molar masses up to $23\,000 \text{ g}\cdot\text{mol}^{-1}$ (dispersity of 1.7) after 24 hours of polymerization in solvent at only 50°C . MALDI-TOF MS analyses highlighted the chemical structure of the so-formed PHUs as well as the formation of unwanted urea during the quenching of the polymers. The obtained PHUs were amorphous with glass transition temperatures between -20°C and 0°C .

In the last part of this thesis, some very promising results have been obtained in the synthesis of fatty acid-based diamines in order to reach fully bio-based and non-isocyanate PUs. Two routes have been envisaged to synthesize diamines from castor oil derivatives such as methyl undecenoate and sebacic acid. The first method involved the preparation of diacyl chlorides then primary diamides from diacids. In the second approach, dinitriles have been prepared from diols using a recently reported mild condition procedure with a copper catalytic system, oxygen as oxidant and aqueous ammonia. Reductions of the formed primary amides and dinitriles led to fatty acid-based diamines. The route via dinitriles turned out to be much more promising due to high efficiency and solubility issue with the primary diamides. Fully bio-based non-isocyanate PHUs have been synthesized using both bis 5- and 6-membered cyclic carbonates in comparable polymerization conditions, allowing a clear comparison of their reactivities.

A plethora of vegetable oils-based PUs precursors have been developed: diols, bis 5- and 6-membered cyclic carbonates as well as diamines. The thermo-mechanical properties have

been modulated by designing the chemical structure of the fatty acid-based monomers. The non-isocyanate PUs synthetic route has been studied in details and applied to renewable resources. The work performed during this thesis allowed the registration of four patents of which three are under writing. A review and an article in the journal "Polymer Chemistry" have also been published. Additional manuscripts are under preparation.

Research perspectives in this subject are numerous. The carbonate/amine reaction produces PU materials avoiding the use of toxic diisocyanates. However, the research to improve the polyaddition kinetic of bis cyclic carbonates and diamines remains an important concern to overcome. Indeed, in isocyanate chemistry, high reactivity even at room temperature can be obtained, which allows fast curing as well as facilitate the preparation of solid foams (chemical reaction rate competes with gas release speed, thus enabling gas trapping). Therefore the development of catalysts, for the curing at room temperature with enhanced selectivity of cyclic carbonate-amine systems, is a challenge that seems unavoidable to industrial growth. Moreover, progress in using more sustainable solvents such as water needs to be further carried out regarding both routes to PUs. Besides, the obtained materials from the cyclic carbonate-amine polyaddition bear hydroxyl groups which impart some specific properties to the non-isocyanates PUs. Nevertheless, too little data is available to accurately compare them to classical PUs notably in terms of thermal and chemical stabilities. Another route could be to explore the use of bis-(dialkyl carbonate)s as recently reported by the group of Hedrick in order to prepare non-isocyanate and "real" PUs.¹ The development of non-isocyanate segmented PUs would also be a great advance. Finally, the production of recyclable and biodegradable PUs by microbial or enzymatic routes can be of further interest to go one step further into sustainable development.²

References

1. H. Sardon, A. Engler, J. M. W. Chan, D. Coady, J. M. O'Brien, D. Mecerreyes, Y.-Y. Yang and J. Hedrick, *Green Chemistry*, 2013, **15**, 1121-1126.
2. S. Matsumura, Y. Soeda and K. Toshima, *Applied Microbiology and Biotechnology*, 2006, **70**, 12-20.

Materials and Measurements

1- Materials

Methyl 10-undecenoate (>96.0%), 2-mercaptoethanol (98%), butane-1,4-diamine (4DA, 99%), dianhydro-D-glucitol (isosorbide, >98%), dodecane-1,12-diamine (12DA, >98%), 1,3-bis[3,5-bis(trifluoromethyl)phenyl]thiourea (Schreiner catalyst, >98%), 1,3-dioxane-2-one (trimethylene carbonate, >98%), 4-(hydroxymethyl)-1,3-dioxolan-2-one (glycerol carbonate, 5CCOH, >90%) and decane-1,10-diamine (10DA, >97%) were supplied by TCI, Europe.

1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%), 1,3-aminopropanol (99%), isophorone diisocyanate (IPDI, 98%), 4,4'-methylene-diphenyl-diisocyanate (MDI, 98%), 2,2'-azobisisobutyronitrile (AIBN, 98%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%), lithium chloride (LiCl, anhydrous >98%), N,N-dimethylformamide (DMF, anhydrous grade), N-Methyl-2-pyrrolidone (NMP), lithium aluminum hydride (LiAlH₄) (95%), sodium hydrate (NaH) (60 % dispersion in mineral oil), ethyl chloroformate (97%), 1,4-butanedithiol (>97%), ethylvinyl ether (99%), Grubbs 2nd and 3rd generation metathesis catalyst, hexylamine (99%), 10-undecenoyl chloride (97%), 3-chloroperbenzoic acid (≤77%), tetrabutylammonium bromide (TBABr, >98%), poly(propylene glycol) bis(2-aminopropyl ether) (Jeffamine, $\bar{M}_n=400$ g.mol⁻¹), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98%), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, 98%), 4-(dimethylamino)pyridine (DMAP, >99%), zinc acetate (ZnAc, 99.99% trace metals basis), ethylene carbonate (5CC, 98%), ammonium hydroxide solution (ACS reagent, 28.0-30.0% NH₃ basis), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 98%), 1-10-decanediol (98%), oleyl alcohol (85%), citronellol (>95%), phytol (97%), Raney[®]-Nickel, slurry in H₂O, active catalyst) and Palladium on carbon (10 wt. % loading, matrix activated carbon support) were obtained from Sigma-Aldrich.

Dibutyl tin dilaurate (DBTDL, 95%), methyl oleate (96%), 1,3-propanediol (99%), dimethyl carbonate (DMC, 99%), triethyl amine (TEA, 99%), piperazine (Pip, anhydrous, 99%), N,N'-dimethylpropane-1,3-diamine (PMe, 97%), sebacyl chloride (97%), 10-undecenoic acid (99%), methyl thioglycolate (98%), oxalyl chloride (98%), 10-undecen-1-ol (99%), copper(I)

iodide (CuI, 98%), 2,2'-bipyridine (bpy, >99%), sebacic acid (>98%), 1,4-butanediol (99%) and 1,2-epoxy-9-decene (96%) were purchased from Alfa Aesar.

The 4-vinyl-1,3-dioxolan-2-one (5CCvinyl, 98%) and thionyl chloride (99.5%) were supplied by ABCR and Acros Organics respectively. Isophorone diamine (IPDA, >99%) and propylene carbonate (5CCMe, 99.5%) were obtained from Fisher. The dimer fatty acid-based diamine (Priamine 1075) was purchased from CRODA.

The catalyst 1-methyl-3-methylimidazolium iodide salt (MMII) was purchased from Solvionic and the 1,5,7-triaza-bicyclo[4.4.0]dec-5-enium bromide (TBD.HBr) was synthesized by our partners from the research group of Landais and coll. (S. Foltran, J. Alsarraf, F. Robert, Y. Landais, E. Cloutet, H. Cramail and T. Tassaing, *Catalysis Science & Technology*, 2013, **3**, 1046-1055.)

All products and solvents (reagent grade) were used as received except otherwise mentioned. The solvents were of reagent grade quality and were purified wherever necessary according to the methods reported in the literature.

2- Measurements

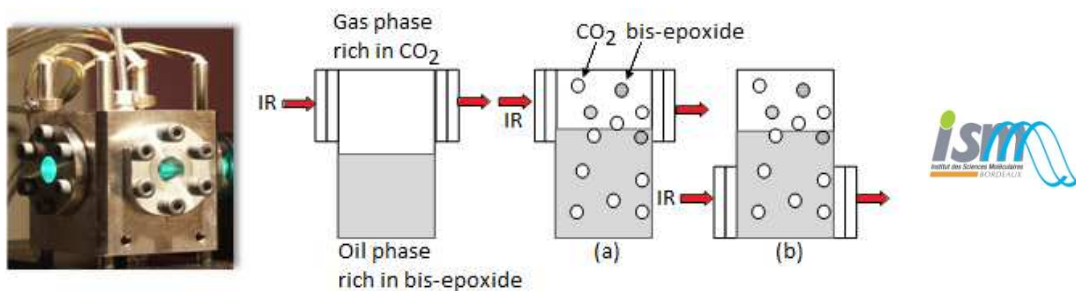
2.1- Nuclear Magnetic Resonance (NMR) analysis

^1H and ^{13}C -NMR spectra were recorded on Bruker Avance 400 spectrometer (400.20 MHz or 400.33 MHz and 100.63 MHz for ^1H and ^{13}C , respectively) by using CDCl_3 as a solvent at room temperature, except otherwise mentioned. Two-dimensional analyses such as ^1H - ^1H COSY (Homocorrelation Spectroscopy) and ^1H - ^{13}C HSQC (Heteronuclear single quantum coherence) were also performed on the monomers.

2.2- Fourier Transformed Infra-Red-Attenuated Total Reflection (FTIR-ATR)

Infrared spectra (FTIR-ATR) were obtained on a Bruker-Tensor 27 spectrometer, equipped with a diamond crystal, using the attenuated total reflection mode. The spectra were acquired using 16 scans at a resolution of 4 wavenumbers.

