Les acides gras comme source de matériaux polycarbonates aliphatiques originaux

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Pierre-Luc Durand. Les acides gras comme source de matériaux polycarbonates aliphatiques originaux. Polymers. Université de Bordeaux, 2017. English. NNT : 2017BORD0710 . tel-03081266

HAL Id: tel-03081266

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université de BORDEAUX

THÈSE PRÉSENTÉE

POUR OBTENIR LE GRADE DE

DOCTEUR DE

L'UNIVERSITÉ DE BORDEAUX

ÉCOLE DOCTORALE DES SCIENCES CHIMIQUES

SPÉCIALITÉ: Polymères

Par Pierre-Luc DURAND

Fatty acids as a source of original aliphatic polycarbonate materials

Les acides gras comme source de matériaux polycarbonates aliphatiques originaux

Sous la direction de : Pr. Henri CRAMAIL
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Soutenue le 27 octobre 2017

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List of abbreviations

Techniques:

COSY: COrrelation SpectroscopY

DMA: Dynamic Mechanical Analysis

DSC: Differential Scanning Calorimetry

FTIR: Fourrier Transformed InfraRed

HSQC: Heteronuclear Single Quantum Coherence

NMR: Nuclear Magnetic Resonance

SEC: Size Exclusion Chromatography

TGA: ThermoGravimetric Analysis

UV: Ultra-Violet

Chemicals

BnOH: benzyl alcohol

$CDCl_3$: deuterated chloroform

ε-CL: ε-caprolactone

DABCO: 1,4-diazabicyclo[2.2.2]octane

DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene

DCM: dichloromethane

DMAP: dimethylaminopyridine

DMC: dimethyl carbonate

DMPA: 2,2-dimethoxy-2-phenylacetophenone

DMF: dimethylformamide

DTC: 5,5-dimethyl-1,3-dioxan-2-one

EC: ethylene carbonate

Et_3N: triethylamine

HCl: hydrochloric acid

L-LA: L-lactide

mCPBA: *meta*-chloroperbenzoic acid

MeOH: methanol

sec-BuLi: sec-butyllithium

$Sn(Oct)_2$: Tin(II) 2-ethylhexanoate

TBD: 1,5,7-triazabicyclododecene

THF: tetrahydrofuran

TMC: trimethylene carbonate

TU: thiourea

VL: δ-valerolactone

Characteristic parameters

ΔH: enthalpy

ΔS: entropy

Đ: dispersity

DP: polymerization degree

E: Young's modulus

E': storage modulus

E'': loss modulus

G': storage modulus

G'': loss modulus

$\bar{M}_n$: number average molar mass

$\bar{M}_w$: mass average molar mass

RT: room temperature

$T_{d:}$ temperature corresponding to 5 wt.% loss

T_g: glass transition temperature

T_m: melting temperature

Tα: α-relaxation temperature

tanδ: loss factor

Polymerization techniques

ROP: ring-opening polymerization

AROP: anionic ring-opening polymerization

Others

CC: cyclic carbonate

xCC: x-membered cyclic carbonate

CL: cross-linked

CTA: chain transfer agent

APC: Aliphatic polycarbonate

CONFIDENTIAL

Résumé en français:

Les acides gras comme source de matériaux polycarbonates aliphatiques originaux

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Cette thèse s'inscrit dans le cadre du projet CARBOLIP (WP3P14) financé par la SAS PIVERT,[1] impliquant le Laboratoire de Chimie des Polymères Organiques (LCPO) et le Centre Technique Industriel des Huiles et Corps Gras (ITERG, Pessac, France). Ce partenariat avec l'ITERG et la SAS PIVERT a permis l'accès à des ressources renouvelables telles que les acides gras et leurs dérivés, dans le but de synthétiser des matériaux polycarbonates plus respectueux de l'environnement.

Les polymères sont largement utilisés dans de nombreux domaines tels que l'emballage, l'automobile, le bâtiment, la cosmétique, etc… En quelques décennies, leur production est passée de 2 millions de tonnes en 1950 à environ 311 millions de tonnes en 2014 dont 39.5% uniquement dédié au domaine de l'emballage.[2] Les « plastiques » consomment 7% des ressources pétrolières produites.[3] Même si cette production n'augmente plus depuis quelques années, la demande de matériaux polymères, en revanche, ne cesse de croître (environ 4%/an) en raison de l'accroissement de la population. A cela se rajoutent les tensions géopolitiques autour de ces réserves fossiles qui génèrent de fortes variations du prix du baril de pétrole et des matières premières et les problématiques environnementales comme l'émission croissante des gaz à effet de serre qui conduisent industriels et académiques à trouver des solutions plus durables pour substituer une partie des ressources pétrolières par des ressources renouvelables.

Dans ce contexte, la Biomasse est considérée comme la principale ressource de carbone renouvelable disponible sur Terre. Son temps de régénération se compte en dizaines d'années alors que celui des ressources fossiles en millions d'années.[4] La valorisation de la Biomasse pour la synthèse de polymères s'oriente autour de deux stratégies principales : (i) l'utilisation directe ou la modification chimique de bio-polymères tels la cellulose, la lignine ou l'amidon[5] et (ii) la polymérisation de monomères obtenus par déconstruction ou extraction de la Biomasse.[6–8] Des

polymères bio-sourcés nouveaux, tel le polylactide, ou ceux similaires aux polymères pétro-sourcés, tel le bio-polyéthylène, sont aujourd'hui proposés sur le marché. Le développement des polymères bio-sourcés (non biodégradables et biodégradables) ne cesse de croître pour atteindre, en 2016, une production mondiale de 5,8 millions de tonnes.

Parmi les bio-ressources disponibles, les huiles végétales représentent une plateforme intéressante pour le développement de synthons permettant de concevoir de nouveaux polymères.[8,9] En effet, l'extraction de ces huiles conduit à l'obtention de glycérol et d'esters d'acides gras. Ces derniers contiennent des insaturations, des fonctions ester (parfois alcool) qui peuvent être directement utilisées ou dérivatisées pour la préparation de polymères originaux (Figure 1).

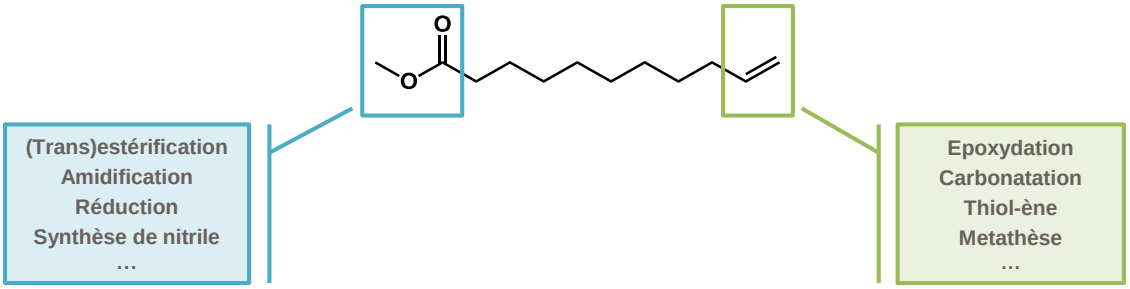

Figure 1: Quelques réactions chimiques possibles sur les acides gras (exemple : Undécénoate de méthyle)

Dans le domaine des 'plastiques', les polycarbonates représentent une classe importante de polymères de spécialité depuis leur invention au milieu des années 1950. On distingue deux familles de polycarbonates : les polycarbonates aromatiques et les polycarbonates aliphatiques.

Particulièrement légers, hautement transparents et faciles à mettre en forme, les polycarbonates aromatiques sont utilisés dans de nombreux domaines de la vie moderne, de l'électronique aux composants informatiques, en passant par l'automobile et les dispositifs optiques. Bien que le terme « polycarbonate » puisse être utilisé pour nommer tous polymères, aromatiques ou aliphatiques, comportant l'unité répétitive -O-C(O)-O, il désigne souvent le polycarbonate de bisphénol-A. Sa production annuelle étant de 2.7 million de tonnes, il est très utilisé dans la fabrication de matériaux optiques, de CD ou de protections contre les chocs (casques, boucliers,…). Cependant l'utilisation de composés toxiques tels que le bisphénol-A ou le phosgène devient un frein à son utilisation.

Contrairement aux polycarbonates aromatiques, les polycarbonates aliphatiques (PCAs) sont non seulement restés commercialement inexploités mais n'ont également reçu que peu d'attention de la part des chercheurs jusqu'aux années 1990. Cependant, comme la synthèse de PCAs implique souvent l'utilisation de CO_2, de tels polymères sont redevenus attractifs afin de réduire la pollution des gaz à effet de serre. De plus, une demande grandissante des matériaux dégradables et polyvalents a également ravivé l'intérêt des PCAs pour des applications biomédicales dans lesquelles leur biocompatibilité, leurs basses températures de transition vitreuse (T_gs) et leur élasticité sont devenus des avantages par rapport à beaucoup d'autres polymères.

Grâce au regain d'intérêt pour les PCAs, de nombreux progrès ont été faits en termes de méthodes de polymérisation,[10–13] de synthèse de monomères fonctionnels[14–16] et des nouvelles applications ont été ciblées.[17–19] De plus, les avancées des techniques de polymérisation, particulièrement celles impliquant l'utilisation du CO_2, ont rendu possible la préparation de PCAs à l'échelle industrielle avec des coûts relativement faibles.

Dans le contexte d'une chimie plus durable, la préparation de précurseurs bio-sourcés pour la synthèse de polymères est de plus en plus étudiée. Plusieurs groupes de recherche ont réalisé la préparation de polycarbonates aliphatiques bio-sourcés à partir de l'oxyde de limonène[20,21] ou d'acides bio-sourcés (acides levulinique et itaconique).[22] Cependant, à l'exception des travaux de More et ses collaborateurs,[23] peu d'attention a été accordée à la préparation de polycarbonates aliphatiques à partir d'acides gras.

Cette thèse porte donc sur la modification chimique de dérivés d'acides gras dans l'objectif d'élaborer des matériaux polycarbonates aliphatiques bio-sourcés originaux.

Ce manuscrit est divisé en quatre chapitres. Le premier chapitre illustre l'état de l'art concernant la synthèse de polycarbonates aliphatiques obtenus par polymérisation par ouverture de cycle (POC). Il permet de donner aux lecteurs les bases nécessaires à la compréhension des objectifs et des accomplissements de cette thèse. Parmi toutes les méthodes d'obtention de polycarbonates aliphatiques,[24] la POC est celle qui nécessite les conditions réactionnelles les plus douces et qui permet la synthèse de polycarbonates fonctionnels de manière contrôlée. Dans ce contexte, les différentes voies d'accès aux carbonates cycliques (CCs) sont détaillées dans un premier temps incluant la synthèse de CCs de 5 à 8 chaînons. Les nouvelles tendances sur le développement de CCs bio-sourcés sont aussi décrites. La seconde partie de ce chapitre couvre les différents travaux

traitants de la POC de carbonates cycliques particulièrement par voie anionique ou par coordination-insertion. Une attention particulière est finalement portée sur les polycarbonates aliphatiques fonctionnels afin d'introduire le contexte de cette thèse.

Fort de cet état de l'art, cette thèse a été développée suivant trois grands axes : (i) la synthèse de carbonates cycliques à 6 chaînons à partir d'acides gras, (ii) la production de PCAs fonctionnels bio-sourcés et (iii) la conception de matériaux polycarbonates réticulés réversiblement ou pas.

Le chapitre 2 de ce manuscrit souligne la problématique rencontrée avec les carbonates cycliques à 5 chaînons (5CCs). En effet, la taille de cycle du carbonate est un paramètre clé pour la polymérisation par ouverture de cycle. Bien que les 5CCs sont facilement synthétisables à partir d'acides gras[25] (par époxydation de la double liaison puis carbonatation), leur homopolymérisation ne permet pas l'obtention de polycarbonates purs en raison de caractéristiques thermodynamiques défavorables. Néanmoins, à haute température, une réaction secondaire de décarboxylation rend la polymérisation possible donnant lieu à des polycarbonates comportant des séquences d'unités éther en grande quantité. Cependant, les 5CCs peuvent, dans une certaine mesure, être copolymérisés avec des monomères cycliques plus réactifs (lactones, lactides, autres carbonates cycliques, etc…). En effet, contrairement aux 5CCs et malgré le fait qu'ils soient plus difficilement accessibles à partir d'acides gras, les carbonates cycliques à 6 chaînons (6CCs) peuvent être facilement polymérisés par ouverture de cycle de manière contrôlée.[16,26–29] Non décrite dans la littérature, la copolymérisation du carbonate d'éthylène (EC) et du carbonate de triméthylène (TMC) a donc été étudiée dans ce chapitre comme réaction modèle (Figure 2).

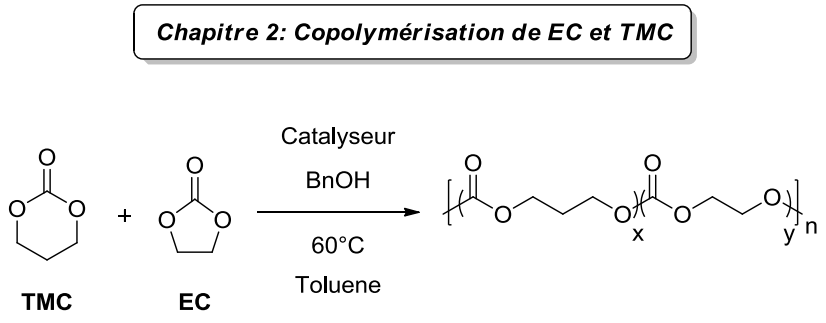

Figure 2: Copolymérisation entre EC et TMC étudiée dans le chapitre 2

L'influence de plusieurs paramètres tels que la nature du catalyseur, le ratio des monomères ou encore le ratio amorceur/monomères a été investiguée. Grâce à cette étude, nous avons été capables d'optimiser le procédé permettant l'incorporation de 15 mol.% d'unités EC dans un squelette de PTMC, sans réactions secondaires de décarboxylation. Une telle incorporation de carbonate d'éthylène a permis d'améliorer la stabilité thermique ainsi que la T_g des copolymères ainsi formés. Une fois la réaction modèle validée, des essais de copolymérisation entre des 5CCs issus d'acides gras et le TMC ont été effectués. Malheureusement, ces expériences ont échoué menant seulement à la synthèse de PTMC.

Par conséquent, le chapitre 3 est dédié à la synthèse et polymérisation de 6CCs issus d'acides gras plus réactifs que leurs homologues 5CCs (Figure 3). Deux plateformes de carbonates cycliques à 6 chaînons ont été synthétisés en utilisant des voies d'accès impliquant soit la formation d'un intermédiaire de type malonate (inspiré des travaux de Maisonneuve *et al.*[30]) ou un couplage entre un acide gras et le 2-amino-1,3-propanediol (inspiré des travaux de Venkataraman *et al.*[31]). Il est important de noter que le rendement global de la seconde voie d'accès (avec le 2-amino-1,3-propanediol) est beaucoup plus élevé que celui de la première voie, ce qui est un avantage non négligeable en vue des réactions de post-polymérisation. La polymérisation par ouverture de cycle a également été décrite dans ce chapitre. La première plateforme de 6CCs a été polymérisée en présence de $Sn(Oct)_2$ comme catalyseur, donnant accès à des polycarbonates de faible T_g allant de -60.8°C jusqu'à -26.1°C du fait de longues chaines alkyle pendantes. La polymérisation de la seconde plateforme de 6CCs a été effectuée de manière contrôlée en utilisant un système catalytique composé du DBU et d'une thio-urée. Étonnamment, les polycarbonates issus de cette seconde plateforme présentent des T_gs relativement hautes (supérieures à 20°C) expliquées par la présence de liaisons hydrogène dues aux fonctions amide pendantes.