2.3- Kinetic experiments monitored by in-situ FTIR of the carbonation reaction (ISM)



The in situ infrared absorption measurements were performed at the *Institut des Sciences moléculaires (ISM)* on a Biorad interferometer (type FTS-60A) equipped with a globar as the infrared source, a KBr/Ge beam splitter and a DTGS (deuterated triglycine sulfate) detector in order to investigate the spectral range 400–6000 cm^{-1} . Single beam spectra recorded with a 2 cm^{-1} resolution were obtained after the Fourier transformation of 50 accumulated interferograms. The kinetic studies of the carbonation reaction were performed using the ISM home-made stainless steel cell equipped with two cylindrical germanium windows with a path length of 100 mm in order to measure the infrared spectra in the wavenumber range extending from 700 to 5000 cm^{-1} . Heating was achieved by using four cartridge heaters distributed throughout the body of the cell. Two thermocouples were used, the first one located close to a cartridge heater for the temperature regulation and the second one close to the sample area to measure the temperature of the sample with an accuracy of about 2°C. The cell was connected *via* a stainless steel capillary to a hydraulic pressurizing system which allows the pressure to be raised up to 50 MPa with an absolute uncertainty of ± 0.1 MPa and a relative error of $\pm 0.3\%$.

2.4- Gas chromatography (GC-FID)

The gas chromatography analyses (GC) were performed by *Iteq* using a Shimadzu GC equipped with: Flame ionization detectors (FID, 380 °C) and Zebron ZB-5HT (5% phenyl - 95% dimethylpolysiloxane) 15 m x 0.25 mm ID, 0.1 μm thickness capillary column. The carrier gas was hydrogen. The column temperature was initially set at 60 °C (volume injected: 1 μl), then increased to 370 °C at a rate of 10 °C. min^{-1} and held isothermally for 10 min.

2.5- Size exclusion chromatography (SEC)

Size exclusion chromatography (SEC) analyses were performed in THF (40°C) on a PL-GPC 50 plus Integrated GPC from Polymer laboratories-Varian with a series of four columns from TOSOH (TSKgel TOSOH: HXL-L (guard column 6.0 mm ID x 4.0 cm L); G4000HXL (7.8 mm ID x 30.0 cm L); G3000HXL (7.8 mm ID x 30.0 cm L) and G2000HXL (7.8 mm ID x 30.0 cm L)) for monomers.

SEC analyses of PUs were performed in DMF (80°C) on a PL-GPC 50 plus Integrated GPC from Polymer laboratories-Varian with a series of three columns from Polymer Laboratories (PLgel: PLgel 5 μ m Guard (guard column 7.5 mm ID x 5.0 cm L); PLgel 5 μ m MIXED-D (7.5 mm ID x 30.0 cm L) and PLgel 5 μ m MIXED-D (7.5 mm ID x 30.0 cm L)). In both cases, the elution times of the filtered samples were monitored using RI detectors.

2.6- Differential Scanning Calorimetry (DSC) and modulated Differential Scanning Calorimetry (ModDSC)

Differential scanning calorimetry (DSC) thermograms were measured using a DSC Q100 apparatus from TA instruments. For each sample, two cycles from -50 to 160 °C (or 200 °C for higher melting point polyurethanes) at 10 °C.min⁻¹ were performed and then the glass transition and crystallization temperatures were calculated from the second heating run. Some semi-crystalline polymer samples were also analyzed with modulated DSC (ModDSC) in a temperature window depending on the T_g and T_m at a rate of 2 °C.min⁻¹ with a modulation amplitude of 0.64 °C and a modulation period of 60 s.

2.7- Thermogravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were performed on TGA-Q50 system from TA instruments at a heating rate of 10 °C.min⁻¹ under nitrogen atmosphere from room temperature to 600°C.

2.8- Dynamic Mechanical Analysis (DMA) and Tensile tests

The PUs viscoelastic properties were recorded by dynamical mechanical analysis (DMA) with RSA-III apparatus from TA Instruments equipped with a liquid nitrogen cooling system. Forced strain was used on cylindrical compression geometry at a frequency of 1 Hz, a strain of 0.1% and a temperature monitoring between T_g -50 °C and T_g +50 °C or T_m +15 °C at a rate of 5 °C.min⁻¹. The values of the Young's modulus E, ultimate strength and strain at break were obtained from uniaxial traction measurements using a Dynamic Mechanical Analysis

(RSA-III from TA Instruments) in a transient mode (Static Mode). The experiments were performed using a crosshead speed of $0.05 \text{ mm}\cdot\text{s}^{-1}$ and a load cell of 35 N sensitivity (force resolution: 1 mN). After adjusting the parameters, experiments were carried out 5 times for each sample. Tensile tests were performed on PUs processed into films using a simple hot-press technique and annealed at their corresponding crystallization temperatures.

2.9- X-Ray diffraction

X-ray diffraction patterns at wide angles (WAXS) were obtained by Marie-France Achard from the *Centre de Recherche Paul Pascal (CRPP)* with a microfocus rotating anode X-ray source (Rigaku MicroMax-007 HF) combined with performant multi-layers optics and a 3-pinholes collimation that provide an intense X-ray intensity on the sample. The sample, mounted on X-Y stage, was held in a Lindemann capillary and placed in an oven providing a temperature control of 0.1 K. A 2-dimensionnal detector (Image plate from Mar Research) was collecting the scattered radiations. Calibration of the sample-detector distance was performed using silver behenate as reference.

2.10- Atomic Force Microscopy (AFM)

AFM measurements were performed progressively at different temperatures (20, 65, 70, 75, 85 and 110°C) using a Veeco Dimension Icon AFM system equipped with a Nanoscope V controller. Both topographic and phase images of sample films were obtained in Tapping Mode using a rectangular silicon cantilever (AC 160-TS, Atomic Force, Germany) with a spring constant of 26 N m^{-1} , a resonance frequency lying in the 270-320 kHz range and a radius of curvature of less than 10 nm. Samples were prepared by solvent casting at ambient temperature from dilute solutions. Freshly cleaved mica pieces were placed in a spin-coating apparatus (G3P-8 Spin Coater, PI-Kem, UK) and excess solvent was removed by spinning for 300 s at an angular rotation of 500 rpm.

2.11- Optical microscopy

Optical images were obtained using an Axioskop 40 Zeiss polarizing microscope equipped with a digital camera (Canon Powershot A640) connected to the computer. The spherulite morphology was observed in thin films prepared between microscope coverslips

2.12- Time-of-flight mass spectrometer with electrospray ionization (ESI-TOF MS)

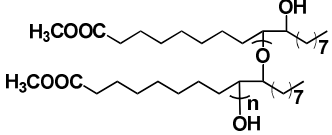
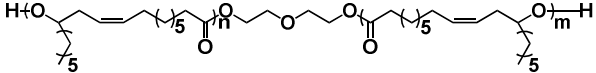
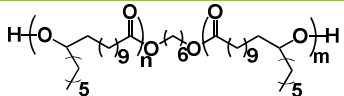
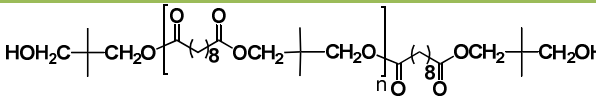
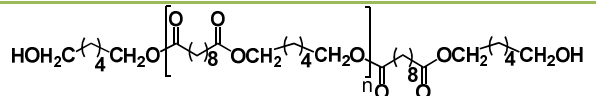
Mass spectra were performed by the *Centre d'Etude Structurale et d'Analyse des Molécules Organiques (CESAMO)* on a QStar Elite mass spectrometer (Applied Biosystems). The instrument is equipped with an ESI source and spectra were recorded in the negative/positive mode. The electrospray needle was maintained at 4500 V and operated at room temperature. Samples were introduced by injection through a 20 μ L sample loop into a 400 μ L/min flow of methanol from the LC pump. Samples were dissolved in THF at 1 mg/ml, and then 10 μ l of this solution was diluted in 1 ml of methanol.

2.13- Time-of-flight mass spectrometer with matrix-assisted laser desorption/ionization (MALDI-TOF MS)

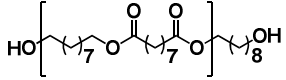
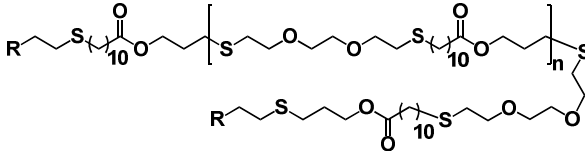
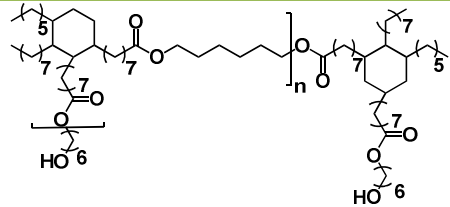
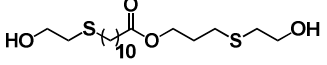
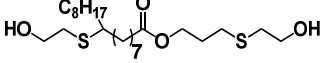
MALDI-MS spectra were performed by the *Centre d'Etude Structurale et d'Analyse des Molécules Organiques (CESAMO)* on a Voyager mass spectrometer (Applied Biosystems). The instrument is equipped with a pulsed N₂ laser (337 nm) and a time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron and with an accelerating voltage of 20 kV.

Samples were dissolved DMF at 10 mg/ml. The IAA matrix (trans-3-Indoleacrylic acid) solution was prepared by dissolving 10 mg in 1 ml of DMF. A methanol solution of cationisation agent (NaI, 10 mg/ml) was also prepared. The solutions were combined in a 10:1:1 volume ratio of matrix to sample to cationisation agent. One to two microliters of the obtained solution was deposited onto the sample target and vacuum-dried.

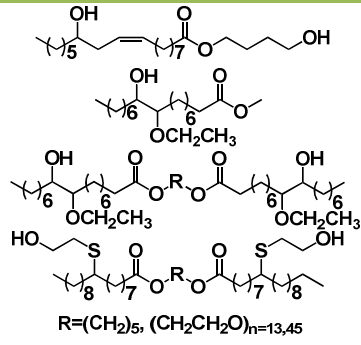
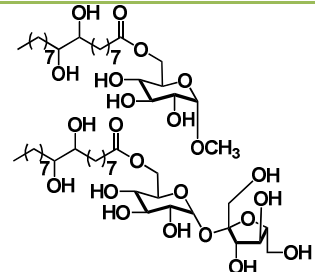
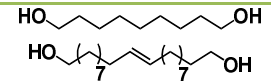
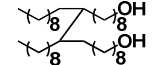
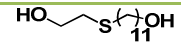
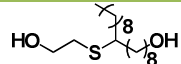
Table A-1- Summarized literature concerning fatty acid based precursors for thermoplastic polyurethanes.

Monomer 1	Monomer 2	\bar{M}_n (g.mol ⁻¹)	T _g	T _m	Comments	Ref.
 <p style="text-align: center;">2580g.mol⁻¹</p> <p style="text-align: center;">and 1,4-butanediol with SSC form 40% to 70%</p>	MDI	-	-15°C	-	T _{5%} =307°C	1 2006 (Lligadas et al.)
 <p style="text-align: center;">2580g.mol⁻¹</p> <p style="text-align: center;">and 1,4-butanediol with SSC form 40% to 70%</p>	MDI	ns (40%SSC) ⁽¹⁾ 23 400 (50%SSC) ⁽¹⁾ 21 500 (60%SSC) ⁽¹⁾ 14 850 (70%SSC) ⁽¹⁾	from -71°C to -56°C (SS) and from 65°C to 115°C (HS)	from 170°C to 220°C (HS)	- TPE-U - presence of "spherulitic-like" superstructures - faster degradation rates than the corresponding petrochemical poly(ester urethane)s	2-4 2008 (Xu et al.)
 <p style="text-align: center;">1552g.mol⁻¹</p> <p style="text-align: center;">and 1,4-butanediol with SSC of 50% and 70%</p>	MDI	27 000 (50%SSC) ⁽¹⁾ 19 700 (70%SSC) ⁽¹⁾	-40°C / -39°C (SS) and 100°C (HS)	-18°C / -14°C (SS) and 175°C / 180°C (HS)		5 2010 (Omprakash et al.)
 <p style="text-align: center;">1320g.mol⁻¹</p> <p style="text-align: center;">and 1,3-propanediol with SSC from 54% to 83%</p>	HMDI	71 100 (83%SSC) ^(nr) 73 100 (75%SSC) ^(nr) 56 300 (68%SSC) ^(nr) 48 500 (61%SSC) ^(nr) 39 200 (54%SSC) ^(nr)	below 0°C (SS) and between 40°C and 60°C (HS)	between 40°C and 60°C (SS) and around 150°C (HS)	- TPE-U	6 2012 (Saralegi et al.)
 <p style="text-align: center;">1900g.mol⁻¹ and 3500g.mol⁻¹</p> <p style="text-align: center;">and 1,3-propanediol</p>	HMDI	74 500 and 63 400 (83%SSC) ^(nr) 76 200 and 63 400 (75%SSC) ^(nr) 35 700 and 64 100 (68%SSC) ^(nr) 31 700 and 59 700 (61%SSC) ^(nr) 34 350 and 42 100 (54%SSC) ^(nr)	below 0°C (SS) and between 40°C and 60°C (HS)	between 40°C and 60°C (SS) and around 150°C (HS)		6 2012 (Saralegi et al.)

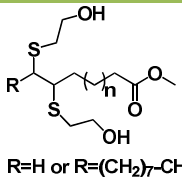
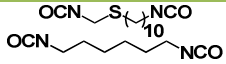
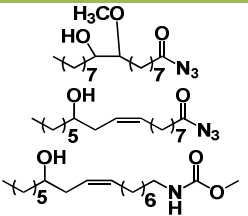
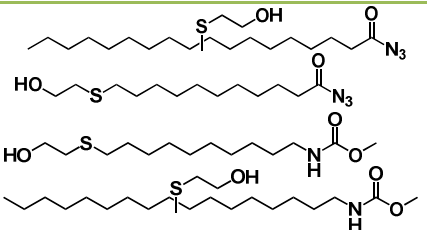
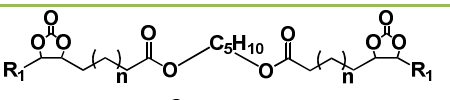
Appendix: PART I - Chapter 1

 <p>azealic acid + 1,9-nonanediol polyesters from 534g.mol⁻¹ to 1488g.mol⁻¹</p>	HPMDI	from 17 000 to 27 000 ⁽²⁾	-28°C or not visible in DSC	from 54°C to 71°C	HPMDI : fatty acid based diisocyanate	7 2012 (Hojabri et al.)
 <p>R=OH, COOH, CH₂-Si(OCH₃)₃ 3100g.mol⁻¹ and 1,4-butanediol</p>	MDI	-	-45°C (SS) and 55°C (HS)	-9°C (SS) and 190°C (HS)		8 2010 (Lluch et al.)
 <p>3000g.mol⁻¹ and 1,4-butanediol with SSC from 60% to 90%</p>	MDI	38 000 (90%SSC) ⁽²⁾ 28 300 (80%SSC) ⁽²⁾ 25 400 (70%SSC) ⁽²⁾ 14 700 (60%SSC) ⁽²⁾	from -51.3°C to -47.8°C(SS) and from 118.1°C to 122.8°C (HS)	not clearly observable in DSC curves but around 200°C		9 2012 (Bueno-Ferrer et al.)
	MDI	50 900 and 71 200 ⁽¹⁾	20°C	124°C	Promising materials for biomedical purposes thanks to good thermal and mechanical properties as well as no cytotoxic response for MTT testes	10 2011 (Gonzalez-Paz et al.)
	MDI	61 900 ⁽¹⁾	8°C	-	Promising materials for biomedical purposes thanks to good thermal and mechanical properties as well as no cytotoxic response for MTT testes	10 2011 (Gonzalez-Paz et al.)

Appendix: PART I - Chapter 1

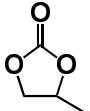

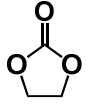
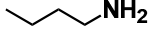
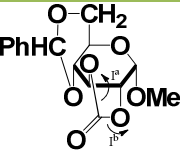
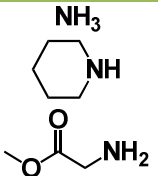
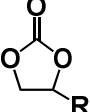
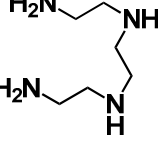
 <p>R=(CH₂)₅, (CH₂CH₂O)_{n=13,45}</p>	IPDI	from 2400 to 18 700 ⁽¹⁾	-49°C to -11.5°C	-		11-13 2012 (Palaskar et al.)
 <p>Sugar lipid based fatty acid polyols</p>	IPDI	5700 to 32000 ⁽³⁾	35°C to 149°C	-		14 2012 (Boyer et al.)
 <p>and 1,9-nonanediol</p>	HMDI and HPMDI	38 000 and 41 000 ⁽⁴⁾	-5.6°C and 0.3°C	101.9°C and 126.7°C	1,7-heptamethylene diisocyanate : fatty acid based diisocyanate	15, 16 2010 (Hojabri et al.)
 <p>Dimer diol idealized structure</p> <p>1000 to 2000g.mol⁻¹</p>					commercially available	17 2000 (Hill et al.)
	MDI	83 300 ⁽¹⁾	56°C	115°C and 141°C		10
	MDI	36 300 ⁽¹⁾	28°C	104°C		10 2011 (Gonzalez-Paz et al.)

Appendix: PART I - Chapter 1

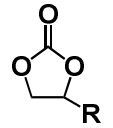
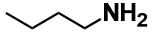
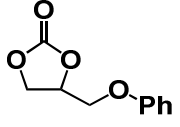
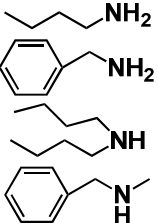
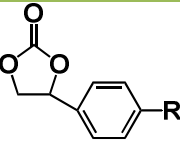
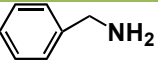
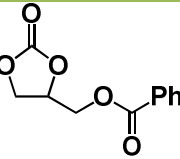
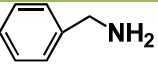
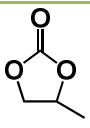
 <p>R=H or R=(CH₂)₇-CH₃</p>	MDI	18 200 and 48 200 ⁽¹⁾	15°C and 20°C	-	Triol monomer can also been obtained after reduction of the ester function	18 2012 (Gonzalez-Paz et al.)
	Aliphatic, cycloalliphatic, fatty acid based diols	from 7 900 to 26 000 ⁽³⁾	from -42.2°C to 162.5°C	from 45.1 to 171.4°C	Fatty acid based diisocyanates using Curtius rearrangement without the use of sodium azide	19 2013 (More et al.)
	Up to 8 900 ⁽¹⁾	from -22°C to -53°C (SS) and around 26°C (HS)	-	Macrocycles formation	20 2010 (Palaskar et al.)	
	Up to 11 800 ⁽¹⁾	from -44.5°C to -7.7 (SS) and from 25.3°C to 78.6°C (HS)	not or from 93.4°C to 116.2°C	- Preparation of copolymers - Macrocycles formation	21, 22 2012 (More et al.)	
 <p>R₁=C₈H₁₇ or R₁=H</p>	EDA, IPDA	from 3 900 to 9 000 ⁽¹⁾	from -25°C to -13°C	-	Side reaction of amide formation with EDA only	23, 24 2010 (Boyer et al.)