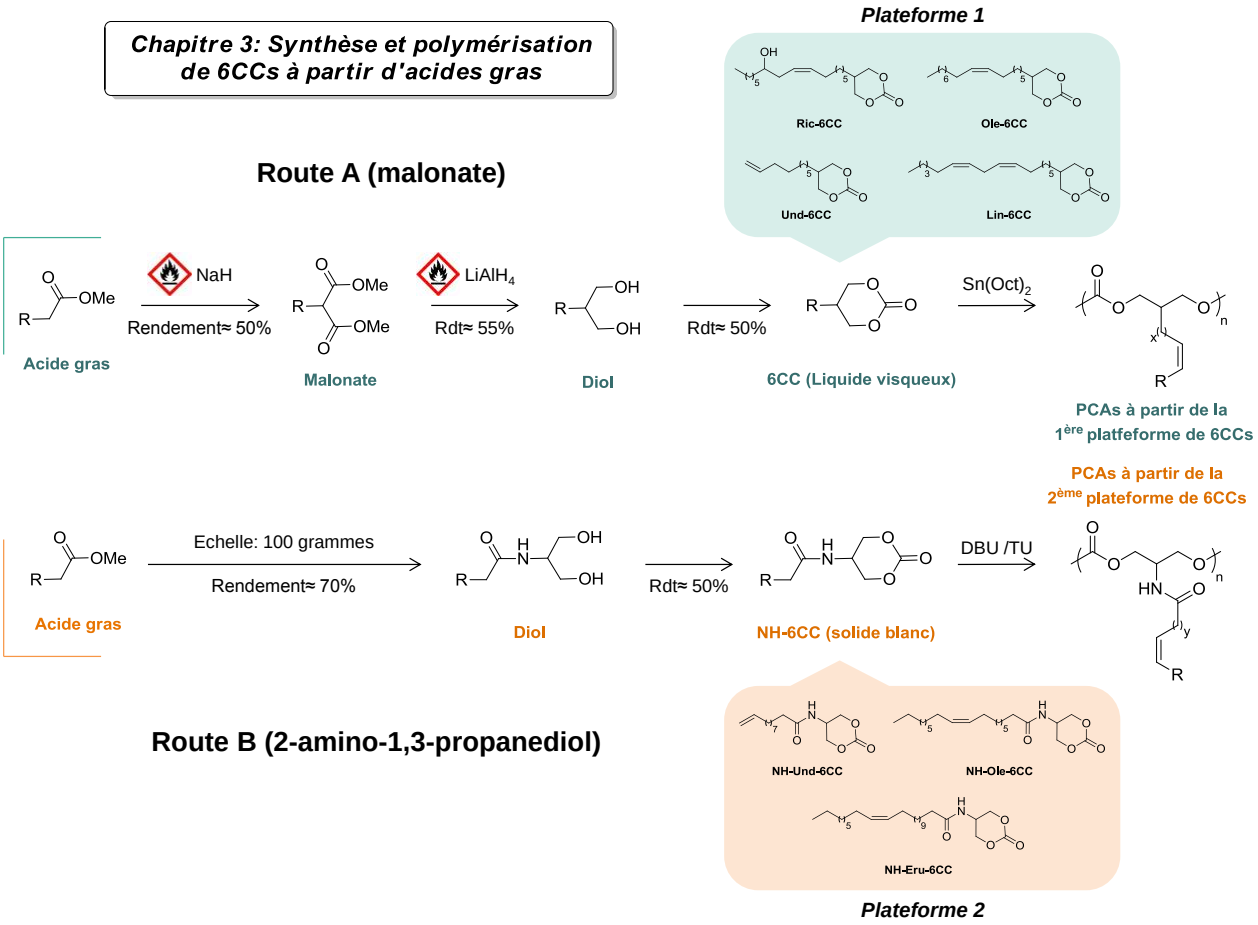

Figure 3: Stratégies utilisées dans le chapitre 3 pour concevoir des polycarbonates aliphatiques bio-sourcés

Dans la continuité du chapitre précédent et tirant profit de ces polycarbonates aliphatiques bio-sourcés linéaires porteurs d'insaturations, le chapitre 4 détaille la conception de matériaux polycarbonates originaux réticulés (Figure 4). Nous avons démontré qu'à partir d'un seul polymère conçu dans le chapitre 3 (polycarbonate issu de NH-Und-6CC), il est possible d'élaborer de nombreux matériaux réticulés selon plusieurs méthodes.

Le couplage thiol-ène direct entre une insaturation terminale et un dithiol a d'abord été utilisé pour préparer des matériaux polycarbonates réticulés. Les propriétés mécaniques de ces matériaux sont contrôlables allant d'un matériau rigide à un matériau avec un comportement élastomère.

Ensuite, des matériaux auto-cicatrisants ont été développés impliquant soit la température soit l'irradiation sous UV comme stimulus. En effet, des réseaux polycarbonates thermo-sensibles ont

été synthétisés à travers le greffage de groupements furane sur les chaines latérales du polymère et la réaction de Diels-Alder consécutive grâce à des molécules bis-maléimide comme agents réticulants. Le taux de furane greffé par couplage thiol-ène est compris entre 31 et 88 mol.% permettant de faire varier les propriétés mécaniques des matériaux réticulés obtenus. De plus, nous avons démontré que ces réseaux pouvaient être recyclés au moins 3 fois sans altérer leurs propriétés mécaniques.

De manière analogue, des groupements cinnamate photo-sensibles ont aussi été greffés par couplage thiol-ène sur le polymère. Ainsi, la réaction de cyclo-addition [2+2] photo-induite entre deux groupements cinnamate a permis la formation de matériaux polycarbonates réticulés de manière photoréversible. Cette méthode de réticulation réversible permet de s'affranchir de la température qui peut, dans une certaine mesure, endommager le matériau.

Par conséquent, des PCAs réticulés issus d'acides gras ont été synthétisés et caractérisés; ces derniers possèdent des propriétés physico-chimiques modulables selon la nature des monomères de départ et la densité de réticulation des réseaux.

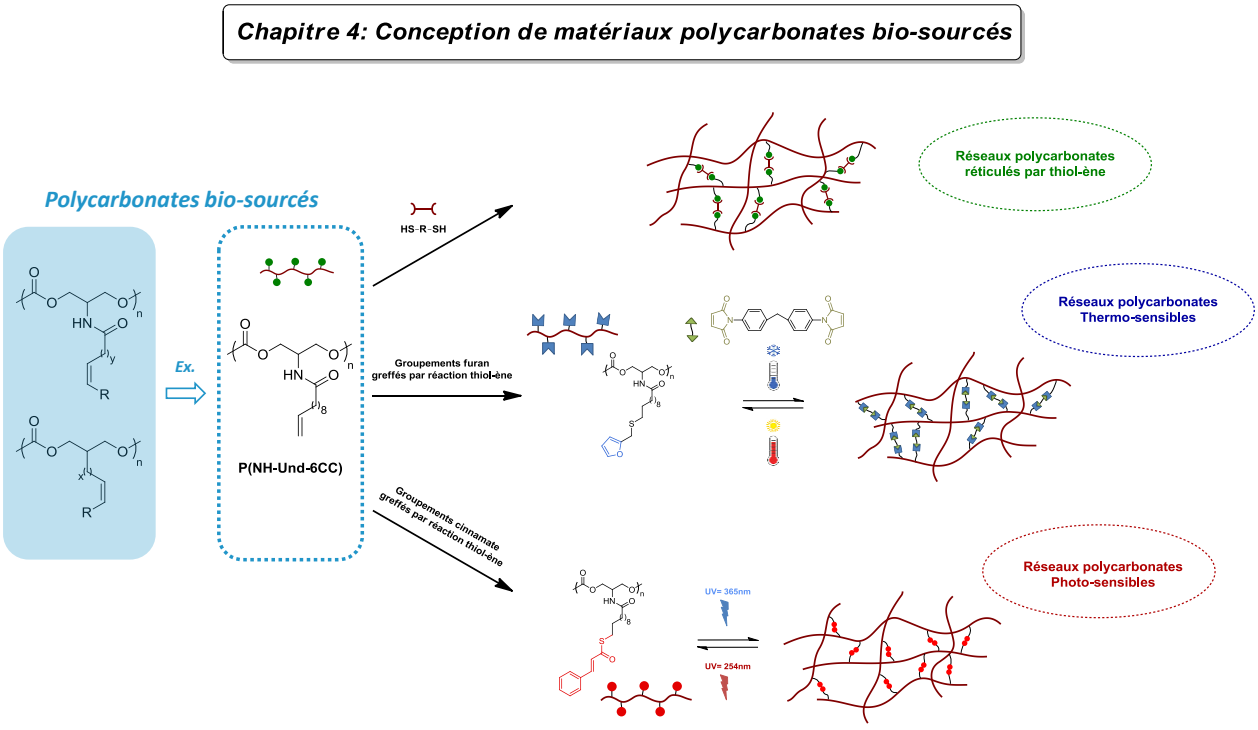

Figure 4: Méthodes de réticulations permettant la conception de matériaux polycarbonates bio-sourcés

En conclusion, ces travaux de thèse ont permis la synthèse de matériaux polycarbonates bio-sourcés. Plusieurs carbonates cycliques issus d'acides gras ont été conçus afin d'étudier leur réactivité en tant que monomères. Ces derniers ont été polymérisés par ouverture de cycle permettant la formation de polycarbonates aliphatiques bio-sourcés possédant des insaturations pendantes. Tirant avantage de cette fonction, des matériaux polycarbonates bio-sourcés à propriétés modulables ont été obtenus par différentes méthodes de réticulation. De plus, certains d'entre eux ont été conçus avec l'idée qu'ils soient recyclables ou qu'on puisse les remettre en forme grâce à la réversibilité des réactions de réticulation.

Afin d'assurer le transfert de ces réactions à l'échelle industrielle, il est nécessaire d'entreprendre des recherches ultérieures. L'étude des procédés de polymérisation sans solvant et leurs effets sur les matériaux obtenus ou encore l'analyse détaillée des propriétés physico-chimiques des polycarbonates sont des axes de développement à considérer pour les futures recherches dans le domaine des polycarbonates aliphatiques.

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General introduction

Polymers are widely used in daily life in many domains such as packaging, automotive, constructions, cosmetics, etc... Over the past decades, their production increased from 2 million tons in 1950 to 311 million tons in 2014 with 39.5% dedicated only to packaging.[1] Besides, the production of 'plastics' consumes 7% of the global oil resources annually produced.[2] However, the growing demand of fossil resources along with their scarcity represent issues to the synthetic plastic production durability. In addition, environmental concerns such as the limitation of greenhouse gas emission motivate researchers to develop sustainable solutions replacing oil-based resources by renewable ones.

In this context, Biomass and CO_2[3] constitutes the main available resources of renewable carbon. The regeneration time of carbon from biomass is evaluated in decades contrarily of fossil resources that can reach several million years.[4] From these observations, the concept of bio-refinery was developed in the respect of the principles of green chemistry.[5] Such a concept considers the use of biomass as a low-cost feedstock for the chemical and biological industries (Figure 1).

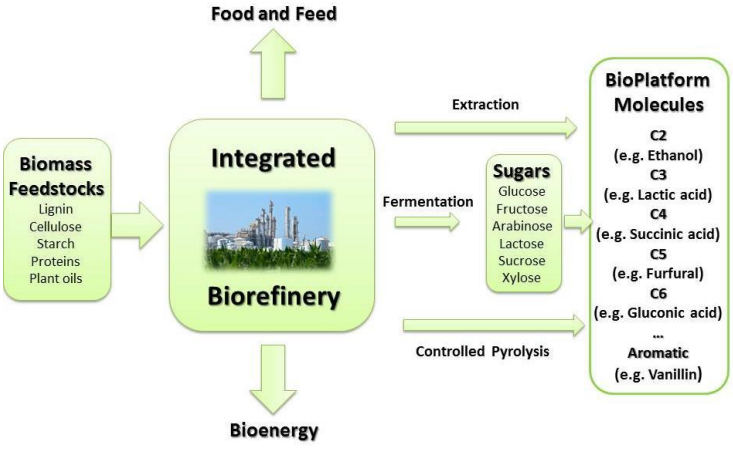

Figure 1: Schematic idealized concept of an integrated bio-refinery

In this framework, over the two last decades, a large community of scientists (academy and industry) has targeted the development of green and sustainable polymers.[6] The valorization of Biomass for the synthesis of polymers has been oriented around two main strategies: (i) direct use

or modification of available biopolymers such as lignin, cellulose and starch;[7] (ii) polymerization of building blocks obtained from Biomass deconstruction or extraction.[8–10]

Among the available bio-resources, vegetable oils appear as an interesting platform for the development of new building blocks for the design of polymers.[11,12] Indeed, the triglyceride transesterification leads to the production of glycerol and fatty esters. These latter display functionalities such as double bonds, ester or alcohol functions that can be directly used or derivatized for the preparation of original polymers (Figure 2).

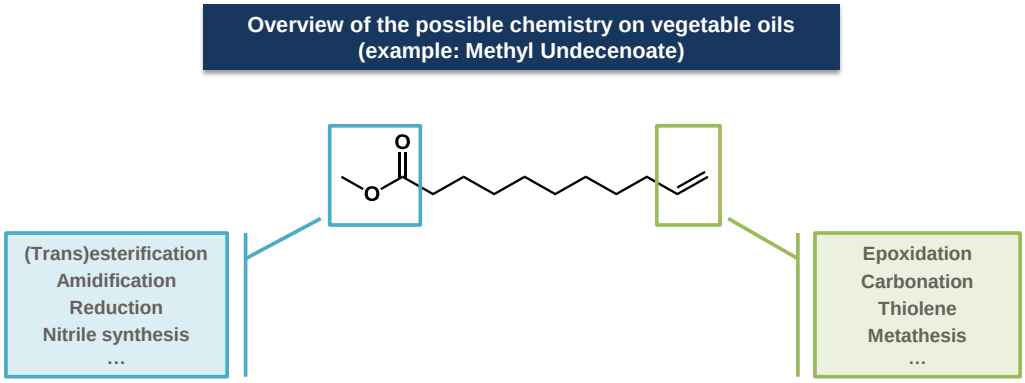

Figure 2: Methyl undecenoate as a source of various building blocks

In midst of available plastics, polycarbonates (PCs) represent an important class of specialty polymers since their invention in the mid 1950's. Two families of polycarbonates can be distinguished: aromatic polycarbonates and aliphatic polycarbonates.

Especially lightweight, highly transparent, and easy to shape, aromatic polycarbonates are used in many areas of modern life, from electronic and IT appliances to automotive and optical devices. Although the term "polycarbonate" can be used to refer to any polymer, aliphatic or aromatic, with the repeating -O-C(O)-O unit, it often refers to the specific polymer derived from 2,2-bis(4-hydroxyphenyl)propane (Bisphenol-A) (Figure 3). 2.7 million tons of Bisphenol-A polycarbonate is produced annually worldwide.

However, the toxicity of Bisphenol-A is a serious limitation to the use of such a polymer in domestic applications. For example, Bisphenol A was shown to release from drinking bottles and mimics the neurotoxic actions of estrogen in developing cerebellar neurons.[13]

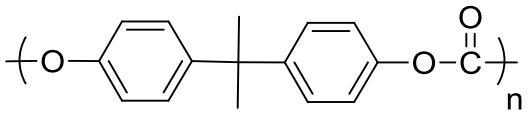

Figure 3: Bisphenol-A polycarbonate repeating unit

Unlike aromatic polycarbonates, aliphatic polycarbonates (APCs) not only remained largely unexplored commercially but also received little attention from the research field until the 1990s. However, since the synthesis of APCs often involves the use of CO_2, such polymers have received significant renewed attention in order to reduce greenhouse gas pollution. Moreover, an increasing demand for more versatile, degradable biomaterials has also revived the interest in APCs for biomedical applications for which their degradability, low glass-transition temperatures, and elasticity became competitive advantages over many other polymers.

Due to the renewed interest of APCs, new progresses have been achieved in terms of polymerization methodologies,[14–16] functional monomer syntheses[17–19] and many new applications were targeted.[20–22] In addition, the advance of polymerization techniques, especially CO_2-based copolymerization techniques, makes it possible to prepare APCs at the industrial scale with a relatively low cost.

In the context of sustainability, another key point is the preparation of fully bio-based APCs. Few research groups carried out the preparation of bio-based APCs from limonene oxide[23,24] or bio-sources acids (levulinic and itaconic acids).[25] However, except the work of More *et al.*[26] not much attention has been paid in the preparation of polycarbonates starting from fatty acid derivatives.

Consequently, the purpose of this thesis was to synthesize vegetable oils-based aliphatic polycarbonates. Besides, the ring-opening polymerization (ROP) method has been chosen for the preparation of bio-based APCs since it requires mild reactions conditions and allows the synthesis of well-controlled functional polymers. Therefore, the synthesis and polymerization of lipidic cyclic carbonates were studied towards new functional APCs. The final goal of this work was to prepare APCs cross-linked materials which can be used in high value-added applications particularly in the biomedical field.

This thesis takes place in the frame of the CARBOLIP project (WP3P14) involving the *Laboratoire de Chimie des Polymères Organiques* (LCPO), the *Centre Technique Industriel des Huiles et Corps Gras* (ITERG, Pessac, France) and the *Unité de Catalyse et de Chimie du Solide (UCCS, Lille, France)*. This project has been financially supported by the SAS PIVERT.[27] The partnership with the ITERG enabled the convenient access to lipidic cyclic carbonate precursors in order to prepare new bio-based APCs.