SEC in THF⁽¹⁾, chloroform⁽²⁾, DMF⁽³⁾, chloroform/DMSO (1:1)⁽⁴⁾ or not referenced^(nr) with PS standards; T_g determined by DSC or DMA; SSC and HSC are the acronyms for soft and hard segment content; SS and HS are the acronyms for soft and hard segment; MDI=4,4'-diisocyanate de diphenylméthylène; IPDI=Isophorone diisocyanate; HMDI=1,6-hexaméthylène diisocyanate, HPMDI=1,7-heptaméthylène diisocyanate; IDPA=isophorone diamine; EDA=ethylene diamine.

Table A-2- Summarized literature on cyclic carbonates / amines model reactions.

Cyclic carbonates	Amines	Reaction conditions & Mechanism	Kinetic data	Cyclic carbonate effect	Amine effect	Isomers	Side reaction / Observations	Ref.
						I:30% II:70%		²⁵ 1957 (Baizer et al.)
			$-dC/dt=k[A][CC][A]_0^{1.5}$ k increase with $[A]_0$ Final product increase k		Primary amines more reactive than secondary			1963 (Tabushi et al.)
		$k_{protic} > k_{aprotic}$ -In aprotic solvent: k increase if ϵ_r increase & in aprotic solvent: k increase if ϵ_r decrease		- Substituent -I on CC decrease reaction rate				1983 (Micheew et al.)
								1988 (Stroganow et al.)
		- DMF, 50°C, 0.2-1.2 mol.L ⁻¹ - Reaction rate increase with $C_0=[A]_0=[CC]_0$	- 2 nd order - Little catalyzed by the final product $-dC/dt=k_2[A][CC]$ $k_2=k_2'.C_0$ where $C_0=[A]_0=[CC]_0$					²⁶ 1967 (Nemirovsky et al.)
					- Influence the isomers ratio	I ^a :60-64% I ^b :36-40%		^{27, 28} 1967-1969 (Stout et al. and Doane et al.)
 R=-CH ₂ OC ₄ H ₉ , -CH ₂ -CH=CH ₂ , -Ph					- Secondary amines less reactive		- OH increase viscosity by intra ant inter H-bonds	²⁹ 1989 (Rokicki et al.)

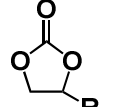
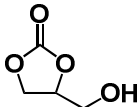
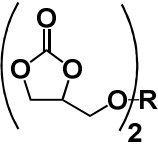
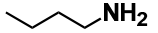
Appendix: PART II - Chapter 1

 <p>R=CH₂OH, -CH₃, CH₂OCOCH₃</p>		- DCM, 60°C, 0.5 mol.L ⁻¹ - Faster reaction without solvent: k between butylamine and glycerol carbonate are equivalent in DCM at 60 °C and without solvent at 25 °C	- 2 nd order - k _{CH₂OH} =1.67 L.mol ⁻¹ .h ⁻¹ ; k _{CH₃} =0.95 L.mol ⁻¹ .h ⁻¹ and k _{CH₂OCOCH₃} =1.83 L.mol ⁻¹ .h ⁻¹ (in DCM at 60°C) - k _{CH₂OH} =1.17 L.mol ⁻¹ .h ⁻¹ ; k _{CH₃} =0.46 L.mol ⁻¹ .h ⁻¹ (without solvent at 25°C)	- Limited influence of R on k - R affect the isomers ratio		I:35-53% II:47-65%		³⁰ 1990 (Couvret et al.)
		- Anisol or toluene, T>50°C, 0.8 to 1.6 mol.L ⁻¹ - Reaction rate increase with the initial concentration	- Uncatalyzed + autocatalyzed (with OH) -dC/dt=k ₁ [A] ^p [CC]+ k ₂ [A] ^q [CC][OH] with [OH] the concentration of the product+initial concentration of OH -P=2.5 / 3 and q=2 (toluene) - k _{1/2} Butylamine=0.0065 / 0.11 L ^{2.5} .mol ^{-2.5} .min ⁻¹ and k _{1/2} Benzylamine=0.0006 / 0.035 L ^{2.5} .mol ⁻¹ min ⁻¹ (in toluene at 65°C, with p=2.5)		- Almost no reaction with secondary amines - Butyl amine more reactive than benzyl amine	I:25% II:75%	- For T>100°C formation of urea with tertiary amines (mecha- nism)	^{31, 32} 1991/1993 (Burgel et al.)
 <p>R= -H (A); -NO₂ (B); -CH₃ (C)</p>		RT, 1h		- R substituant influence isomers ratio		ratio I/II for (C):46/54 (A):41/59 (B):23/77		³³ 2000 (Iwasaki et al.)
		DCM, RT, 1.4 mol.L ⁻¹ , 3d				I:18% II:82% ΔH _{f-I} =-8.1 kcal.mol ⁻¹ ΔH _{f-II} =-9.8 kcal.mol ⁻¹	- No amidation side reaction with the ester function	³⁴ 2000 (Steblyanko et al.)
	large range (17) of primary, secondary mono- di- tri-amines, aliphatic, cyclic or with other functional groups	Propylene glycol monomethyl ether, 80°C, 0.5mol.L ⁻¹ , 14h			- Primary amines more reactive than secondary - k depend on Nu and steric hindrance			³⁵ 2000 (Webster et al.)

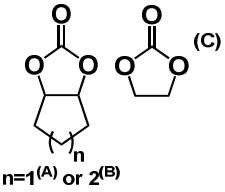
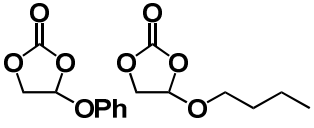
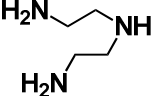
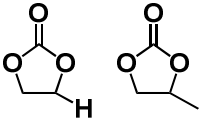
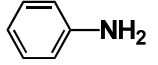
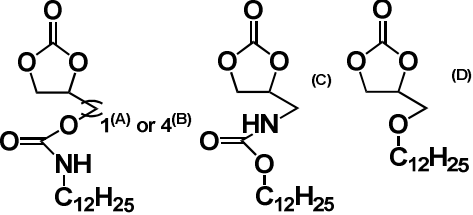
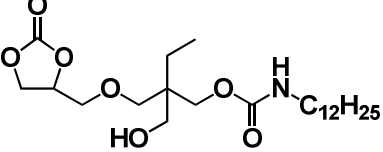
Appendix: PART II - Chapter 1

<p>(A) and (A') are 5-membered cyclic acetals with a vinyl group. (B) and (B') are 6-membered cyclic acetals with a vinyl group.</p>	$C_6H_{13}-NH_2$ 	DMAC, 30-50-70°C, 1 mol.L ⁻¹	- 2 nd order - dC/dt=k ₂ [A][CC] - At 50°C with hexylamine: k _(B) =1.49 L.mol ⁻¹ .h ⁻¹ > k _(A) =0.04 L.mol ⁻¹ .h ⁻¹ - At 50°C with benzylamine: k _(B) =0.29 L.mol ⁻¹ .h ⁻¹ > k _(A) =0.01 L.mol ⁻¹ .h ⁻¹ - With hexylamine: E _{a-(A)} =5.88 kcal.mol ⁻¹ > E _{a-(B)} =2.42 kcal.mol ⁻¹ - k _(B) 29 to 62 times higher than k _(A) (30-70°C)	- (B) more reactive than (A) - The ring-strain energy of 6CC was 2.86 kcal.mol ⁻¹ larger than that of 5CC: (ΔH _{f-(A)})=-1.14 kcal.mol ⁻¹ and ΔH _{f-(B)} =-4.00 kcal.mol ⁻¹	- Hexylamine pKa=10.56 more reactive than benzylamine pKa=9.33 - importance of basicity and steric hindrance		36 2000 (Tomita et al.)
	$C_6H_{13}-NH_2$ 	- Toluene or DMSO, 30-70°C, 0.5mol.L ⁻¹ , 30-40d - Solvent influence the isomers ratio (less II OH in DMSO than in toluene) - CONV _{DMSO} <CONV _{toluene}			- Influence the isomers ratio (less II OH with benzylamine than with hexylamine)	I:15-21% II:79-85%	37 2001 (Tomita et al.)
<p>R=-CF₃, -CH₂OPh, -Ph, -H, -CH₃</p>	$C_6H_{13}-NH_2$ 	- Toluene or DMSO, 70°C, 1 mol.L ⁻¹ , 1h-50d - Very slight better conv and Y for toluene compared to DMSO - Mechanism proposed	- 2 nd order - k _{CF₃} =64 L.mol ⁻¹ .h ⁻¹ > k _{CH₂OPh} =0.42 L.mol ⁻¹ .h ⁻¹ > k _{Ph} =0.38 L.mol ⁻¹ .h ⁻¹ > k _H =0.23 L.mol ⁻¹ .h ⁻¹ > k _{CH₃} =0.05 L.mol ⁻¹ .h ⁻¹ (in DMSO)	- k increase with the inductive effect of R - With R=-CH ₃ , conv=75% after 50d - A closer substituent is inductively more effective than a further one		- Increase of inductive effect R ₁ => difference of the bond order (L ^I -L ^{II}) increase & Y, conv, k and II:I ratio increase	38 2001 (Tomita et al.)
	$C_6H_{13}-NH_2$ 	DMSO, 30-50-70°C, 0.1-1 mol.L ⁻¹	- 2 nd order - k not calculated at 50°C and 70°C because 7CC to reactive - At 30°C with hexylamine (0.1mol.L ⁻¹) : k=48.5 L.mol ⁻¹ .h ⁻¹	- 7CC more reactive than 6CC and 5CC	- Hexylamine more reactive than benzylamine	I ^a :I ^b ≈50/50%	39 2001 (Tomita et al.)

Appendix: PART II - Chapter 1

 <p> $R_1 = \text{H}, -\text{CH}_3,$ $-\text{CH}_2\text{OC}_4\text{H}_9,$ $-\text{CH}_2\text{OPh}$ </p>	$\begin{array}{c} \text{H} \\ \\ \text{R}_2 - \text{N} - \text{R}_3 \\ \\ \text{R}_2 / \text{R}_3 = \\ -\text{H} / -\text{CH}_3, \\ -\text{CH}_3 / \text{CH}_3, \\ -\text{H} / \text{C}_2\text{H}_4\text{OH}, \\ -\text{C}_4\text{H}_9 / \text{C}_4\text{H}_9, \\ -\text{H} / \text{C}_8\text{H}_{17}, \\ -\text{H} / \text{C}_6\text{H}_{11} \end{array}$	<ul style="list-style-type: none"> - Aprotic solvents (toluene, DMF, DMSO) : k increase with the permittivity (ϵ_r) - Protic solvents (various alcohols) : k decrease with the permittivity (ϵ_r) / effect of H bonds - 50-90°C, 1 mol.L⁻¹ - Mechanism proposed in 3 steps 	<ul style="list-style-type: none"> - Overall 2nd order (aprotic solvents) - Overall 3rd order with 2nd order with respect to the amine (protic solvents) 	<ul style="list-style-type: none"> - R₁ affect the isomers ratio - Electron-releasing R₁ decrease the reactivity of the CC - Electron-withdrawing R₁ increase the reactivity of the CC 	<ul style="list-style-type: none"> - R₂ and R₃ volumes affect the isomers ratio - Secondary amines less reactive - k increase with higher nucleophilicity of the amine 			⁴⁰ 2003 (Garipov et al.)
	$\text{C}_6\text{H}_{13}\text{-NH}_2$	- DMSO, 1.2 mol.L ⁻¹ , RT				I:47% II:53%		⁴¹ 2004 (Ubaghs et al.)
Laprolate-803 (aliphatic tricyclic carbonate)	11 various amines: primary with ether linkages or internal secondary amines	-bulk, RT			<ul style="list-style-type: none"> - Aliphatic amines with no α / β substituents more reactive - Lower \bar{M}_n amines more reactive - Primary amines activated by secondary amines in β 		Test of various catalysts	⁴² 2004 (Diakoumakos et al.)
 <p> (A) $\text{R} = \text{-Ph-Ph-}$ (B) $\text{R} = \text{-(CH}_2\text{)}_4\text{-}$ </p>		Water, 1mol.L ⁻¹ , 70°C, 24 h					Hydrolysis of the CC: hydroxyurethane : diol = 84 : 16 (A) but quant. hydrolysis for (B) due to different hydrophobicity of the CC	⁴³ 2005 (Ochiai et al.)

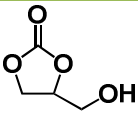
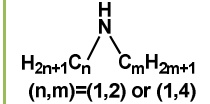
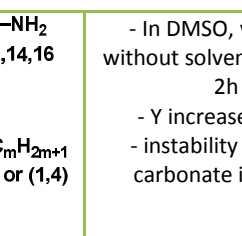

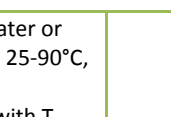
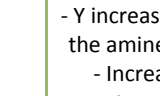
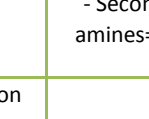
Appendix: PART II - Chapter 1

 <p>$n=1^{(A)}$ or $2^{(B)}$</p>	$C_6H_{13}-NH_2$	No solvent or DMAC, 70°C, 2mol.L ⁻¹ , 110h	$k_{(C)} > k_{(B)} = 0.0132 \text{ L.mol}^{-1} \cdot \text{h}^{-1}$ $> k_{(A)} = 0.0059 \text{ L.mol}^{-1} \cdot \text{h}^{-1}$	- (B) more reactive than (A) - $Y_{(A)} = 54\%$ and $Y_{(B)} = 82\%$ - $E_{a-(A)} = 29.9 \text{ kcal.mol}^{-1}$ and $E_{a-(B)} = 22.4 \text{ kcal.mol}^{-1}$			44 2005 (Ochiai et al.)
 <p>2 or 3eq</p>		chloroform, 30°C, or DMSO 100°C, or bulk 170°C, 24h			Pseudo-diamine to PHU bearing a secondary amine: with 2/1eq 100% conv CC but for 3/1eq, only 66% conv CC for T<100°C and 76-86% conv or T=170°C		45 2005 (Ochiai et al.)
						hydroxyalkylation of aniline over it acylation using i) zeolites ii) phosphonium-based ionic liquids	46 2010 (Selva et al.)
 <p>$1^{(A)}$ or $4^{(B)}$</p>	$C_6H_{13}-NH_2$	DMSO, RT, 0.5 mol.L ⁻¹	- 2 nd order : $k_{(C)} = 0.204 \text{ L.mol}^{-1} \cdot \text{h}^{-1} > k_{(A)} = 0.124 \text{ L.mol}^{-1} \cdot \text{h}^{-1} > k_{(D)} = 0.057 \text{ L.mol}^{-1} \cdot \text{h}^{-1} > k_{(B)} = 0.018 \text{ L.mol}^{-1} \cdot \text{h}^{-1}$	- (A) with the urethane function in α position to the CC more reactive than (B) - (C) more reactive than (A)			47 2010 (He et al.)
	$C_{12}H_{25}-NH_2$ 1.1 eq.	Ethyl acetate, 60°C, 24h				I:18% II:82%	48 2011 (He et al.)

Appendix: PART II - Chapter 1

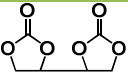
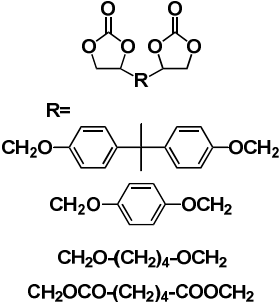
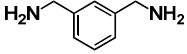
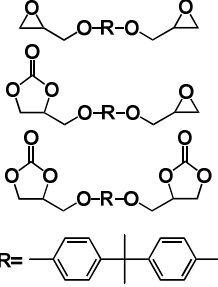
	<p>C₁₂H₂₅-NH₂ Jeffamine M1000</p>	- THF, 2.6-3.3 mol.L ⁻¹ , RT, 18h - Ethyl acetate, 2 mol.L ⁻¹ , 60°C, 18h		- different reactivity 5CC & 6CC toward amines - THF, RT, dodecylamine: only 6CC reacts - Ethyl acetate, 60°C, dodecylamine: 5CC and 6CC react			
		DMSO:water=3:2, 72 mmol.L ⁻¹				Hydrolysis CC - RT, 20d: 5CC=0% & 6CC=15% - 60°C, 7d: 5CC=0% & 6CC=40% - 90°C, 7d: 5CC=0% & 6CC=100%	
	<p>C₈H₁₇-NH₂ 2 eq.</p>	Bulk, 80°C, no cat. or LiBr	Quantitative conversion after 21h without cat but quantitative conversion after 2h with LiBr				⁴⁹ 2011 (Tang et al.)
		Bulk, RT, 50°C, 70°C, 100°C - 100°C, 24h, Y=99%					⁵⁰ 2012 (Bahr et al.)
						- Intra molecular etherification study of 5CC bearing OH groups	^{51, 52} 2012 (Tomczyk et al.)

Appendix: PART II - Chapter 1

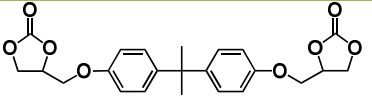
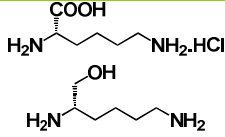
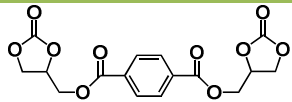
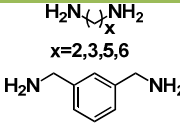
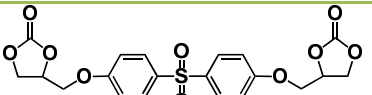
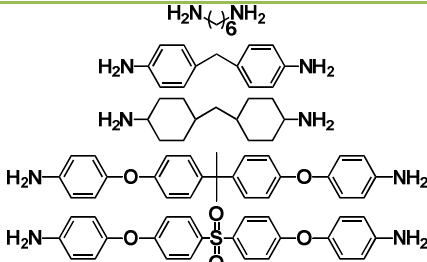
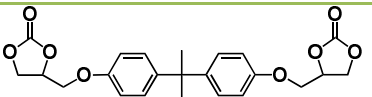
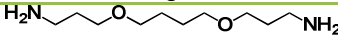
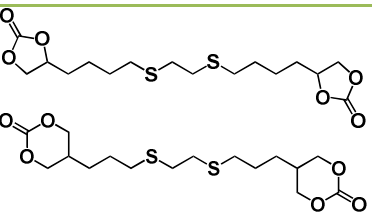
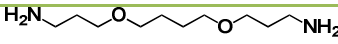
	$\text{H}_{2n+1}\text{C}_n\text{—NH}_2$ $n=4,6,8,12,14,16$  $(n,m)=(1,2) \text{ or } (1,4)$	<ul style="list-style-type: none"> - In DMSO, water or without solvent, 25-90°C, 2h - Y increase with T - instability of cyclic carbonate in water 			<ul style="list-style-type: none"> - Y increase with the amine / CC - Increase amine alkyl chain = Y decrease & ratio I:II increase - Secondary amines => I≈II 	I:35% II:65% (no solvent, 50°C, octyl-amine)	<ul style="list-style-type: none"> - By-product =glycerol (quantity increase with water, primary and short amines link to a decrease of I:II) 	53 2012 (Nohra et al.)
		80°C, 1h		<ul style="list-style-type: none"> - Faster reaction with (B) compared to (A) 				54 2012 (Nohra et al.)
	$\text{H}_3\text{C—NH}_2$	<ul style="list-style-type: none"> -DFT calculations => one-stage and multistage paths mechanisms - $10^{(A)}$ and $40^{(B)}$ conformers and isomers possible - $\Delta H_{\text{reaction}}^{(A)} = -15.1 \text{ kcal.mol}^{-1}$ - $\Delta H_{\text{reaction}}^{(B-I)} = -13.5 \text{ kcal.mol}^{-1}$ and $\Delta H_{\text{reaction}}^{(B-II)} = -14.0 \text{ kcal.mol}^{-1}$ - 2 amines involved in the mechanism lead to better stability of the intermediate 			<ul style="list-style-type: none"> - Second amine molecule acts as a catalytic assistant 			55 2012 (Zabalov et al.)
	 <p>0.5eq.</p>					only OH II owing to the -I character of -CH ₂ Cl		56 2012 (Ochiai et al.)