This manuscript is divided in four chapters. The first chapter attempts to illustrate the state of the art regarding aliphatic polycarbonates in order to provide the reader the basics to better understand the objectives and the achievements of this thesis. It will be focusing on the synthesis of cyclic carbonates and their ring-opening polymerization towards the preparation of APCs. In this respect, the different routes to produce cyclic carbonates are first depicted, including the synthesis of five-, six-membered and larger cyclic carbonates. New trends for the development of bio-based cyclic carbonates are also described. The second part of this chapter covers the different works dealing with the ROP of cyclic carbonates especially by the anionic and coordination-insertion pathways. An extra focus is finally made on functional aliphatic polycarbonates to introduce the context of this thesis.

The synthesis of five-membered cyclic carbonates (5CCs) being straightforward from fatty acids, the second chapter of this manuscript investigates the capability of 5CCs to undergo ring-opening copolymerization with more reactive six-membered cyclic carbonates (6CCs). In the purpose of understanding the polymerization process, an optimization of experimental conditions with model molecules (ethylene carbonate (EC) and trimethylene carbonate (TMC)) and a mechanistic study were performed.

Considering the results of the second chapter, the third chapter covers the achievements related to the synthesis and the ROP of lipidic 6CCs. In this context, two platforms of fatty acid-based 6CCs were elaborated with tuneable characteristics such as length of the side chain or nature and number of unsaturations. These monomers were then successfully used for the synthesis of bio-based functional APCs either catalyzed by a tin-based compound $Sn(Oct)_2$ or an organo-based system composed of DBU and Schreiner thiourea. The structure-property relationships of the so-formed APCs were further investigated.

Lastly, the fourth chapter presents the work dedicated to the design of novel cross-linked polycarbonate materials in order to enhance the thermo-mechanical properties of the bio-based functional APCs developed in the third chapter. In a first part, such polymers were irreversibly cross-linked using the thiol-ene reaction. In a second part, the lipidic bio-based APCs were reversibly cross-linked through thermal or photo-chemical processes yielding original self-healed materials.

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Chapter 1

State of the art: Towards aliphatic polycarbonates obtained by ring-opening polymerization

Keywords: Cyclic carbonates, ring-opening polymerization, aliphatic polycarbonates, bio-sourced.

Mots-clés: Carbonates cycliques, polymérisation par ouverture de cycle, polycarbonate aliphatiques, bio-sourcé.

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Table of contents

1. Introduction

Environmental concerns along with the need to replace hazardous chemicals and harsh conditions have driven academic research groups and industries to develop greener processes and materials free of any toxic compounds. In this context, aliphatic polycarbonates (APCs) are raising a lot of attention over the last decades due to their non-toxicity, their relative low degradation rate in water and their non-production of acidic degradation products. These features make them very suitable materials for green technologies and biomedical applications such as scaffolds for tissue engineering[1–4] or drug carriers[5,6]. In addition, the incorporation of the carbonate moiety makes the rigid and brittle polyesters more flexible and tough.[7] Even if APCs are less industrially produced than their aromatic analogous (around 3 million tons in 2016), this class of materials has an important potential and is still the object of developments.

Three different synthetic methods can afford the synthesis of aliphatic polycarbonates (Figure 1): (1) polycondensation between a diol and phosgene derivatives, (2) copolymerization of carbon dioxide with epoxides and (3) ring-opening polymerization (ROP) of cyclic carbonate monomers.

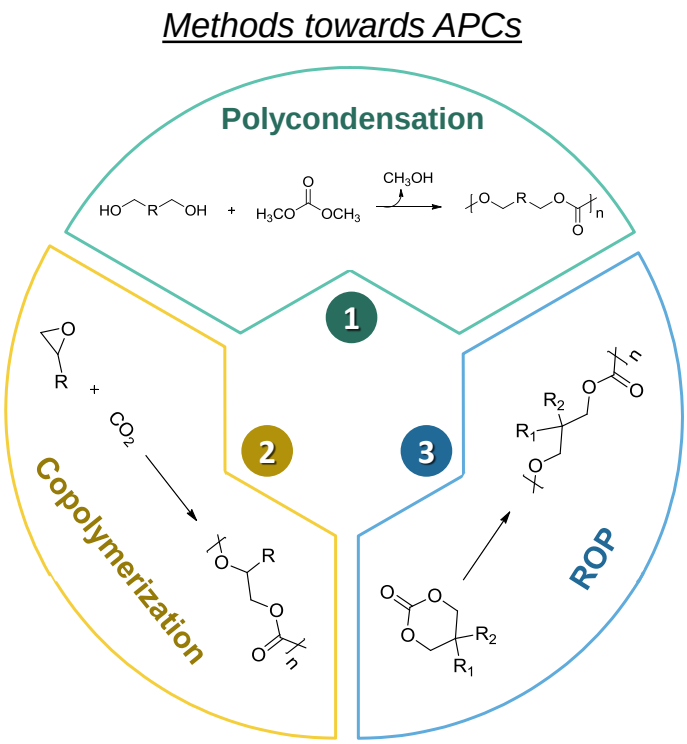


Figure 1: Overview of synthetic routes to aliphatic polycarbonates

From an industrial viewpoint, the most common method to produce APCs is the polycondensation between alkanediols with phosgene, triphosgene or dialkylcarbonates. However, because of the high toxicity of phosgene[8], many efforts were raised to find a greener alternative for producing aliphatic polycarbonates.

From an ecological point of view, one of the most promising areas of CO_2 utilization is its application as a direct material for polymer synthesis. Since the work of Inoue,[9,10] great progresses have been made in the formation of polycarbonates by the reaction between CO_2 and epoxides. This topic has been reviewed by several authors.[11–14] Nevertheless, major drawbacks of this method are the synthesis of 5-membered cyclic carbonates as side-products and ether linkages formation in the polycarbonate backbone.[15]

Another alternative method for APCs synthesis is the ring-opening polymerization of cyclic carbonates. This method is by far the most used technique since it requires mild reactions conditions and allows the synthesis of well-controlled functional polymers. The present state of the art will only focus on the latter mentioned method, which has been the most studied over the past decades.[16–22]

Thus, the first part of this chapter will be devoted to the synthesis of cyclic carbonate monomers required for aliphatic polycarbonates production. The syntheses of five-, six-membered and larger cyclic carbonates will be reviewed. In a second part, main ROP methods of cyclic carbonates will be detailed. In each part, available routes for bio-based products will be discussed.

2. Aliphatic cyclic carbonate syntheses

In the early 1930s, pioneering work of Carothers *et al.*[23–25] gave first insights regarding the synthesis of cyclic carbonates (CCs). CCs were obtained by the depolymerization of respective linear oligocarbonates at high temperature in the presence of several catalysts combined under reduced pressure. Nowadays, this method is still applied in the synthesis of CCs but many other routes have emerged. Below are reported the different approaches for their synthesis.

2.1. Synthesis of 5-membered cyclic carbonates (5CCs)

The synthesis of 5-membered cyclic carbonates (5CCs, or 1,3-dioxolan-2-one, presented in Figure 2) has been extensively studied along the years, through various methods. Ethylene carbonate and propylene carbonate have been commercially available for over 45 years.

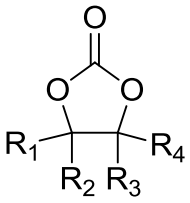


Figure 2: Chemical structure of 5-membered cyclic carbonates

Also recently available commercially, bio-based glycerol carbonate gained significant interest from international scientific community.[26–28] This monomer and its derivatives are also key compounds in the synthesis of multiple cyclic carbonates which are used for the preparation of non-isocyanate polyurethanes.[29,30] Such monomer can be synthesized either from glycerol (obtained from vegetable oils by saponification or methanolysis) following the methods developed below, or from activated glycerol (3-chloro-1,2-propanediol) or epichlorydrin using CO_2 or alkaline (hydrogen) carbonate (Figure 3). The more suitable processes are up to date the reaction of glycerol with of ethylene carbonate or dialkyl carbonates.[28]

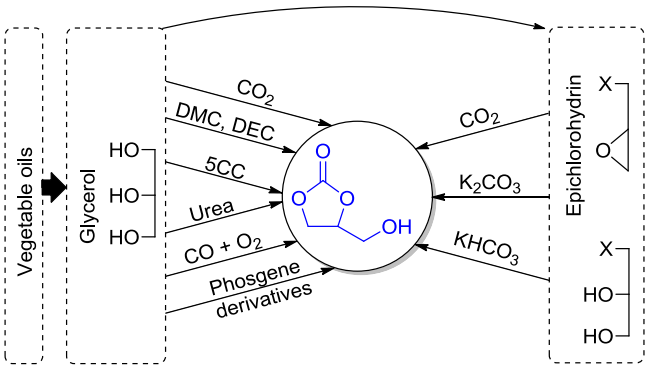


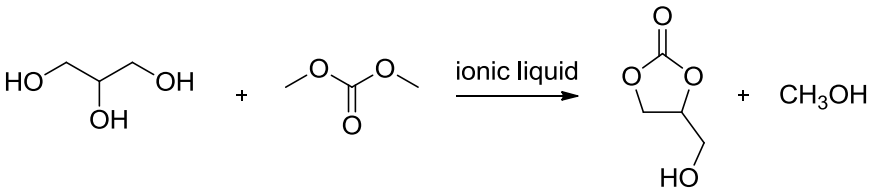
Figure 3: Synthesis of glycerol carbonate. (DMC=dimethyl carbonate, DEC=diethyl carbonate, 5CC=ethylene carbonate).

Besides the depolymerization of linear oligocarbonates above-mentioned (Scheme 2-(13)), various approaches have been developed to access 5CCs, as summarized in Scheme 2.

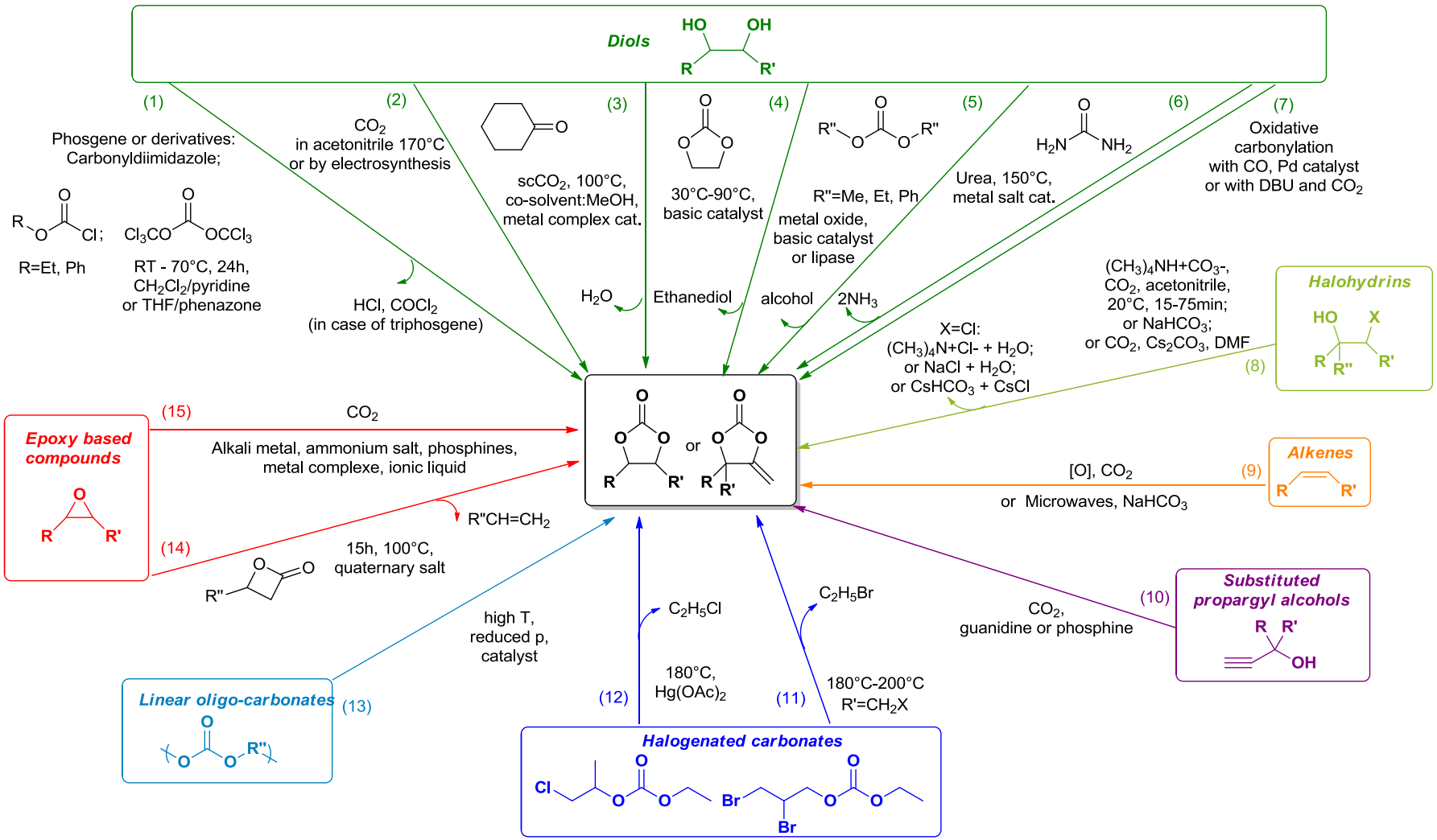
Among all these methods, there are two main synthetic routes leading to five-membered cyclic carbonates: the reaction of an epoxy precursor with carbon dioxide (Scheme 2-(15)) or the reaction of 1,2-diol with phosgene and its derivatives (Scheme 2-(1)) or with dialkyl carbonates (Scheme 2-(5)).

1,2-Diols are one of the main precursors for the synthesis of 5CCs. For the first time in 1883, Nemirovsky synthesized ethylene carbonate directly by using phosgene and ethylene glycol.[31] As another example, Burk and Roof [32] synthesized 5-membered cyclic carbonates from 1,2-diols and triphosgene using pyridine in CH_2Cl_2 at 50°C with yields in the range of 87% to 99%. Endo and coll. also used triphosgene for the synthesis of cyclic carbonates.[33,34] The high toxicity and hazards of phosgene make this way not suitable even if high yields of cyclic carbonates could be reached.

A greener alternative, is the carbonate interchange reaction between 1,2-diols and ethylene carbonate[35] (Scheme 2-(4)) or dialkyl carbonates (dimethyl carbonate, diethyl carbonate or diphenyl carbonate) (Scheme 2-(5)). This route leads to 5CCs with good yields (40-80%) in the presence of catalysts such as organic bases, metal oxide (MgO, CaO, La_2O_3) catalysts, hydrotalcite or enzymes.[36–41] The transcarbonatation of glycerol with dialkyl carbonate was also performed using different ionic liquids (ILs) as catalysts under solvent-free conditions (See Scheme 1).[42]



Scheme 1: Transcarbonatation of glycerol with DMC catalyzed by ILs[42]



Scheme 2: Main routes for the synthesis of five-membered cyclic carbonates[43–46]

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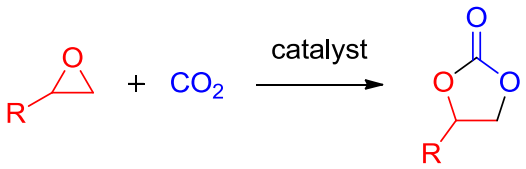
Still from 1,2-diols, other less used methods are the reactions with carbon dioxide using metallic acetates in acetonitrile[47] or by electrosynthesis[48,49] (Scheme 2-(2)), and the oxidative carbonylation with carbon monoxide using, for instance, palladium-based catalysts (Scheme 2-(7)).[50,51] The approach involving the formation of a ketal from ethylene glycol and cyclohexanone, which then reacts in the presence of supercritical CO_2, is also a route to 5CCs (Scheme 2-(3)).[52]

The reaction of 1,2-diols with urea in the presence of catalysts is another way for the synthesis of 5CCs (Scheme 2-(6)).[53,54] Lim *et al.*[55] achieved the synthesis of cyclic and linear carbonates from diols and alcohols by using a transition metal-free synthesis. The cyclization process was carried out with DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) in dibromomethane under 5 to 10 bars of CO_2, leading to good yields (47-86%).

Nevertheless, the insertion of gaseous carbon dioxide into the epoxy ring still remains the most convenient method of obtaining five-membered cyclic carbonates (Scheme 2-(15) and Scheme 3).