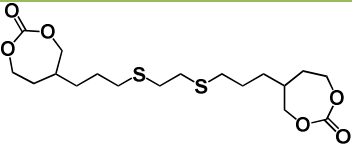

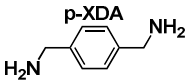
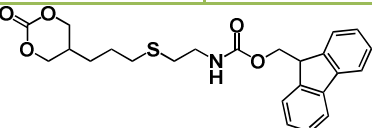
CC=cyclic carbonate; A=amine; nCC=n-membered cyclic carbonate (n=5, 6, 7); Y=Yield; conv=conversion; d=days; T=temperature; RT=room temperature; I and II are the % of the hydroxyurethanes with primary OH and secondary OH respectively; [CC]=cyclic carbonate concentration; [A]=amine concentration; [OH]=hydroxyl concentration; Nu=nucleophilicity

Table A-3- Summarized literature about poly(hydroxyurethane)s.

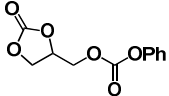
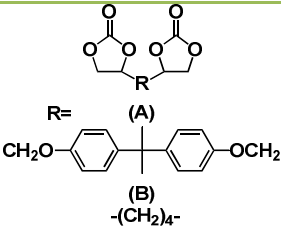
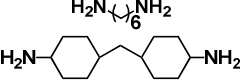
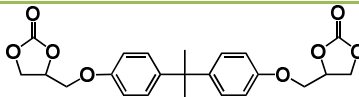
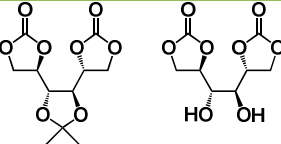
Bis-Cyclic carbonates	Diamines	Reaction conditions, yield and kinetic	\bar{M}_n (g.mol ⁻¹) and Dispersity Đ	Thermo-mechanical properties and thermal stability	Selectivity / Side reaction / Observations	Ref.
	<p>Primary aliphatic unhindered diamine C2-C20</p> <p>Secondary aliphatic diamine are less reactive</p>	<p>0-140°C</p> <p>EtAc, DMSO, DMF, benzene</p> <p>- purified by vacuum distillation of the solvent or precipitation in water or short alcohol</p>	<p>Higher \bar{M}_n in solvent</p>	<p>Hard and brittle polymers to more rubbery and tough polymers</p>		<p>patent⁵⁷ 1960 (Whelan)</p>
	<p>$\text{H}_2\text{N}(\text{CH}_2)_x\text{NH}_2$ $x=2,3,6,12$</p> 	<p>70°C or 100°C (no reaction at RT)</p> <p>DMSO, 24h</p> <p>- purified by precipitation in water</p>	<p>- Lower \bar{M}_n with ethylenediamine and 1,3-diaminopropane</p> <p>- \bar{M}_n increase with T : surprising because same conv but \bar{M}_n different</p> <p>\bar{M}_n:13000-28000</p> <p>Đ:1.39-2.16 (DMF/LiBr, PS St)</p> <p>- \bar{M}_n not as step growth polymerization</p> <p>- The presence of 2eq. / tot amounts reactants of water, methanol, ethyl acetate almost no influence \bar{M}_n</p>	<p>- Same thermal decomposition than model PU : around 310°C</p> <p>- Tg=34°C (10°C/min)</p>	<p>-More OH II bCC with ester group: no amidation reaction</p> <p>- Post-crosslinked with hexamethylene diisocyanate or Al triisopropoxide in DMAC or THF</p> <p>- Less soluble in organic solvent than model PU</p> <p>- Hypothesis: Side reaction with ethylene diamine and 1,3-diaminopropane by cyclization with the neighboring urethane to afford cyclic urea (low quantity, not confirm)</p>	<p>⁵⁸ 1993 (Kihara et al.)</p>
	<p>- 1,6-diaminohexane, xylylene diamine, 1,8-diamino-3,6-dioxaoctane and piperazine</p> <p>- Many secondary diamines (N,N'-dibenzyl ethylene diamine) almost do not react because of steric hindrance</p>	<p>75°C</p> <p>DMSO</p> <p>- purified by precipitation in cold water</p>	<p>- Low \bar{M}_n explained by the high reaction order with respect to the amine : Reaching high conv, [A] decreases and k decrease</p> <p>\bar{M}_n:3170-7700</p> <p>Đ:1.6-2.35 (THF, PS St)</p>		<p>If high T without solvent : side reaction = urea formation</p>	<p>⁵⁹ 1993 (Burgel et al.)</p>

Appendix: PART II - Chapter 1

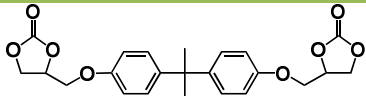
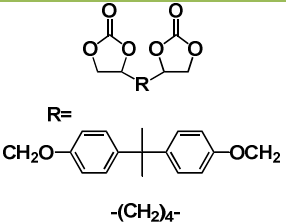
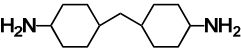
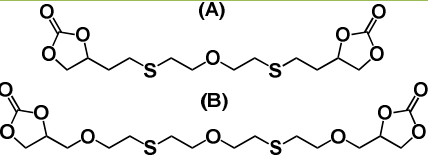
		- DMAC, 24h (heterogeneous-> not reproducible) 1eq. DBU or 2eq. TEA - NMP (L-Lysinol) - Y increase with T but not with amount of DBU and [reactant]	\bar{M}_n increase with T but not with amount of DBU and [reactant] \bar{M}_n :13000-24000 \bar{D} :1.3-1.58 (DMF/LiBr, PS St)		- Cross-linked with with copper acetate, sodium tetrahydroborate, and titanium tetraisopropoxide - optically active polymer	60 1996 (Kihara et al.)
		- DMF, RT, 72 h, 10 mol.L ⁻¹ - Xylylene diamine less reactive and less soluble = lower Y	\bar{M}_n :6300-7700 \bar{D} :1.52-1.80 Xylylene diamine less reactive and less soluble= lower \bar{M}_n (DMF/LiBr, PS St)	Tg:3-29°C T _{10%} :177-277°C Lower Tg for hexamethylene diamine compared to shorter diamine = higher urethane concentration (10°C/min)	- I:12-14% II:86-88% - No aminolysis of the ester groups - insoluble in methanol, ethanol, diethyl ether, acetone, methylene chloride, chloroform, hexane, benzene, chlorobenzene, and THF	34 2000 (Steblyanko et al.)
		- DMSO, 1 mol.L ⁻¹ , 100°C, 24h - purified by precipitation in water	\bar{M}_n :4300-12900 \bar{D} :1.18-1.99 (chloroform) (lower \bar{M}_n for aromatic amines because of low structural flexibility)	Thermal properties depend on the structure of the monomers Tg:50-102°C Td:339-388°C function of the amine structure (higher Tg for aromatic amines)	Only soluble in aprotic solvents because of the hydrophilic character of the OH group (10°C/min)	61 2001 (Kim et al.)
		- DMSO, 0.5 mol.L ⁻¹ , 70°C, 30d - purified by precipitation in ether			I:24% II:76%	37 2001 (Tomita et al.)
		- DMAC, 1 mol.L ⁻¹ , 50°C, 24h - purified by precipitation in ether - B6CC converted quantitatively after 48h while a conv of 67% for B5CC - B5CC conv did not reach 100% even	B6CC:26000 (48h) B5CC:15000 (14d) - Typical curve for the evolution of \bar{M}_n with conversion (DMF/LiBr, PS St)			62 2001 (Tomita et al.)