Scheme 3: Coupling oxiranes and CO_2 to yield 5-membered cyclic carbonate

Recently, a significant number of reports have been released concerning the development of carbonation methods of epoxy compounds with CO_2 for cyclic carbonate synthesis.[56–58] Such method presents various advantages compared to the previous presented routes. Indeed, first the recapture of the CO_2 is a benefit regarding both the economical and environmental points of view.[59] 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 a 100% atom economical reaction. The carbon dioxide both acts as an aprotic solvent and as a reagent.[60] The most represented catalytic systems are based on transition-metal complexes. However, simple complexes were replaced by more complex bimetallic ones (See Scheme 4).[61,62]

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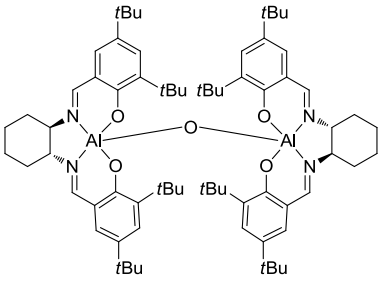
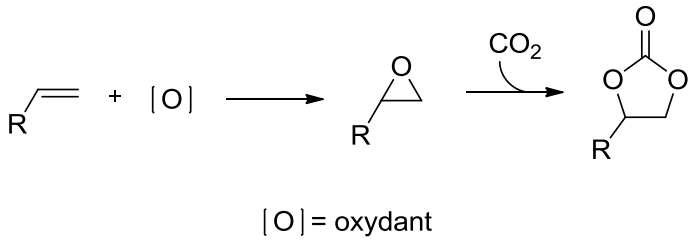


Scheme 4: Bimetallic aluminium(salen) complex [62]

Despite this bimetallic complex structure, these catalysts required harsh reaction conditions and significant amounts of the catalyst. Introducing an ammonium[63,64] or phosphonium salt[65] in the complex appears to be a good compromise to overcome this problem. There are also a number of systems containing tertiary amines as co-catalysts described in the literature.[66,67]

In addition to the latter binary systems, a new group of transition-metal complex catalysts have been developed, called bifunctional catalysts.[68,69] From an industrial approach, the most suitable catalysts for the preparation of 5CCs are quaternary ammonium salts. Recently, new examples of binary[70] and bifunctional[71] catalysts have been developed. Few other catalytic systems have been investigated including ionic liquids,[72] alkali metal halide-based catalysts[73–77] and MOF's (Metal Organic Frameworks)[78–81] with diverse results.



Scheme 5: Two steps synthesis of 5CCs from olefins

Despite the fact that insertion of carbon dioxide into oxiranes is a well-developed route to 5CCs, promising studies have been undertaken to directly convert olefins or alkynes into cyclic carbonates by oxidative carboxylation[82,83] (Scheme 2-(9)). Scheme 5 depicts the straightforward synthesis of 5CCs from olefins. It can be viewed as the coupling of two sequential reactions: epoxidation of olefins and CO_2 cyclo-addition to the epoxides so-formed. The facile synthetic approach combined with the more accessible starting materials make this carbonate synthesis

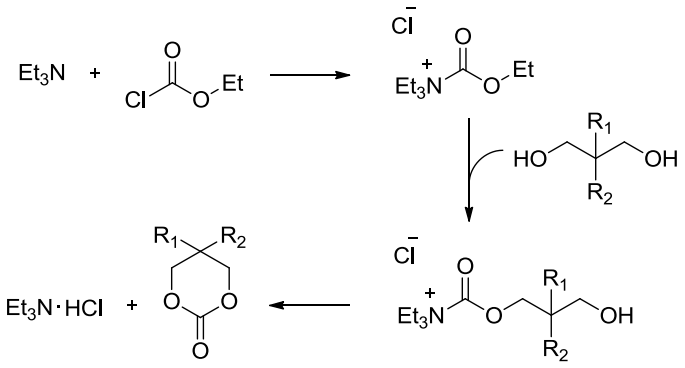
simpler and cheaper, with an industrial potential. Recently, the group of Kleij[84] employed this method to produce 5CCs directly from fatty acids using a binary catalyst comprising an Al(III) aminotriphenolate complex.

5CCs can also be prepared from halohydrins using sodium bicarbonate (Scheme 2-(8))[85] or cesium carbonate in DMF[86] under mild conditions. In addition, in the presence of guanidine catalyst, the reaction of substituted propargyl alcohols with CO_2 (Scheme 2-(10)) can produce 5CCs with yields up to 82%.[87] The phosphine-catalyzed transformation of propargyl alcohol (Scheme 2-(10)) gives also access to 5CCs.[88] From another example, halogenated carbonates can be converted into 5CCs at a temperature between 180°C and 200°C (Scheme 2-(11)-(12)).[89,90]

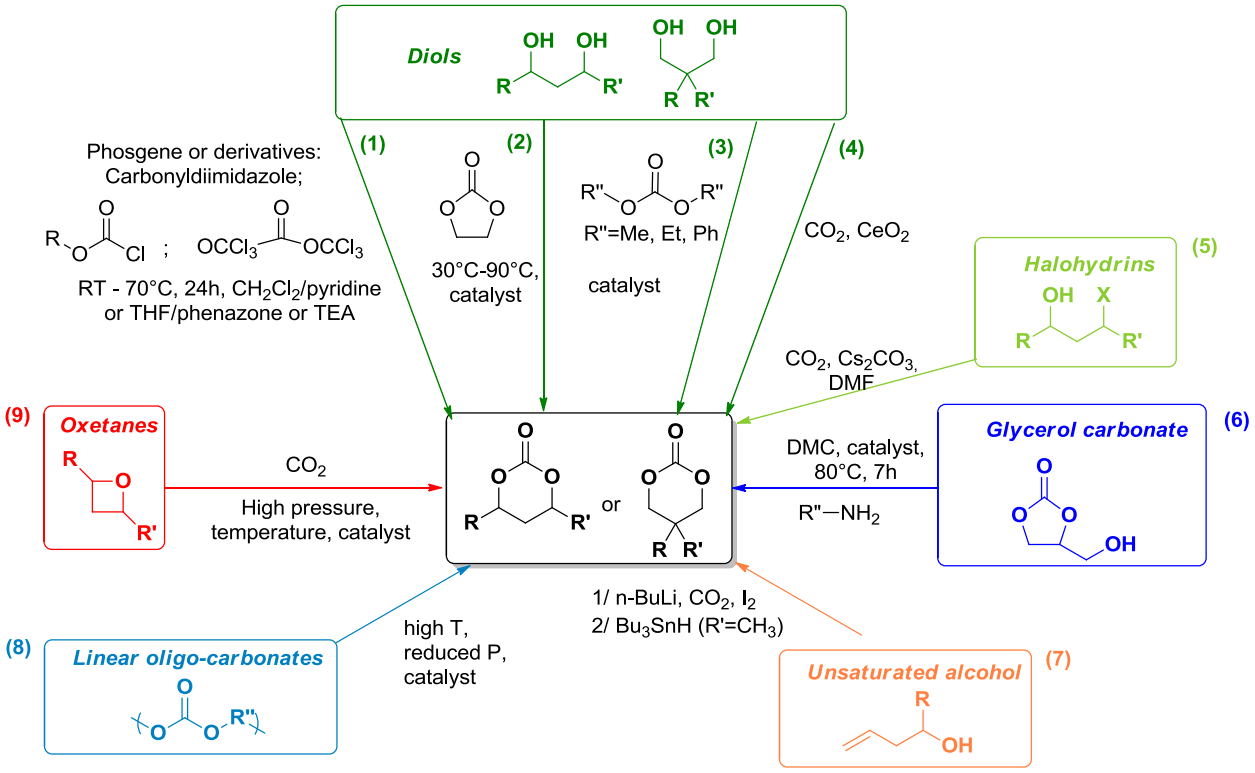
2.2. Synthesis of 6-membered cyclic carbonates (6CCs)

The 6-membered cyclic carbonates (6CCs) can be prepared by number of routes as the ones used for the synthesis of 5CCs. They are commonly obtained via the reaction of 1,3-diols with phosgene derivatives. In a less extent, 6CCs can be prepared from 3,4-unsaturated alcohols, halohydrins or oxetanes with CO_2. These main approaches are summarized in the Scheme 7 and were recently reviewed by Rokicki,[21] Dove[19] and Zhang[5] groups.

A universal method to afford 6CCs has been developed by Matsuo *et al.*[91] involving the use of ethyl chloroformate in the presence of a stoichiometric amount of triethylamine (Scheme 7-(2)). The authors proposed that the formation of a specific ammonium salt as an intermediate derivative is the driving force of the reaction (Scheme 6). The low temperature also favours the ring closure of the six-membered carbonate (yields up to 60%).



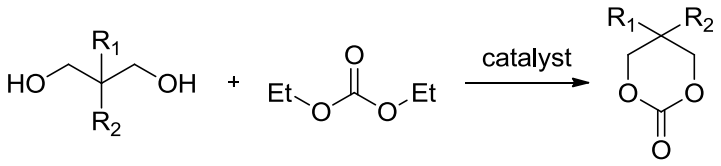
Scheme 6: Synthesis of six-membered cyclic carbonates from 1,3-diols an ethyl chloroformate



Scheme 7: Main synthetic methods for the synthesis of 6-membered cyclic carbonates

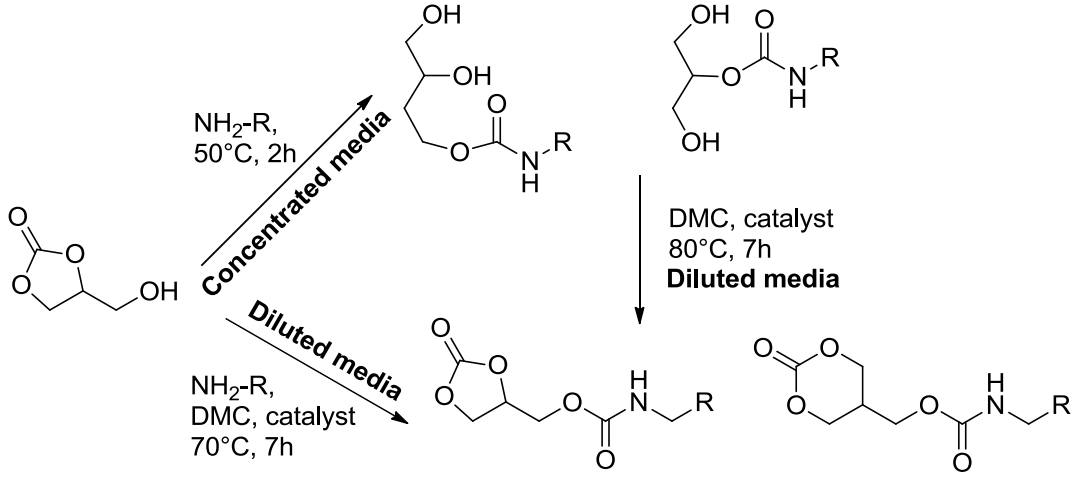
This method is largely used for the formation of functional 6CCs further detailed in the last part of this chapter. Similarly, other phosgene derivatives such as triphosgene also give 6-membered cyclic products with good yields.[34,92]

A similar method to afford 6CCs from 1,3-diols uses dialkyl carbonates as carbonation agent (Scheme 7-(1) and Scheme 8). Carothers and Van Natta[93] first described the synthesis of six-membered cyclic carbonates by transcarbonatation of propane-1,3-diols with diethyl carbonate. The reaction was catalyzed with sodium ethanolate with 40% yield. The presence of a catalyst is essential for this carbonate interchange.[16] Possible catalysts are alkaline metals,[94,95] amines, basic ion-exchange resins,[96] oxides, alkoxides, or carboxylate salt of zinc, titanium, or tin,[97–99] enzymatic catalysts,[100] etc.



Scheme 8: Synthesis of six-membered cyclic carbonates from 1,3-diols and diethyl carbonate

Mouloungui and co-workers[101] have investigated the synthesis of 5CCs and 6CCs with α-urethane group from glycerol carbonate and dimethyl carbonate (DMC) in the presence of various catalysts, without solvents (Scheme 7-(6); Scheme 9). The authors demonstrated that cyclic carbonates having exocyclic urethane functions are hydrophobic systems widely used to switch the hydrophilicity of glycerol carbonate.



Scheme 9: Synthesis of 5- and 6-membered cyclic carbonates with an α-urethane group[101]

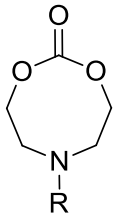
Another approach is about the synthesis of 6CCs from various diols with CO_2 (130-160°C, 5MPa) and CeO_2 as a catalyst (Scheme 7-(4)).[102] The selectivity and the yields are particularly high (up to 99%). The reaction of oxetane with CO_2 (Scheme 7-(9)) can also be used to prepare 6CCs. However, the addition of CO_2 is less efficient with oxetane in comparison to epoxides. Moreover, the efficiency of this reaction dramatically decreases with the number and the size of the substituents.[103,104] The 6CCs have also been synthesized from halohydrins with CO_2 using cesium carbonate in DMF (Scheme 7-(5)).[86]

Therefore, six-membered cyclic carbonates are the most widely studied class of cyclic carbonate monomers because of their stability and ease of synthesis as well as polymerization.

2.3. Synthesis of 7-membered or larger cyclic carbonates

In the case of seven-membered and larger ring size cyclic carbonates, they can be either prepared by the same transcarbonatation reaction pathways as those leading to five- and six-membered rings or by reaction of appropriate diols with phosgene (or its derivative) in the presence of antipyrine.[105,106] However, due to the low stability of seven-membered cyclic carbonates, cyclic dimers are formed almost exclusively.[18] In the transcarbonatation-depolymerization method, dimers are formed when the monomer ring contains 7 to 12 linkages. For larger monomer ring, both monomer and dimer are formed.[23]

The only way to obtain 7CC in its monomeric form is the reaction of butane-1,4-diol with triphosgene in the presence of antipyrine in anhydrous chloroform. It is a versatile method allowing the synthesis of 7CCs with phenyl, methyl, or cyclic acetal side-groups.[107,108]



Scheme 10: 8-membered ring cyclic carbonate[109]

More recently, Venkataraman *et al.*[109] synthesized a 8CC from N-substituted diethanolamine (Scheme 10). Organocatalytic ring-opening polymerization (ROP) of eight-membered cyclic carbonates was explored as a route to access narrowly dispersed polymers of predictable molecular weights. Yuen *et al.*[110] also prepared 8CC monomers and dimers for further polyaddition with diamines to achieve poly(hydroxyurethane)s.

3. Ring-opening polymerization of cyclic carbonates

Ring-opening polymerization (ROP) is, together with chain (radical and ionic) polymerization and condensation polymerization, one of the main routes to industrial polymers. Particularly controlled ROP has proved to be a useful strategy to engineering polymers with specific and tunable properties.

The ring strain, explained by the distortion of the ring angles and bond stretching, is the driving force for monomer conversion into polymer. The five-membered cyclic carbonate monomers are the less strained due to sp^2 hybridization of the carbon atom in the carbonyl group which may be problematic for polymerization purpose. However, the flat geometry of the carbonate moieties in the six-membered cycle increases its strain and thus its polymerizability.

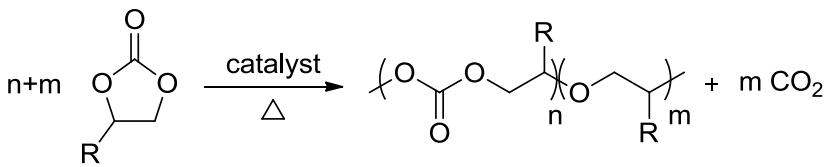
In addition, the ability of cyclic monomers to polymerize *via* ring-opening process depends also on thermodynamics. Indeed, as it is well known, Gibbs energy (free enthalpy) change ($\Delta Gp = \Delta Hp - T\Delta Sp$) should be negative. Most of cyclic monomers have ΔHp and ΔSp both negative. Thus, temperature plays a key role to get negative free enthalpy of polymerization. Monomers can polymerize only below a temperature known as the ceiling temperature.[111]

In the next sections, the state of the art regarding the ring-opening polymerization of both 5CCs and 6CCs will be detailed. Few examples will be also given about the polymerization of 7CCs and larger membered cyclic carbonates.

3.1. Polymerization of 5-membered cyclic carbonates

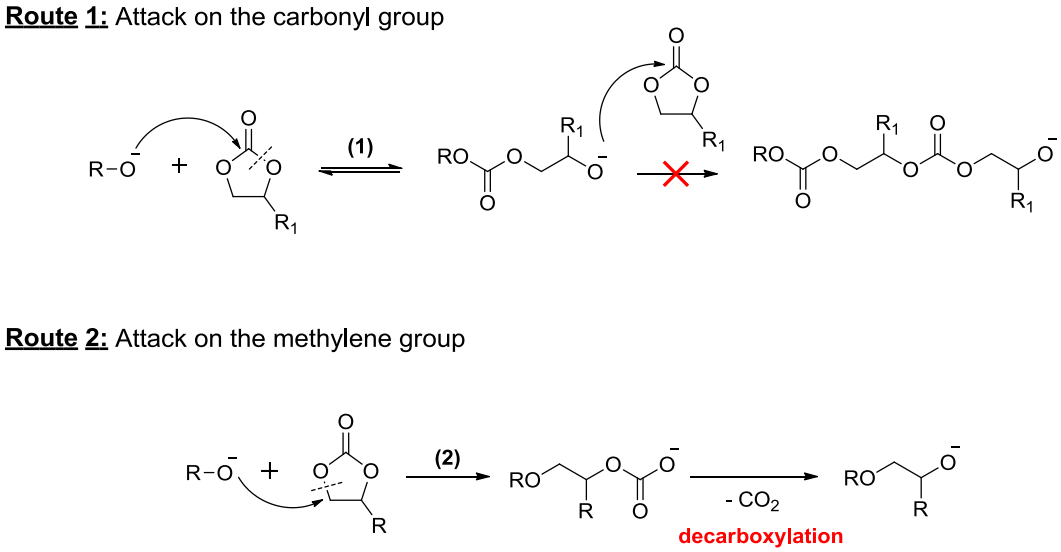
3.1.1. Polymerization of 5CCs

Contrary to most of cyclic monomers, five-membered cyclic carbonates behave differently in ROP. The high polymerization enthalpy of ethylene carbonate (EC) (125.6 $kJ.mol^{-1}$) makes it impossible to synthesize true poly(ethylene carbonate). However, at high temperature (above 120°C), polymerization of ethylene carbonate generally results in a copolymer composed of ethylene oxide (EO) units with a content of carbonate units lower than 50 mol.% (Scheme 11). This is the consequence of the carbon dioxide formation during polymerization. Indeed, decarboxylation during polymerization makes this reaction thermodynamically feasible by increasing the entropy of the polymerization.[112] Ether linkages are undesired especially when polycarbonates are used in biomedical applications.



Scheme 11: Poly(alkylene carbonate-*co*-alkylene oxide) prepared by ROP of 5CCs

Ring-opening polymerization of EC by several different catalysts has been reported.[16] All the catalysts used for polymerization of ethylene carbonate result in copolymers having different content of ether and carbonate linkages. The process of EC polymerization with an alkaline initiator was analyzed and discussed by Lee and Litt.[113] Other research groups[112,114–116] investigated basic catalysts (KOH, CH_3OK, NaI, and NaCl etc.), which revealed that content of carbonate linkages in the copolymers decreases to only 10-20 mol.%. Lee *et al.*[113] polymerized EC in bulk at 150–200 °C using various amounts of KOH as initiator. The authors showed that even in the very early stage of the polymerization, the content of EC units was not higher than 32 mol.% and for longer reaction times, the content of EO units increases. Two possible attacks of the propagating species are considered to explain the decarboxylation side reaction (Scheme 12).



Scheme 12: Formation of poly(ethylene ether-carbonate)s.

The alkoxide ion and EC monomer can react with respect to two pathways. According to route 1 the carbonyl group in EC is attacked by the alkoxide ion thus forming the carbonate function. On the other hand, the route 2 depicts the nucleophilic attack of the anion on the methylene carbon nearby the carbonyl group resulting in a decarboxylation and the irreversible formation of an alkylene oxide unit. It is noteworthy that the carbonyl attack is kinetically favored over the alkylene one; however this reaction is reversible. In addition, the product of reaction (1) cannot react with another EC molecule because the formation of the EC–EC sequence is thermodynamically forbidden. Lee and Litt[113] suggested that the most probable EC

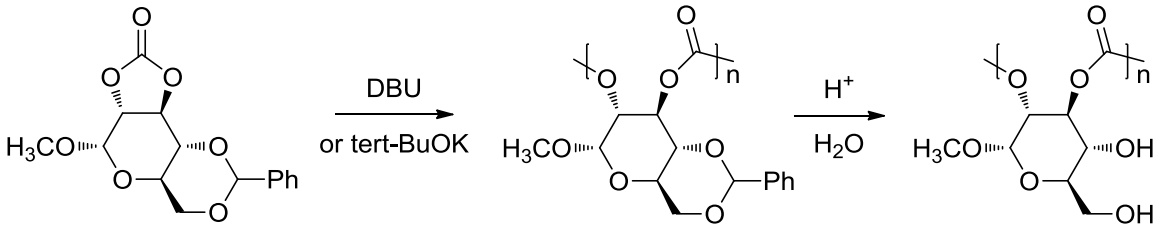
polymerization mechanism under basic conditions should be a combination of a carbonyl carbon attack (1) and an alkylene carbon attack (2).

Other catalysts dealing with 5CCs polymerization were investigated. More specifically, Lewis acids or transcarbonatation catalysts (metal alkoxides of tin, zirconium and metal acetyl acetonates) produce copolymers that contain about 40–50 mol.% ethylene carbonate units along with unwanted ethylene oxide units.[117–120] Organic catalyst (namely *t*-BuP_4) was also used by Zhang *et al.* to polymerize EC.[121] The carbonate units content was about 23-25mol.%, a value that decreases with an increase of the polymerization temperature.

Finally, heterogeneous catalyst like sodium stannate trihydrate was also reported for ethylene carbonate polymerization.[117,122] The copolymer structure was confirmed in a recent study;[123] according to the authors, the EC–EO–EO triad is the major repeating unit in the polymer chain.

3.1.2. Polymerization of 5CCs bearing strained ring of functional group

Interestingly, it has been reported that increase of the 5CCs ring-strain can favor their polymerization. In contrast to typical five-membered cyclic carbonates, which polymerize at high temperatures leading to poly (ether-carbonate)s as described above, five-membered cyclic carbonates with high ring-strain can be polymerized at relatively low temperatures, without decarboxylation side reaction. For example, the 5CC obtained from methyl 4,6-O-benzylidene-glucopyranoside (**MBCG**) was reported as a monomer leading to pure polycarbonate (Scheme 13).[111,124,125]



MBCG

Scheme 13: Polymerization of the five-membered strained cyclic carbonate

Two types of initiators were used: DBU and potassium *tert*-butoxide. It was shown that the polymerization proceeded smoothly even at 30°C leading to PC with a M_n = 14 000 g.mol^{-1} in

good yield (93%). The ring strain may result from the connection of the carbonate ring on the rigid bicyclic structure of methyl 4,6-O-benzylidene-glucopyranoside. The bio-sourced nature of the starting material (natural sugar) is interesting for biomedical applications of the resultant polycarbonate. More recently, the group of Haba[126] investigated the thermodynamic stability of different MBCG isomers. A similar example was patented by Carpentier and co-workers starting from cyclohexene carbonate as a monomer.[127]

In order to bring some functionality to polycarbonate from EC, many derivatives of EC have been developed in the recent years.[84] The latter can contain various reactive groups such as vinyl moieties, esters, ethers and alcohols. Nevertheless, only glycerol carbonate (GC) has been industrialized so far. The synthesis of GC has been discussed in the previous part (Synthesis of 5-membered cyclic carbonates (5CCs)). In terms of polymerization, GC is considered as a latent AB_2-type monomer and can be used for the synthesis of hyperbranched poly(hydroxyether)s.[128] Such branched polymers exhibit a flexible polyether core and a multihydroxyl external sphere. An overview of multiple possible reactions with glycerol carbonate was made by Guittard and co-workers.[28]

Vinylic functionality can also be brought to 5CCs from the corresponding epoxide substrates. The two main cyclic carbonates with vinylic moieties are the vinyl ethylene carbonate[129] (**1**) and the 4-phenyl-5-vinyl-1,3-dioxolan-2-one[130] (**2**) from corresponding oxirane molecules. Their structures are depicted in Figure 4.

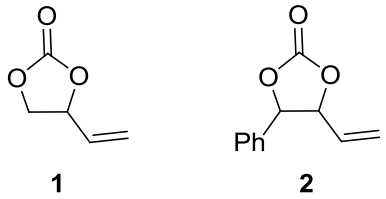


Figure 4: Vinylic-functionalized 5CCs

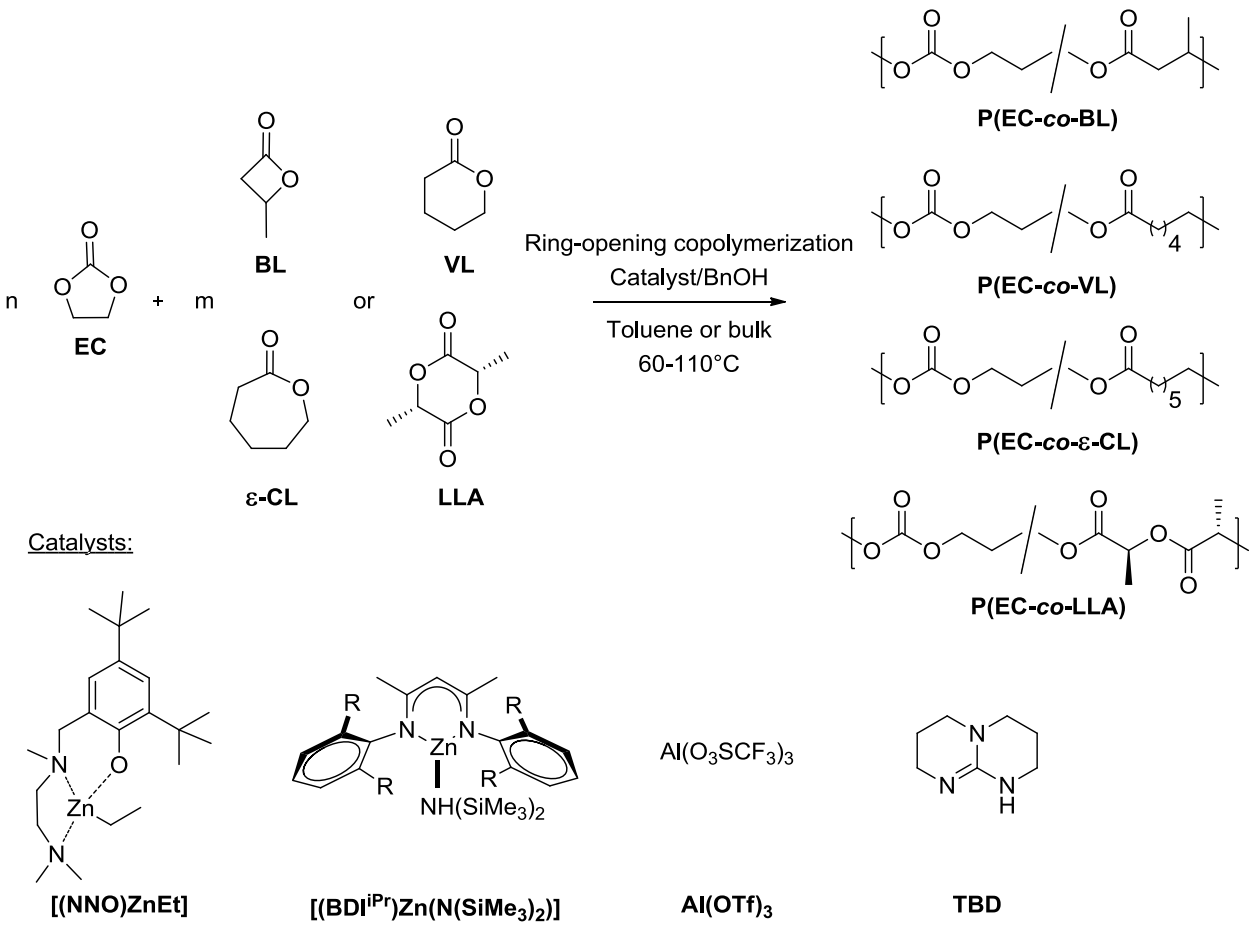
Such monomers can be polymerized by a free-radical process to produce polymeric species with pendent five-membered cyclic carbonate functionality. These polymers can be further cross-linked by reaction with amines. Although the homopolymerization of both monomers produces polymers in relatively low yield, copolymerization with other vinylic monomers effectively provided cyclic carbonate-containing copolymers.

3.1.3. Copolymerization of 5CCs

As mentioned in a previous part, classical five-membered cyclic carbonates do not homopolymerize to afford pure polycarbonates because of unfavorable thermodynamic characteristics. However, these monomers can undergo copolymerization with more reactive heterocyclic monomers.

Many studies have been reported on the 5CC copolymerizations with cyclic esters such as β-butyrolactone (BL), δ-valerolactone (VL), ε-caprolactone (ε-CL) or L-lactide (LLA).[115,121,131–139] Most of these copolymerizations involve rare earth complexes as catalysts. Among these examples, Shirahama and coll.[133] synthesized copolymers of EC with ε-CL or VL using $(C_5Me_5)_2SmMe(THF)$ as a catalyst. The resulting copolymers exhibit really high molar mass (Mn=140 000 $g.mol^{-1}$) with up to 30 mol.% of EC units. They also revealed that the EC/ε-CL copolymers were obtained in better yield compared with that of EC/VL copolymers. Chen and co-workers[135] also prepared EC/ε-CL copolymers in the presence of neodymium as single-component catalyst. With up to 22 mol.% of EC units, the copolymers exhibited increased glass transition temperatures and reduced melting temperatures together with an enhanced elongation percentage at break compared to true Poly(ε-CL).

In addition, Scheme 14 illustrates the work of Guillaume's group about the copolymerization of EC with cyclic ester monomers yielding random poly(ester-carbonate).[131] All polymerizations were carried out under mild conditions (60-100°C) in toluene or bulk affording relatively high molar mass copolymers (M_n=6 000-93 350 $g.mol^{-1}$) combined with moderate dispersity (1.24-2.15). It is worth noticing that most of the polymerizations proceeded without decarboxylation side-reaction.



Scheme 14: Synthesis of poly(ester-carbonate)s by ROCP of EC with BL, VL, CL and LLA

Kuran and coll.[140–142] investigated the copolymerization of 5CCs with oxiranes in the presence of zinc-based organometallic catalysts. However, the poly(ether-carbonate)s obtained were characterized by a lower content of carbonate units with respect to ether units. Rokicki and Nguyen[143,144] described that the reaction of oxiranes with five-membered cyclic carbonates in the presence of $BF_3{\cdot}OEt_2$ as a cationic initiator led to spiroorthocarbonates, poly(ether-carbonate)s, or polyethers, depending on the oxirane ring substituent. It was found that the copolymerization proceeded through a trialkoxycarbenium cation stabilized by adjacent three oxygen atoms, being thermodynamically favored.

Höcker's group reported that unreactive five-membered cyclic carbonates such as EC and PC can be successfully copolymerized with tetramethylene urea (TeU) to afford polyurethanes.[132,145,146] The polyurethanes obtained were characterized by random distribution of TeU–EC and TeU-PC units and containing up to 54 mol.% of PC repeating untis.

At last, unreactive five-membered carbonates can undergo copolymerization with more reactive 6-membered one. Still, the content of EC units in the resulting copolymer was rather small, not exceeding a few mol.%. The group of Shen[147] reported the copolymerization of EC with 2,2-dimethyltrimethylene carbonate catalyzed by Lanthanide Tris(2,6-di-tert-butyl-4-methylphenolate) illustrated in Figure 5.

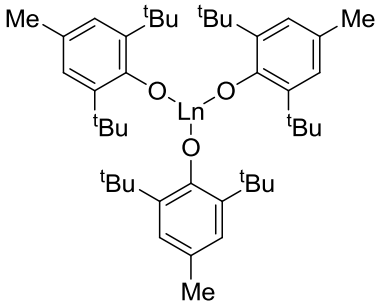


Figure 5: Chemical structure of Lanthanide-based catalyst (Ln = La, Nd, Sm, or Dy).

Best results in terms of yields and intrinsic viscosities were obtained using lanthanum as lanthanide. The authors demonstrated that mechanical properties of these polymers such as the tensile strength, tensile modulus and elongation at break were enhanced significantly with increasing EC incorporation.

3.2. Polymerization of 6-membered cyclic carbonates

In contrast to thermodynamically unfavorable 5-membered cyclic carbonates, 6-membered cyclic carbonates easily polymerize to obtain PCs. 6CCs can be polymerized through 4 methods namely anionic, cationic, coordination-insertion and enzymatic polymerization. Although a brief overview will be given for the cationic and enzymatic pathways, this part will only detail the two most used mechanisms, i.e. the anionic and coordination-insertion pathways.