		<p>after 14d</p> <p>- Second order overall : $k_{B6CC-30^\circ C} = 0.70$; $k_{B6CC-50^\circ C} = 0.89$; $k_{B6CC-70^\circ C} = 1.07$ and $k_{B5CC-30^\circ C} = 0.03$; $k_{B5CC-50^\circ C} = 0.06$; $k_{B5CC-70^\circ C} = 0.10$ ($L \cdot mol^{-1} \cdot h^{-1}$)</p> <p>- $k_{B6CC} < k_{6CC}$: probably because of the smaller mobility of the reaction site of the bifunctional monomers and polymer end</p> <p>- In contrast, $k_{B5CC} \approx k_{5CC}$: because of its slow reactivity</p> <p>- $E_{a-B6CC} = 9.2 \text{ kJ} \cdot mol^{-1}$ and $E_{a-B5CC} = 24.9 \text{ kJ} \cdot mol^{-1}$</p>				
	<p>DODDA</p>  <p>p-XDA</p> 	<p>- DMSO, 0;5 mol.L⁻¹, 30-50-70°C</p> <p>- p-XDA is less reactive</p>	<p>- Hydroxymethyl and 2-hydroxyethyl groups ratio: 52:48 (B7CC with DODDA) and 50:50 (B7CC with p-XDA)</p> <p>- in 6h : \bar{M}_n/\bar{D}: 10900/1.3 - 35700/2.8 (DMF/LiBr, PS St)</p> <p>- Better \bar{M}_n than B5CC and B6CC (same amine comparison)</p>			<p>³⁹</p> <p>2001 (Tomita et al.)</p>
 <p>fluorenylmethoxycarbonyl (Fmoc)-protected amino groups</p>		<p>- 30-50 or 70°C, DMSO, 1 mol.L⁻¹, 14d, with 10%mol. tertiary amines for deprotection</p> <p>- precipitated with ether to purify</p>	<p>\bar{M}_n: 3200-11000g.mol⁻¹</p> <p>\bar{D}: 1.1-1.2 (DMF/LiBr, PS St)</p> <p>\bar{M}_n decrease with the temperature</p>	<p>- Stability 6CC with N,N-diisopropylethylamine and 4-(dimethylamino)pyridinene: 50°C (14d) <1%conv but 70°C (7d) 55%conv</p> <p>6CC + TEA (morr nucleophilic) 30°C =>rapidly converted</p>		<p>⁶³</p> <p>2001 (Tomita et al.)</p>

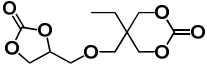
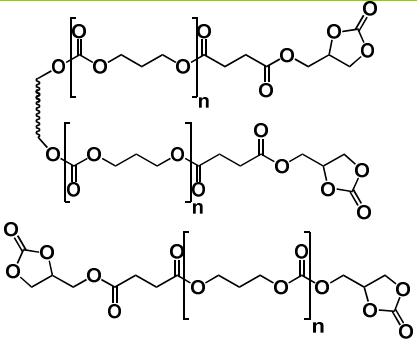
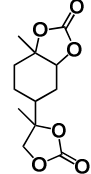
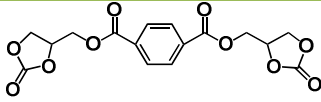
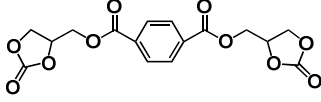
Appendix: PART II - Chapter 1

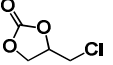
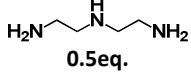
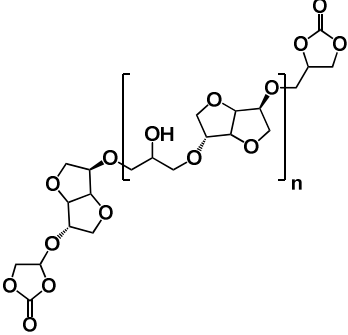
 <p>AA* monomer</p>	$\text{H}_2\text{N}-(\text{CH}_2)_x-\text{NH}_2$ $x=2,3,4,5,6$	DMAC, 2 mol.L ⁻¹ , RT, 20h precipitation in diethyl ether	- low D= low \bar{M}_n material is soluble in diethyl ether - \bar{M}_n :6400-8700 \bar{D} :1.46-1.57 (DMAC / LiCl / PS St)	- Amorphous: Tg decrease with the increase of the number of methylene groups between urethane functions Tg:22.6-52.8°C (10°C/min) - Stable up to 225°C. T _d increases with increasing number of methylene groups between the urethane groups (10°C/min)	Removal of phenol	⁴¹ 2004 (Ubagh's et al.)
 <p>(A) (B) -(CH₂)₄-</p>	$\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$ 	- Water, 0.5 mol.L ⁻¹ , organic solvent and surfactant free, 24h/48h, various T°C:50-100°C - (A): always heterogeneous "protection of CC from hydrolysis" -(B): heterogeneous then homogeneous - Higher T°C = higher conv - (A)+1,6- diamino-hexane 50- 60°C possible polymerization	\bar{M}_n lower than in DMSO containing water probably because the excess amounts of water resulted in the slight hydrolysis of the cyclic carbonate under the basic conditions \bar{M}_n :500-4400 \bar{D} :1.03-2.16 (DMF, phosphoric acid, LiBr, PS St)		Hydrolysis of the CC as in model reaction	⁴³ 2005 (Ochiai et al.)
	$\text{H}_2\text{N}-(\text{CH}_2)_{12}-\text{NH}_2$	- DMSO, 1.7 mol.L ⁻¹ , 70°C, 6h + 5mol% - Additives such as lithium salts, NaCl, Bu ₄ NCl, CaCl ₂ , Bu ₄ Sn, Bu ₂ Sn(OAc) ₂ , K ₂ CO ₃ , CaH ₂	Consequent higher \bar{M}_n with LiF, LiCl, Bu ₄ Sn - without additive: 19300 / 1.88 - with additive: 14600 /1.73 - 36700/1.84 (DMF, phosphoric acid, LiBr, PS St)	- I:21-40% II:60-79% Study of the effect of additives		⁶⁴ 2005 (Ochiai et al.)
	$\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$	- DMAC, diglyme, dioxane, THF, 0.1-0.2 mol.L ⁻¹ , 25- 80°C, 12-24h - purified by dissolving in DMF and	- Higher \bar{M}_n in less polar solvents (dioxane, THF:7000-87000 g.mol ⁻¹) than in more polar ones (DMAC, diglyme: 5000-18000	(A) Amorphous, Tg:50-70°C (B) Tg:64-79°C and Tm:160- 190°C - Td=180-224°C (10°C/min)	- I:6-19% II:81-94% - Acylation of the hydroxyl groups	⁶⁵ 2005 (Proempers et al.)

Appendix: PART II - Chapter 1

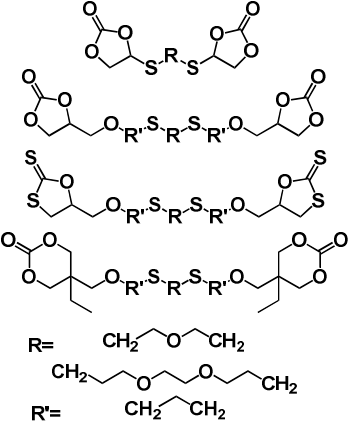
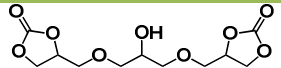
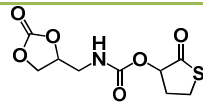
		precipitation in ether - Y:45-99%, higher yields in less polar solvents (dioxane, THF) than in more polar ones (DMAC, diglyme) - An increase in the concentration lead to an increase of Y	g.mol^{-1} - In THF, 25°C, 45°C, 65°C: higher \bar{M}_n at 65°C - An increase in the concentration lead to an increase of \bar{M}_n - \bar{M}_w :5000-122000 \bar{D} :1.4-1.6 ($\bar{M}_n < 76250$) (DMAC, LiCl, PS St)			
	$\text{H}_2\text{N}(\text{C}_6\text{H}_4)_2\text{NH}_2$	- DMSO, 1 mol.L ⁻¹ , LiCl, 70°C, 24h, Y=93% - Functionalization: with phenyl or ethyl or 3-(triethoxysilyl)propyl isocyanates with DBTDL, 1,4-dioxane	$\bar{M}_n = 26200 \text{g.mol}^{-1}$ $\bar{D} = 1.71$ (DMF, phosphoric acid, LiBr, PS St) - Increase of \bar{M}_n in some cases with functionalization	Tg=46°C - Increase of Tg to 53°C and 74°C with Et-NCO and Ph-NCO respectively (10°C/min)	- I:24% II:76% - Modification of the OH of the PHU	⁶⁶ 2007 (Ochiai et al.)
	$\text{H}_2\text{N}(\text{C}_6\text{H}_4)_6\text{NH}_2$ $\text{H}_2\text{N}(\text{C}_6\text{H}_4)_2\text{NH}_2$ 	1/ Ionic liquid, 0.2-1 mol.L ⁻¹ , 70°C, 24h (All the reaction mixtures became heterogeneous), high Y:88-92% or or 2/ water : N-n-butylimidazolium hexafluorophosphate (0.5:1), different T°C, 24h, Y:51-94% - Purification: diluted and precipitated in water and diethyl ether	1/ comparative \bar{M}_n than those obtain in organic solvent \bar{M}_n :4200-20800 \bar{D} :1.7-2.11 2/ \bar{M}_n :600-5100 \bar{D} :1.57-7.54 (DMF, LiBr, PS St)		1/ Not accompanied by the alkyl-exchange reaction between the diamines and the imidazolium ionic liquids - Ionic composites formed; originated from the interactions between hydroxyl groups in the side chains and the ionic liquids - ratio identical than the one in DMSO: I:29-33% II:67-71% 2/ Hydrolysis of the CC - I:36-38% II:62-64%	⁶⁷ 2009 (Ochiai et al.)
	$\text{H}_2\text{N}(\text{C}_6\text{H}_4)_{10}\text{NH}_2$	- DMF, 75°C, 24h - Purified by precipitation in methanol	\bar{M}_n :7000g.mol ⁻¹ (A) and 9000g.mol ⁻¹ (B) \bar{D} :1.5 (A) and 3.2 (B) (DMF, PMMA St)	Tg:-31°C (B) and -14°C (A) Td _{5%} =227°C (A) and 250°C (B) (20°C/min)	- I:25% and II:75% - Preparation of the monomers by thiolene-reaction: neither solvent nor photoinitiator and stoichiometric quantities	⁶⁸ 2011 (Benyahya et al.)

Appendix: PART II - Chapter 1

	1,6-diaminohexane, 4,9-dioxadodecane-1,12-diamine, triethylenetetramine and combination	- solvent, RT or T°C (60-90°C), in one or two step, 3d (°C) or 60d (RT), Y:85-96% - Purification by precipitation in pentane/diethyl ether (1:1)	\bar{M}_n :1340-8800 \bar{D} :1.45-2.11 (DMF, LiBr, PS St) - \bar{M}_n influence by the polarity of the solvent: $\bar{M}_{n\text{-DMF}}$:1300-1700; $\bar{M}_{n\text{-DMAc}}$:3200-3900; $\bar{M}_{n\text{-THF or CHCl}_3}$:3300-7100		48 2011 (He et al.)
	$\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ 5eq.	- DCM, 43 mmol.L ⁻¹ 70°C, 5d - Purification by precipitation in methanol	\bar{M}_n :68100g.mol ⁻¹ \bar{D} :1.2 (DMF, LiBr, PS St) From $\bar{M}_{n\text{-bisCC}}$ =5300-5700 g.mol ⁻¹ (THF)		69, 70 2011 (Helou et al.)
	1,4-diaminobutane, 1,6-diaminohexane, isophorone diamine, 1,8-diaminooctane	bulk, 60°C then gradually until 120°C	\bar{M}_n :960-1840g.mol ⁻¹ \bar{D} :1.2-1.5 (THF, PS St)	Tg:33-70°C amorphous or Tm:80-100°C (by DMA, max tanδ)	50 2012 (Bahr et al.)
	$\text{H}_2\text{N}(\text{CH}_2)_{10}\text{NH}_2$	DMF, 1.3 mol.L ⁻¹ , 75-120°C, 48h - Purification by precipitation in diethyl ether - A temperature of 120°C is too high for the polymerization (solvent evaporation)	\bar{M}_n :8000-20000g.mol ⁻¹ \bar{D} :1.9-2.5 (DMF, PMMA St)	Tg:41-48°C depend on the polymerization T°C (10°C/min)	Rheology - Enthalpy of the reaction too small to be detected by DSC 71 2012 (Benyahya et al.)
	Various diamines	- DMF, 75°C, 48h - Purification by precipitation in methanol	\bar{M}_n :3800-18000g.mol ⁻¹ $\bar{D} \approx 2$ (DMF, PMMA St)	Tg:4-78°C Tg depend on the diamine structure: - Lowest Tg with Jeffamine 400 and higher Tg with isophorone diamine, a cycloaliphatic diamine - A shorter aliphatic	72 2012 (Benyahya et al.)

				diamine lead to higher Tg due to the reduction of the macromolecular mobility - Different Tg than Steblyanko because different condition reaction and higher rate for the DSC analyses 20°C/min compared to 10°C/min		
	 0.5eq.	- Polyaddition proceeded through nucleophilic addition of the primary amino group to the cyclic carbonate structure (THF, RT) and quarternization of the secondary amino group with the chloromethyl (in molten salts)	\bar{M}_n :940-3120g.mol ⁻¹ Đ:1.18-1.81 (acetonitrile, 0.1mol.L ⁻¹ NaNO ₃)		- Branched cationic PHU - Used as catalyst for the reaction of carbon dioxide and epoxide owing to the ammonium structure - Used as a capsule for DNA	⁵⁶ 2012 (Ochiai et al.)
 \bar{M}_n :392 and 524g.mol ⁻¹	Jeffamine D-400, 1,10-diaminodecane, diethylenetriamine and isophorone diamine	DMF, catalyst, 12h, RT	\bar{M}_n :7500 and 8600g.mol ⁻¹ Đ:2.6 and 6.3 (DMF, PMMA St)	-Amorphous, Tg:-8 to 59°C (20°C/min) T _{5%} :234 to 255°C (5°C/min)		⁷³ 2013 (Besse et al.)

Appendix: PART II - Chapter 1

 <p>R= $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$ $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2$ R'= CH_2CH_2</p>	Isophorone diamine, diethylenetriamine (addition drop-wise, no cross-linking)	(A) DMF, RT or 60°C, 90h (B) THF, 16h, hydroxyethylacrylate (C) DMF, RT or 60°C, 24h, 2mol% diisopropylethyl- amine	\bar{M}_n :1800-20400g.mol ⁻¹ \bar{D} :1.4-3.1 (DMF, PMMA St) - Higher \bar{M}_n with 6CC but no proof of side reaction and only with DETA - Higher \bar{M}_n with DETA due to flexibility, but does the secondary amine react?	Tg:-29-19°C (10°C/min) T _{20%} :252-296°C (5°C/min- N ₂) - Similar Tg with b5CC and b6CC	(B) disulfide formation in oxidative atmosphere - Dried conditions	⁷⁴ 2013 (Besse et al.)
	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$	25-50-70-100°C, 8h, in a mold T<70°C : the diffusion of cyclic carbonates and amines is adversely affected by this viscosity build- up, thus preventing quantitative PHU formation - Slightly cross-linked due to f>2 in commercial epoxide (precursor of CC)		Tg=20°C (10°C/min) E-Modulus=7±1 MPa Tensile strength=9±2 MPa Elongation at break=280±50%	1wt% DABCO increase the reactivity at 25°C: no cat. conv≈60% and with DABCO conv≈90% within 2min - Tg and mechanical properties increase with cross-linked	⁷⁵ 2013 (Fleischer et al.)
 <p>Thiolactone coupler</p>	Various diamines	- DMF or THF, 0.35 mol.L ⁻¹ , 70°C, 13-43h - Add of 1-5mol% DTT (D,L-dithiothreitol) to prevent cross-linking of the thiol groups of the resulting polymer	\bar{M}_n : 3100-6400g.mol ⁻¹ \bar{D} :1.99-3.33 (DMF/LiBr, PMMA St) - \bar{D} >2: some disulfide bonds formed		- poly(hydroxyurethane amide) formed - preparation of dimer based on the higher reactivity of the thiolactone group - Post polymerization modification of the thio side groups by thio-Michael addition reaction	⁷⁶ 2013 (Keul et al.)

bCC=bis-cyclic carbonate; nCC=n-membered cyclic carbonate; Y=Yield; conv=conversion; T=temperature; RT=room temperature; I and II are the % primary OH and secondary OH formed.

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RESUME

Cette thèse porte sur la synthèse de polyuréthanes thermoplastiques plus durables à partir de dérivés des huiles végétales. La première voie étudiée est basée sur la réaction, largement utilisée, entre un diol et un diisocyanate. Aussi, pour s'affranchir de l'utilisation des diisocyanates toxiques, une approche via la polyaddition entre un bis carbonate cyclique et une diamine a également été étudiée. Pour ce faire des précurseurs bi-fonctionnels : diols, bis carbonates cycliques à 5 et 6 chaînons et diamines ont été préparés à partir de dérivés de l'huile de tournesol (oléate de méthyle) et de l'huile de ricin (undécénoate de méthyle et acide sébacique). Les propriétés thermo-mécaniques des polyuréthanes et poly(hydroxyuréthane)s thermoplastiques obtenus ont pu être ajustées par le choix adapté de la structure chimique des précurseurs (gras) utilisés. Les travaux réalisés démontrent un effet de la taille du cycle du carbonate sur la réactivité. En effet, les (bis) carbonates cycliques à 6 chaînons se sont avérés plus réactifs que leurs homologues à 5 chaînons. De plus, la synthèse de diamines via un intermédiaire dinitrile semble très prometteuse pour le « design » d'une plateforme de diamines issues d'acides gras et de poly(hydroxyuréthane)s entièrement bio-sourcés.

Mots clés : *polyuréthanes, poly(hydroxyuréthane)s, thermoplastiques, bio-sourcé, huiles végétales, acide gras, sans isocyanates, catalyse organique, diol, diisocyanate, (bis) carbonate cyclique, (di)amine.*

SUMMARY

This thesis aims to synthesize more sustainable thermoplastic polyurethanes from vegetable oil derivatives. The first route that has been investigated is based on the well-known reaction between a diol and a diisocyanate. Then to avoid the use of diisocyanates, the route via the polyaddition of a bis cyclic carbonate and a diamine have been studied as well. For this purpose, bifunctional precursors such as diols, bis 5- and 6-membered cyclic carbonates and diamines have been prepared from sunflower oil derivative (methyl oleate) and castor oil derivatives (methyl undecenoate and sebacic acid) The thermo-mechanical properties of the PUs have been modulated by designing and selecting the chemical structure of the (fatty acid-based) monomers. The performed model reaction kinetics revealed the higher reactivity of the 6-membered cyclic carbonates compare to the 5-membered ones. Finally, the developed route to fatty acid-based diamines via dinitriles synthesis in mild conditions was really efficient and this route is really promising to develop a fatty acid based-diamines platform and fully bio-based poly(hydroxyurethane)s.

Keywords : *polyurethanes, poly(hydroxyurethane)s, thermoplastic, bio-based, vegetable oils, fatty acid, isocyanate free, organocatalysis, diol, diisocyanate, (bis) cyclic carbonate, (di)amine.*

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