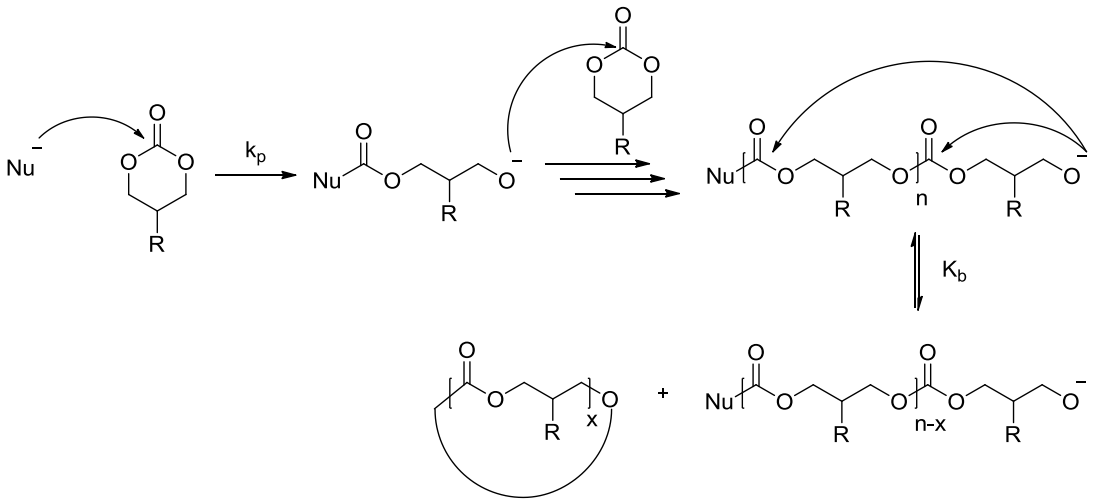
In the case of ROP of 6CCs proceeding through a cationic mechanism, electrophilic reagents are used as initiators. Brønsted and Lewis acids, as well as alkyl esters of strong organic acids (e.g., methyl trifluoromethanesulfonate) are most often involved.[148–159] However, the main drawback of the cationic polymerization of 6CCs is the occurrence of decarboxylation and back-biting side reactions thus leading to low molar mass copolymers.

Enzymatic polymerization appears to be a feasible alternative to prepare aliphatic polycarbonates as chemical methods often require extremely pure monomers and anhydrous conditions. The unnecessary removal of the enzyme from the resultant polymer is also an advantage. Trimethylene carbonate (TMC) was the first cyclic carbonate to be polymerized by ring-opening polymerization in the presence of lipases, particularly CALB[160,161] and porcine pancreatic lipase.[162] Recently, Mespouille *et al.*[20] reviewed this research field.

3.2.1. Anionic Ring Opening Polymerization (AROP)

Anionic initiators afford usually high molar mass APCs from the ring-opening polymerization of 6-membered cyclic carbonates. In addition, contrarily to polymers obtained by cationic ROP, the ones resulting from anionic ROP do not contain ether linkages.

Regarding the mechanism involved (Scheme 15), the initiation reaction consists in the nucleophilic attack of the initiator on the carbonyl group followed by the formation of the active species (an alkoxide) after cleavage of the carbon-oxygen bond. Both the nucleophilicity of the initiator and the electrophilicity of the monomer have a significant impact on the initiation process. A slow initiation in comparison to the propagation step leads to broad dispersity and a loss of molar mass control. Besides these two polymerization steps, transcarbonatation side-reactions can also occur. The most common side reaction is the intramolecular attack of the active species on the carbonyl group leading to cyclic oligomers, known as backbiting reaction. An important feature of AROP of 6-membered cyclic carbonates is its equilibrium feature, with the presence of residual monomer at the end of the polymerization. The reversible mechanism was discussed by Kühling et al.[163,164] According to the authors, the polymerization conditions such as temperature, solvent polarity, monomer concentration and the nature of the active site are essential for a decent polymerization control.

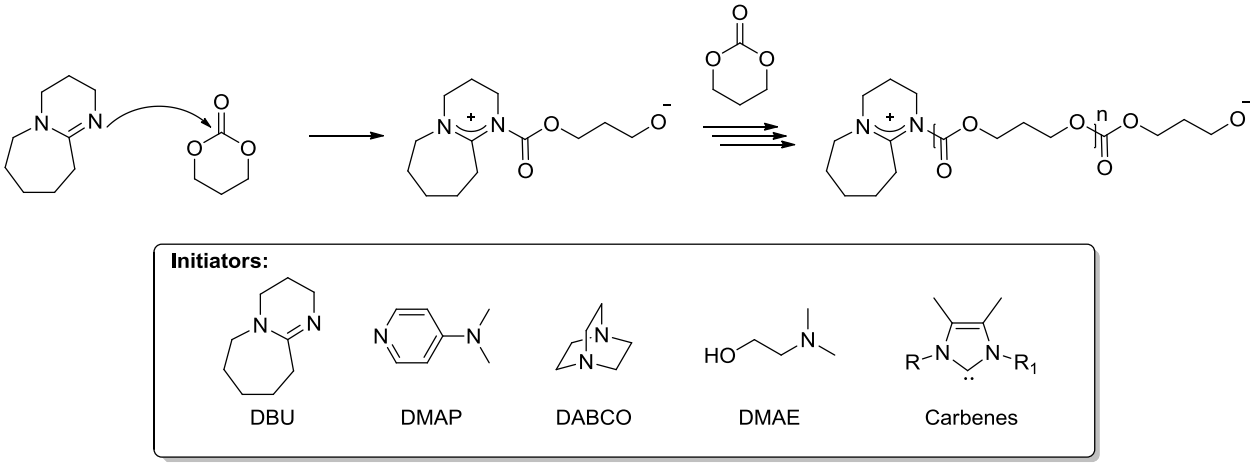


Scheme 15: Anionic polymerization of six-membered cyclic carbonate with nucleophilic initiators

The anionic ROP of TMC was first reported by Carothers and Van Natta[93,165] in the 30s using K_2CO_3 as an initiator. Since then, many other initiators were able to polymerize 6-membered cyclic carbonates. Among them, several studies reported the use of nucleophilic initiators based on alkali metal alkoxides-containing compounds.[98,166–169] Such systems were found to also afford cyclic oligomers during the polymerization. For this type of initiators, the backbiting reaction rate constant (k_b) is close to the one of propagation (k_p). Other initiators based on alkali metals such as sec-butyllithium (sec-BuLi)[170] as well as sodium and potassium naphthalene[171] were also surveyed. Rokicki *et al.*[171] showed that, when potassium naphthalene reacts with cyclic carbonates (1:2 molar ratio), dialkoxide species are formed.

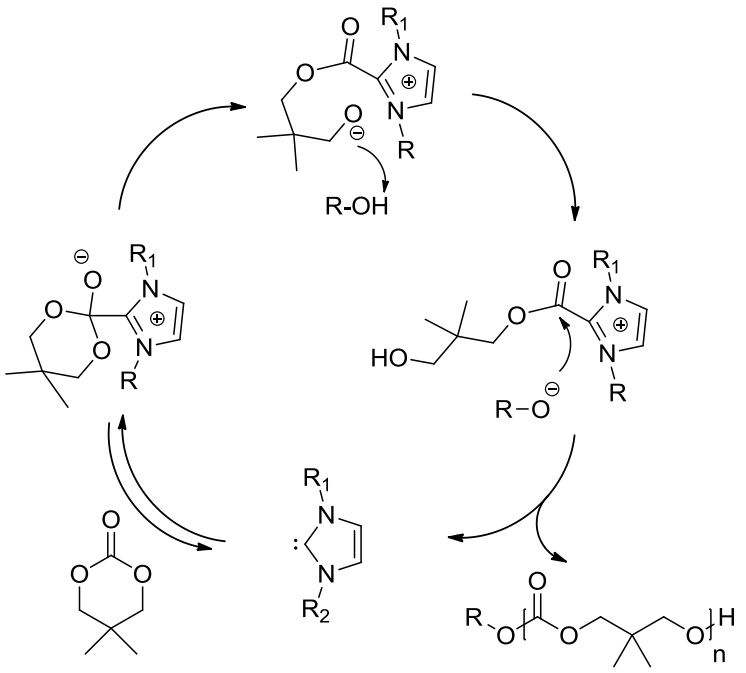
However, an important issue for the polymeric materials used in the biomedical field is the presence of residual toxic catalysts. For this purpose, non-metallic catalysts were thus investigated. Murayama *et al.*[172] were the first to show that tertiary amines such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO), and 4-dimethylaminopyridine (DMAP) afforded the polymerization of 6-membered cyclic carbonates (Scheme 16). Using DBU as initiator at 120°C, a polycarbonate with relatively low molar mass (6 400 $g.mol^{-1}$) was obtained in short time (1 h). However, no polymer was obtained when triethylamine, aniline, N,N-dimethylaniline, or pyridine were used. These low activities might be due to the large steric hindrance around the nitrogen atom for triethylamine or the aromatic resonance decreasing the nucleophilicity of the aromatic amines. The authors proposed a

zwitterionic polymerization mechanism, which was confirmed by FD-MS analysis proving the presence of DBU end-group. Thus, the reaction between DBU and a cyclic carbonate to form an alkoxide anion is the initiating step of the polymerization. In the propagation step, the alkoxide anion attacks the carbonyl group of the cyclic carbonate to yield the corresponding PC. This mechanism is called nucleophilic monomer activation.



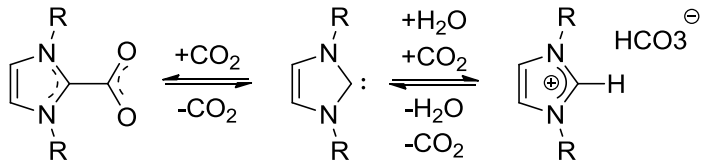
Scheme 16: Anionic ring-opening polymerization of TMC initiated by DBU

N-Heterocyclic Carbenes (NHCs) can also act as organocatalysts for ROP of cyclic carbonates. These catalysts used to be applied for various reactions such as transcarbonatation and benzoin condensation.[173] Lately, NHCs have also been introduced in polymer chemistry as powerful organic catalysts in polymerization of heterocyclic monomers.[174] Hedrick *et al*. reported the NHC-catalyzed ROP of TMC in a controlled manner.[175] The strong nucleophilicity of NHC enables high monomer conversion (>99%) in a short time (30 min). Wang and coll.[176] used recently benzyl, isopropyl and methyl substituted imidazol-2-ylidenes for polymerization of 5,5-dimethyl-1,3-dioxan-2-one (2,2-DTC). According to the authors, polymerization proceeded according to a monomer-activated mechanism (Scheme 17).



Scheme 17: Proposed mechanism for the polymerization of DTC catalyzed by NHC with BnOH

However, the main limitation with the use of NHCs in polymer chemistry is linked to their air and moisture sensitivity.[177] To overcome this drawback, several research groups have developed masked NHC over the past years. Among them, Taton *et al.*[178–180] discovered recently that imidazolium hydrogen carbonates $[NHC(H)]^+$ $[HCO_3]^-$ were a straightforward source of NHCs. Such precursors can be conveniently handled and stored in air without any particular precautions even though their catalytic activities are lower than free NHCs.

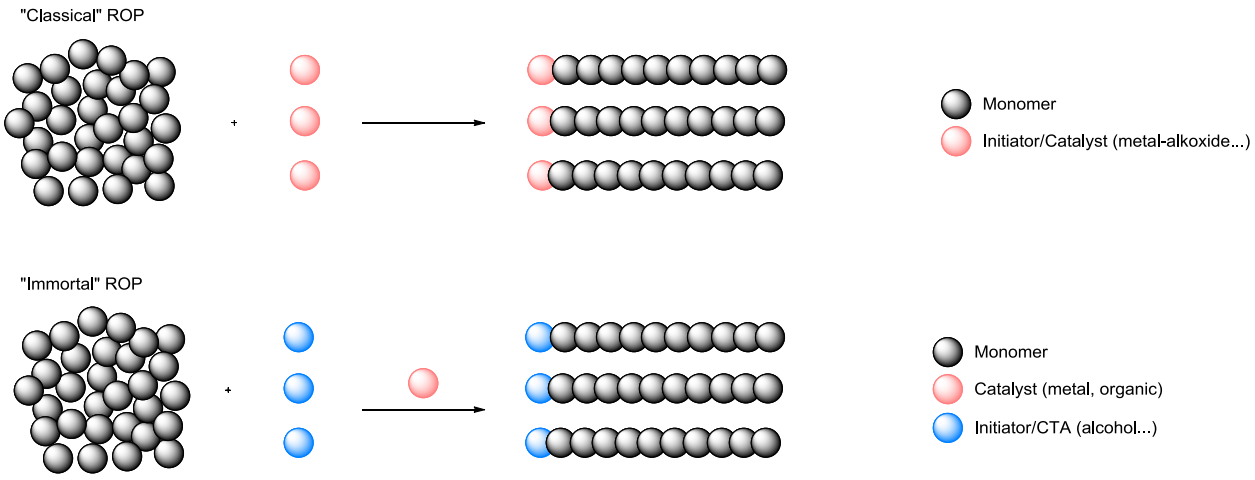


Scheme 18: Reversible generation of NHCs from [NHC(H)] [HCO_3] salts and NHC-CO_2 adducts

Fliedel and coll.[181] investigated the use of NHCs as ligands for transition-metal catalysts in the ROP of cyclic carbonates. The authors reported that the bi-component complex NHC/$Zn(C_6F_5)_2$ mediated the ROP of TMC under mild conditions.[182] These catalytic systems can be used for obtaining PTMC-PLA block copolymers in a controlled and so-called 'immortal' fashion.

In the past years, organocatalysts were then combined with initiators (usually alcohols) to perform the ROP of cyclic carbonates according to an "immortal" process. The concept of 'immortal' ring-opening polymerization (iROP) was invented by Inoue.[183] It was then revisited by Guillaume and Carpentier[184,185] for the iROP of cyclic esters and cyclic carbonates. The "classical" ROP and the "immortal" ROP are outlined in Scheme 19.

In a "classical" ROP, the number of growing polymer chains depends on the number of initiating groups (e.g., alkoxide moieties) attached to the metal center. The number of groups cannot exceed the largest oxidation state of the metal (usually four for the metal used in such a coordination–insertion approach). The catalyst can also be an organic catalyst (Scheme 16). Thus, in a 'classical living' ROP, the molar mass of the polymer can be estimated from the monomer-to-initiator molar ratio. However this approach suffers from several weaknesses. Impurities possibly present in the reaction media may deactivate initiating moieties leading to a drastic decrease of the final molar mass of the polymer. Moreover, possible residues of the metal catalyst are another limitation, as they may disturb material properties, especially those dedicated for microelectronics, biosensors, medicine and food packaging.



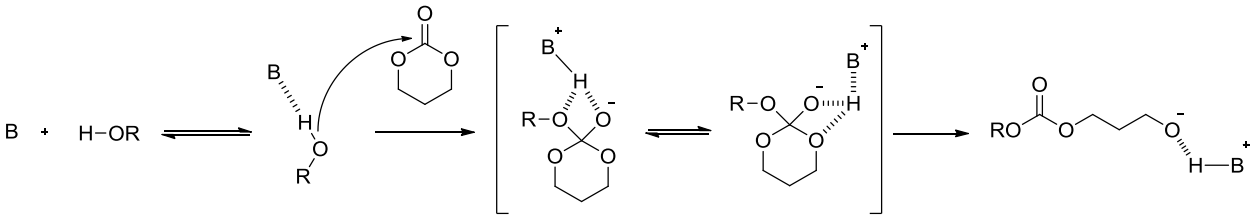
Scheme 19: Schematic illustration of "classical" ROP vs. "immortal" ROP[184]

In constrast, in iROP, an initiator also acts as a chain transfer agent (CTA). The initiator/CTA is a protic source, typically an alcohol, introduced in large excess with respect to the catalyst. In such processes, the initiation is faster than the propagation and the termination step is avoided. The "immortal" feature is due to the reversibility of the chain transfer reactions between dormant and

active macromolecular chains, which leads to the revival of the polymer chains once dead. Thus, the polymer molar mass is given only by the initial monomer/initiator ratio, independently of the catalytic loading. As a result, immortal polymerization can afford polymers with a controlled molar mass and very low amount of catalyst' residues.

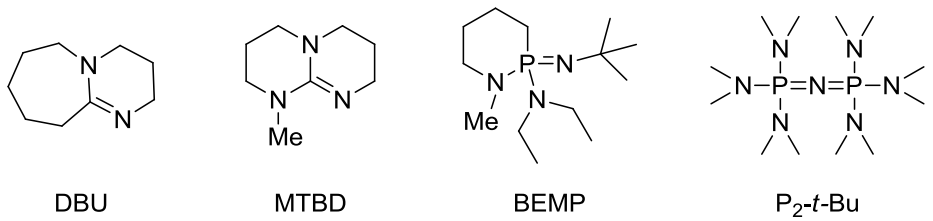
Guillaume's groups have also investigated the use of metallo-organic catalytic systems in combination with benzyl alcohol (BnOH) acting as initiator and CTA in the iROP of six-membered cyclic carbonates.[185–190] The authors used the dual-catalyst systems combining a discrete cationic metal complex with a tertiary amine.[191] The process was carried out under mild conditions. Such a dual approach bridges the gap between the coordination/insertion and activated-monomer pathways.

Like DBU, other "H-bonding" catalysts have been investigated in the iROP of cyclic carbonates. Since the work of Hedrick in 2001 on the organocatalyzed ROP of lactide using DMAP and 4-pyrrolidine-pyridine as organic catalysts,[192] the development of organic catalysis has expanded rapidly. There have been many attempts to elucidate the appropriate combinations of organocatalysts and monomers for producing precisely controlled polymerization systems.[193,194] This type of organocatalysts can be either monofunctional or bifunctional.[195]



Scheme 20: Initiator/chain end mechanism for ROP of TMC catalyzed by mono functional catalyst

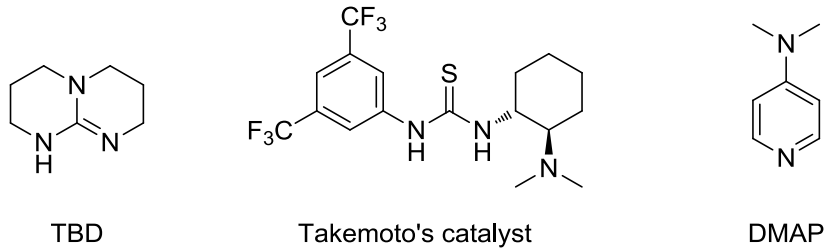
Besides DBU, which is an amidine, other mono functional organocatalyst as MTBD (guanidine) and phosphazenes ((BEMP) and P2-t-Bu) are employed as H-bond acceptor catalysts for ROP of cyclic carbonates (Scheme 21). H-bonding between the initiator BnOH and the catalysts activates the initiator and the growing chain. The catalysts behave as proton shuttles from the nucleophilic reactant to the chain-end, along the ring-opening steps (Scheme 20).



Scheme 21: Mono functional H-bond acceptor catalyst for ROP of cyclic carbonates

Concerning the ROP of TMC, DBU and MTBD combined with BnOH induced a well-controlled process affording the corresponding PTMC. The bulk ROP of TMC was shown to exhibit a 'living' character performing chain extension experiments in the presence of DBU and BnOH.[196] Very recently, Coulembier *et al.* reported the use of an organic catalyst system such as DBU capable of switching between active and dormant propagating states during the ROP of cyclic carbonates.[197]

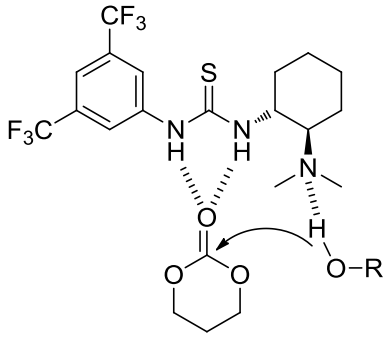
Secondly, in contrast to their monofunctional counterparts, bifunctional catalysts presented in Scheme 22 have the advantage of activating both the monomer and the initiator or the growing chain-end at the same time by forming an H-bonded complex with these two partners. Due to its rigid structure, no self-aggregation of the catalyst was noticed.



Scheme 22: Bifunctional organocatalysts for ROP of cyclic carbonates

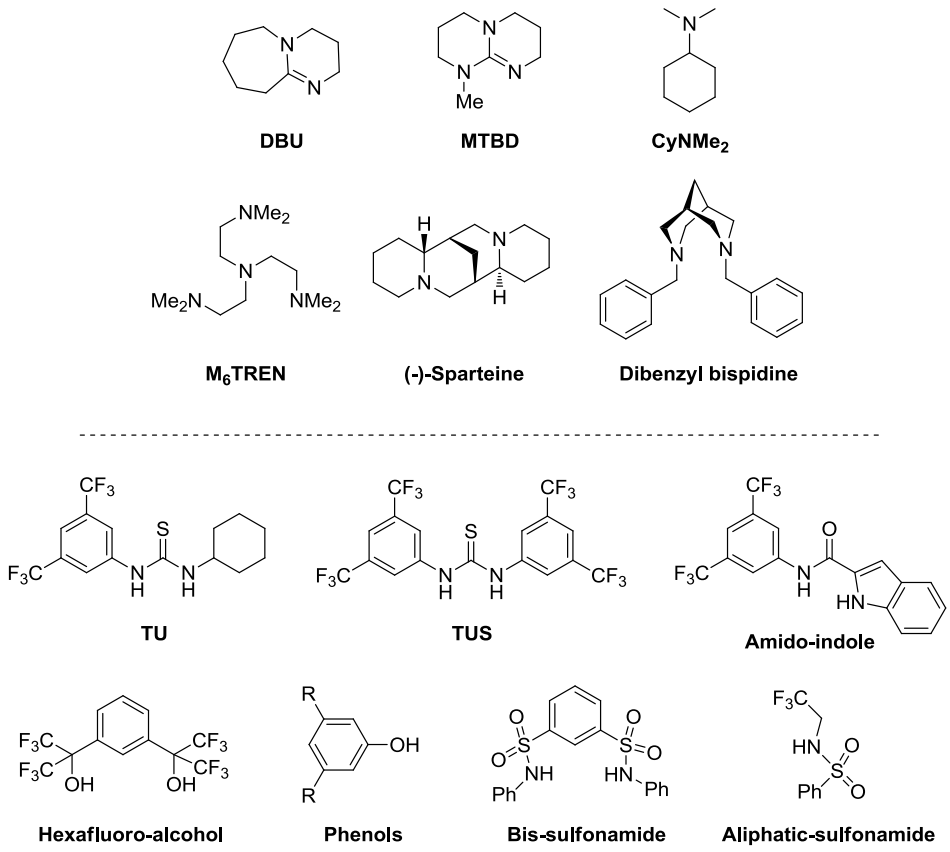
Among these bifunctional molecules, Waymouth and Hedrick groups[198] have first demonstrated the ability of Takemoto's catalyst to afford ROP of lactide. The catalyst behaved as a "proton shuttle", by capturing and transferring a proton during the nucleophilic and ring-opening elementary steps. Guanidine such as TBD also catalyzed the ROP of TMC in a controlled fashion ($Đ<1.15$), if reaction times were short.[199] Finally, methanesulfonic (CH_3SO_3H) and triflic (CF_3SO_3H) acids have proved to be efficient bifunctional organocatalysts for the controlled ROP

of six-membered cyclic carbonates in the presence of an alcohol as an initiator.[152,153,200] The sulfonic acids were predicted to be bifunctional catalysts for both elementary steps, thus acting as an H-bonding moiety with the monomer and the initiator, as well as a proton shuttle *via* their acidic hydrogen and basic oxygen atoms.

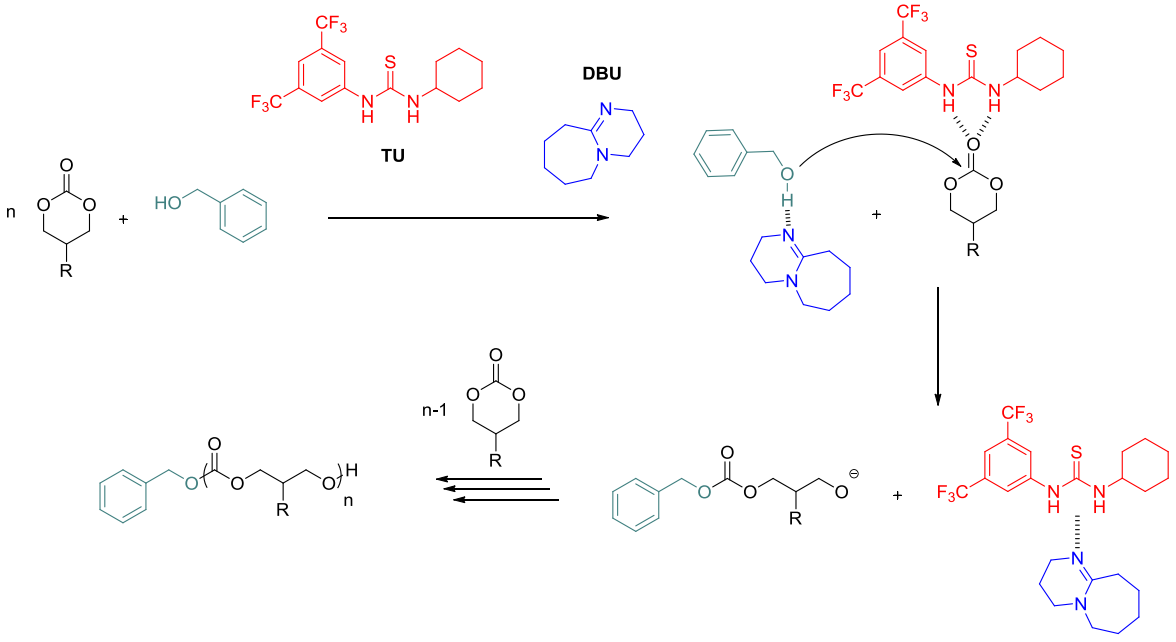


Scheme 23: Dual activation by bifunctional Takemoto's catalyst

Contrarily to the previously mentioned catalysts, the use of a bimolecular catalytic system, composed of a H-bond donor (D) and a H-bond acceptor (A) compound, is also possible. Compared to bifunctional catalysts, the latter may be easily obtained from commercial substrates and numerous D + A combinations are available; however, the possible H-bonding between both species may be an issue. The choice of H-bond acceptor compounds depends on the monomer structure and reactivity and on the catalyst partner. Typical structures of H-bond acceptors are presented in Scheme 24-up. Concerning H-bond donor catalysts, different organic structures have been tested over the past years (Scheme 24-down). The first catalytic systems were studied in 2006, using a combination of thiourea, TU, with various amines to catalyze the polymerization of cyclic esters in the presence of an alcohol as initiator.[201] For the co-catalysts examined, the magnitude of their binding constant has been shown to be proportional to the rate of polymerization. Therefore, the cocatalyst binding constant represents the catalytic activity of the system. Interestingly, the strongly binding TU/DBU system acted kinetically as a unimolecular catalyst species. It could be representative of a hydrogen-bonding analogue of so-called 'cooperative ion pairing' in asymmetric organocatalysis.[202] The mechanism is detailed in Scheme 25.



Scheme 24: H-bond acceptor (up) and donor (down) catalysts for ROP



Scheme 25: Mechanism for ROP of cyclic carbonates catalyzed by the catalytic system TU/DBU

Several authors presented the ROP of cyclic carbonates (often bearing functional groups) catalyzed by catalytic quantities of DBU and a cocatalyst such as TU, with a primary alcohol as initiator.[109,199,203–214] The alcohol initiator is activated by DBU, while the electrophilic carbonyl group of the monomer is activated by the thiourea *via* hydrogen bonding in both cases. The terminal hydrogen-bonded alcohol becomes 'dormant' when all the monomer is consumed but the chain-growth process restarts after addition of a second batch of cyclic carbonate. When desired, the reaction is terminated by protonation with an acid (e.g., benzoic acid), or by end-capping the terminal alcohol with acetyl chloride or acetic anhydride.

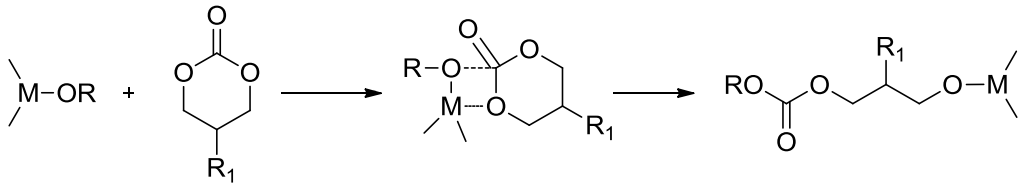
Other tertiary amines, (-)-sparteine or dibenzyl bispidine for instance, are used more sporadically with TU as cocatalyst for the controlled ROP of cyclic carbonates.[215]

Few examples have been reported in the literature about the ROP of cyclic carbonates with different couples such as hexafluoro-alcohol/sparteine[216] or phenols/tertiary amines.[217]

To conclude this part, the anionic polymerization of cyclic carbonates is the most widely used method affording aliphatic polycarbonates in a controlled manner without undesirable decarboxylation side reactions.

3.2.2. Coordination-Insertion polymerization

An alternative mechanism for the ROP of six-membered cyclic carbonates is the coordination–insertion pathway. In this mechanism, the propagating species and its counterion share a covalent bond. In addition, this method requires the use of a metal-based catalyst since the propagation is proceeding by coordination of the monomer to the active species, followed by insertion of the monomer into the metal–oxygen bond by rearrangement of the electrons (Scheme 26). Generally, no ether linkages are observed in the afforded polycarbonates obtained by this pathway. The reaction is terminated by hydrolysis forming a hydroxyl end-group.



Scheme 26: Coordination-insertion mechanism for ROP of 6CCs

For the metal-catalyzed ROP of 6CCs, a variety of catalytic systems have been proposed and reported in the literature. This section will be divided into the different metal catalysts.

Tin-based catalysts

In the last decades, the tin complexes with bidentate ligands attracted much attention as active catalyst for the ROP of cyclic esters and cyclic carbonates. Tin(II) 2-ethylhexanoate (Figure 6), commonly referred to as stannous octoate ($Sn(Oct)_2$), is the most frequently used catalyst due to a high activity and a rather low toxicity, as approved by the American Food and Drug Administration (FDA).

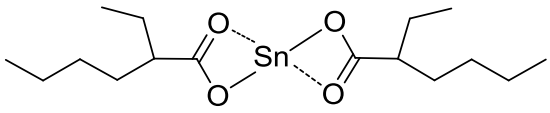
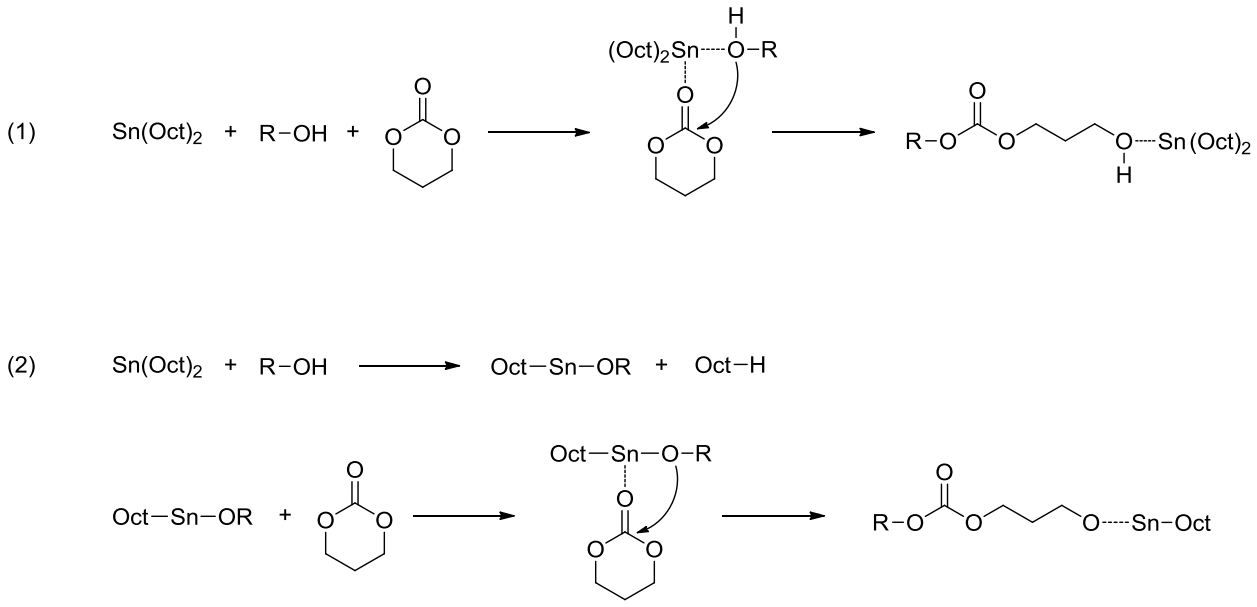


Figure 6: Structure of $Sn(Oct)_2$

Using $Sn(Oct)_2$ and an alcohol as initiator, studies of the coordination-insertion mechanism have resulted in two slightly different reaction pathways. Hovestadt *et al.*[218] and Kricheldorf *et al.*[219] have respectively proposed a mechanism in which the initiating alcohol function and the monomer are both coordinated to the $Sn(Oct)_2$ complex during the initiation step (Scheme 27-(1)). Other groups[220–222] have presented a mechanism in which $Sn(Oct)_2$ is converted into a Tin alkoxide before complexation and ring-opening of the monomer (Scheme 27-(2)). In addition, Kricheldorf and coll.[223] proved that addition of benzyl alcohol accelerated the polymerization reaction and allowed the control of the polymer molar mass by adjusting the [monomer]/[alcohol] ratio. Without the use of initiator, very high molar mass can be obtained (M_n = 450 000 $g.mol^{-1}$) by TMC polymerization at 130°C for 3 days.[224] The control of the temperature around 100–120°C is also an important parameter.[223] Below these values, an alcohol-type initiator is needed to obtain a fast polymerization. This initiator is incorporated into the chain and thus forming alkyl carbonate end-groups. Above 120°C, TMC can obviously undergo direct insertion into the metal-carbonate bond resulting in octanoate ester end-groups.



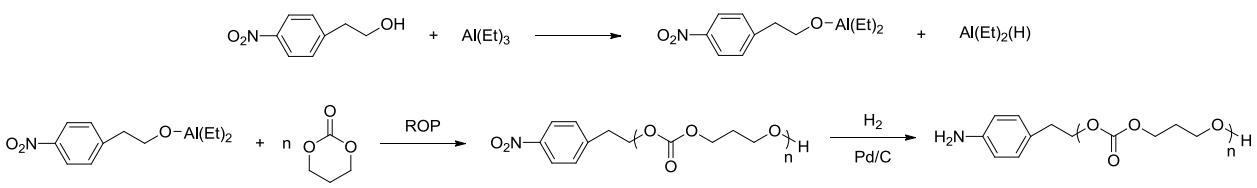
Scheme 27: Mechanisms proposed for the ROP of TMC catalyzed by $Sn(Oct)_2$

Other tin-based catalysts can also be applied for the polymerization of six-membered cyclic carbonates. For instance, Kricheldorf and Stricker[219] showed that $Bu_2Sn(Oct)_2$ could be used for the ROP of TMC with similar reactivity than $Sn(Oct)_2$. Recently, Ruzicka and coworkers[225] reported on the catalytic activity of bisamidinato and bisguanidinato tin(IV) diolates for the ROP of TMC.

Aluminum-based catalysts

Due to their high selectivity, aluminum alkoxides are frequently used to obtain well-defined PCs. Indeed, the PC molar masses are well controlled thanks to the fast propagation reaction compared to transcarbonatation. Moreover, various aluminum alkoxides can be prepared by reaction of triethylaluminum with selected alcohol. Consequently, end-groups can be easily tuned.

Duda and Penczek[226,227] investigated the coordination-insertion ROP mechanism catalyzed by aluminium-based compound through kinetic studies. An interesting example dealing with Al-based catalyst in ROP was reported by Hedrick.[228] The catalysts were efficient for the polymerization of TMC leading to polymers terminated by a single nitrophenyl group (M_n = 9500 $g.mol^{-1}$). These nitro groups after reduction under mild conditions afforded aminophenyl end-capped PCs (Scheme 28).



Scheme 28: NH_2 terminated PTMC catalyzed by Al-based compound

More recently, Koller[229] reported an highly active aluminum-based catalyst bearing phenylene-diamine ligands affording synthesis of well-defined polymers. Interestingly, the catalyst is cheap, versatile and highly active toward the polymerization of TMC and other cyclic esters without the need of solvent and exhibits turnover frequencies (TOF) of up to 36 900 h^{-1}.

Rare earth-based catalysts

A large variety of rare earth derivatives have been used to initiate the ROP of cyclic carbonates. In contrast to the conditions required for tin-based or aluminum-based catalysts, mild conditions are sufficient to polymerize TMC with Lanthanide-based catalyst, for instance $Ln(OAr)_3$[230]. As rare earth metals, La (lanthanum), Ce (cerium), Nd (neodymium), Sm (samarium), Gd (gadolinium), Dy (dysprosium), Er (erbium), Yb (ytterbium), Sc (scandium), and Y (yttrium) are the most often used.[231]

Carpentier and co-workers developed cationic divalent rare earth complexes to mediate controlled ROP reactions. The general aspects of the synthesis of rare earth borohydride complexes and their applications as initiators for the ROP of polar monomers have been reviewed recently.[232,233] Guillaume and coll. synthesized and applied β-diketiminate borohydrides of both divalent and trivalent rare earth elements[234] and bis(phosphinimino)methanide borohydride complexes of lanthanum, yttrium, and lutetium[235] for the ROP of TMC.

3.2.3. Copolymerization of 6-membered cyclic carbonates

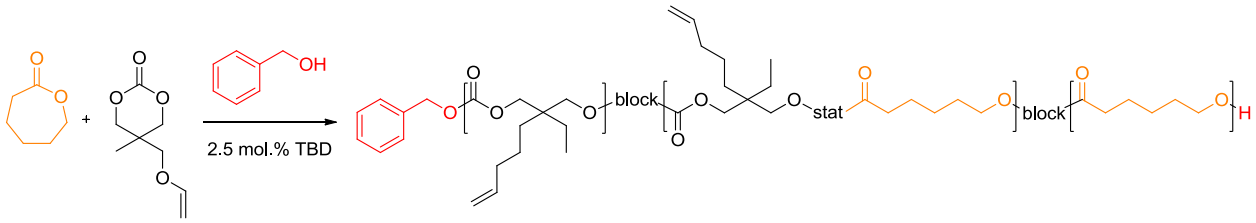
Six-membered cyclic carbonates can be easily copolymerized with different heterocyclic monomers such as different cyclic carbonates (five-, six-, and seven-membered), lactones or oxiranes. The copolymerization between cyclic carbonates is often used to bring functionality to the PTMC backbone. Such a topic is covered in Part 4: Towards functional APCs. Besides, since biodegradable polymers are mainly based on brittle polyesters, many studies have been undertaken on the copolymerization of lactones, lactides or glycolides with cyclic carbonates.

The objective is to prepare polyesters more flexible by introducing elastic aliphatic carbonate segments. Moreover, the introduction of carbonate monomer units enables a regulation of the polymer biodegradation rate.

For instance, Katz *et al.*[236] reported the synthesis of a bioabsorbable suture material produced by copolymerization of glycolide with approximately 32.5 mol.% of softer TMC units. As mentioned above, the incorporation of carbonate linkages improve the polyesters performance. In addition, the carbonate linkages are more stable to hydrolysis *in vitro* because of the absence of acidic groups (which catalyze the hydrolysis). However, the hydrolysis of the carbonate proceeds faster *in vivo* and the copolymer can be used as a bioabsorbable material.[237,238]

Yang *et al.* copolymerized randomly TMC with ε-CL to enhance the properties of PTMC for the preparation of the implanted devices.[239,240] Peruch and coworkers[241] prepared also dihydroxyl-telechelic ε-CL/TMC random copolymers catalyzed by methanesulfonic acid. The authors claimed that the poly(TMC-*co*-ε-CL) samples presented the expected microstructural characteristics, a unimodal molar mass distribution and a very narrow dispersity.

Remarkably, Albertsson and coworkers[242] employed a monomer-specific "on/off switch" to synthesize a nine-block copolymer composed by a functional cyclic carbonate and ε-CL with a controlled molar mass with a narrow distribution (Scheme 29). The authors played on the dependence of polymerization rate with temperature for the two monomers. Under similar reaction conditions, the ratio of the apparent rate constant of the functional cyclic carbonate (AOMEC) and ε-CL [K_p^{app}(AOMEC)/ K_p^{app} (ε-CL)] changes from 400 at T = -40 °C to 50 at T = 30 °C and 10 at T = 100 °C. Thus, the conversion of ε-CL can be switched "off" at -40°C and switched "on" again at 30°C. This study provides a new straightforward synthetic route to degradable multiblock copolymers, yielding new interesting materials with endless structural possibilities. This type of copolymers can be also used as drug carriers.[243]



Scheme 29: Synthetic route for the copolymerization of AOMEC and ε-CL with TBD as catalyst

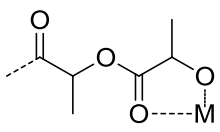
Zhu *et al*.[244] prepared biodegradable antimicrobial copolymers by copolymerization of ε-CL with 5,5-dibromomethyl trimethylene carbonate (DBTC) followed by the quaternization reaction between the functional polymer and a series of N,N-dimethyl alkylamines.

Considering the poor dimensional stability under physiological conditions of the copolymers of TMC and ε-CL with intermediate compositions (30-70% TMC), Grijpma and coll. used gamma irradiation to cross-link PTMC-*co*-ε-CL (co)polymers.[245] The mechanical properties of the obtained networks range from flexible and elastomeric to relatively rigid materials. Similarly, by adjusting the composition, the erosion behavior of the networks can be tuned from relatively rapid surface erosion to slow bulk erosion processes. The authors claimed that such materials can be used for biomedical applications.

Similarly, Gu's group also improved the form stability and lowered the degradation rate of PTMC by cross-linking with a bis-lactone.[246]

Finally, Guillaume's group described the first examples of β-benzyl malolactonate/carbonate copolymers.[247,248] Such copolymers appeared to be promising precursors to nano-vectors derived from the corresponding amphiphilic poly(carbonate-*co*-(β-malic acid) copolymers.

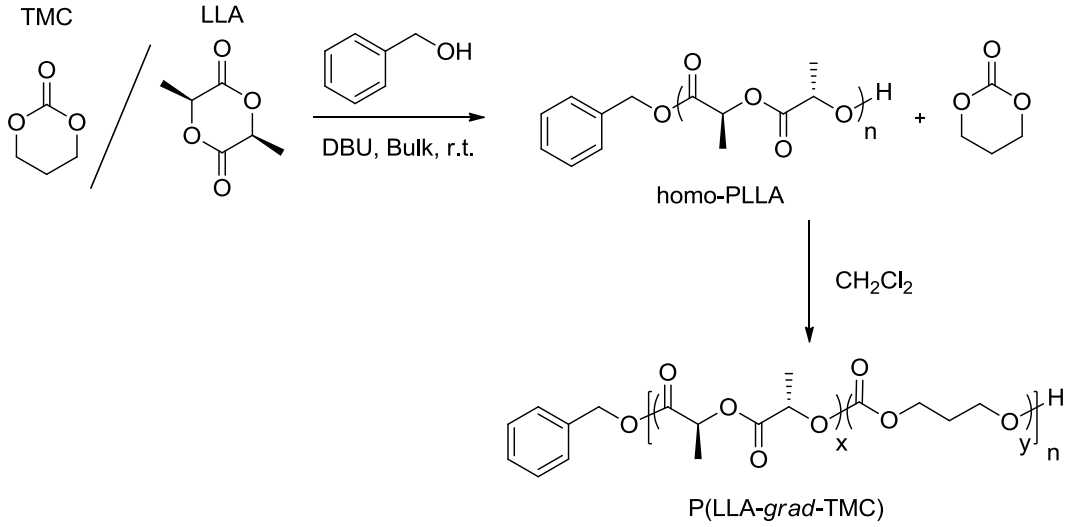
Regarding the copolymerization between cyclic carbonates and lactides catalyzed by a metallic species, several studies revealed that the microstructure of the copolymer depends on the order in which the monomer was polymerized first.[249,250] It has been noticed that when L,L-Lactide (LLA) was polymerized first, a random copolymer was formed, whereas the addition of LLA to a living polycarbonate resulted in a block copolymer. In addition, the copolymerization of a mixture of LLA and cyclic carbonate also resulted in a random copolymer. Taking these results into account, the authors proposed the following mechanism: the PLLA active centers are well-stabilized by the adjacent carbonyl group (enol formation) and by the formation of a five-membered cyclic complex including the metallic species (Scheme 30). Once the active center of PLLA has reacted with the cyclic carbonate, the newly formed active site has a reduced capability of stabilization.



Scheme 30: LLA active species in ring-opening polymerization[249]

More recently, Guillaume's and Carpentier's groups reported the synthesis of L-lactide/trimethylene carbonate block copolymers as thermoplastic elastomers.[251] Several metallic complex (namely β-diiminate zinc complex) and organic catalytic systems (such as DMAP, BMEP and $Al(OTf)_3$) have been used to enable the controlled copolymerization of TMC and LLA. By tuning the size of the amorphous polycarbonate segment, the authors managed to improve the ductility of the polymer by a factor of 25 while maintaining the stiffness of the material. The same group also synthesized gradient copolymers having PLLA and PTMC blocks of significant lengths.[252]

Surprisingly, Coulembier and coworkers[253] discovered that LLA and TMC were able to form a fluid eutectic melt within few minutes at 23.1°C, temperature at which each monomer is solid (melting temperature of LLA=98.3 °C and TMC= 46.0 °C). Taking advantage of this phenomenon, the authors synthesized L-lactide and gradient copolymers from a LLA/TMC eutectic melt without any solvent. The authors reported that when DBU was used as a catalyst, the homopolymerization of LLA from its eutectic LLA/TMC melt at room temperature was only observed. They exploited the discrimination between the two monomers for the preparation of poly(L-lactide-gradient-trimethylene carbonate) (Scheme 31).



Scheme 31: Preparation of LLA/TMC gradient copolymers from the eutectic melt of monomers[253]

Lastly, Han *et al.* used TMC/LLA copolymers for reinforcement of short poly(lactide-co-glycolide) (PLGA) fibers[254] as well as bioresorbable composites.[255]

3.3. Polymerization of 7-membered or larger cyclic carbonates

Due to relatively high ring strain, the ROP of seven-membered cyclic carbonates (7CCs) proceeds easier than that of the six-membered ones. However, because of difficulty in the synthesis of the monomer,[18] the number of reports concerning the polymerization of 7CCs is rather limited. Nevertheless, cationic ROP of seven-membered cyclic carbonates has been reported for the first time by Hayakawa in 1997.[156] It was achieved using a zirconocene complex as a catalyst. Endo *et al.* also found that such monomers underwent polymerization in the presence of an alcohol and a Brønsted acid as the initiator and activator, respectively.[157,256]

It is worth noticing that in contrast to a six-membered cyclic carbonates, the cationic polymerization of seven-membered cyclic carbonates leads to the corresponding polymer without ether linkages thanks to the faster propagation reaction compared to the backbiting degradation.[257]

Anionic polymerization can also be used to polymerize seven-membered cyclic carbonates. It was found that ring strained monomers easily undergo ring-opening reaction. As an example, the polymerization of a 7CC initiated with sec-BuLi and carried out in THF afforded the corresponding polycarbonate in a relatively high yield in a short time.[106]

More recently, Guillaume and co-workers obtained and polymerized methyl substituted seven-membered cyclic carbonates such as 4-methyl- and 5-methyl-1,3-dioxepan-2-one.[258] Similarly to six-membered cyclic carbonates, ROP of these monomers were carried out using various catalysts combined with an alcohol acting as an initiator and a chain transfer agent.

4. Towards functional APCs

As mentioned in the introduction, owing to their biocompatibility and biodegradability, aliphatic polycarbonates are suitable materials for bio-medical applications such as drug delivery carriers and tissue engineering scaffolds. In order to enable specific interactions with cells or organs, their chemical structure must be tailored. For this purpose, properties of non-functional aliphatic polycarbonates can either be tuned by copolymerization with other heterocyclic monomers or by introducing functional end-groups.[255,259–262] However, to precisely control the properties of polycarbonate structure, the best strategy is the post-derivatization of pendent functionalities in

the polymer backbone. Such pendent functional groups may be introduced via the ROP of cyclic carbonate monomers bearing the desired functionality. However, some functional groups can disturb the ROP process and, in some cases, the added functionality limits the polymerization efficiency. Consequently, further modifications of the polymer backbone post-polymerization is often required.

This part will describe first the ring-opening polymerization of cyclic carbonates bearing various functional groups. Then, several post-polymerization modifications of functional polycarbonates will be detailed.

4.1. Ring-opening polymerization of functional cyclic carbonates

4.1.1. Telechelic polycarbonates

Telechelic polycarbonates are polymers with well-defined functional end groups. For instance, PCs with terminal reactive hydroxyl groups at each chain-end are highly valuable starting materials for various ABA or multiblock copolymer architectures. Various synthetic strategies have been developed over the past few years for the preparation of such telechelic polycarbonates. The ROP of TMC catalyzed by different systems can directly afford the corresponding difunctionalized hydroxyl telechelic PTMC. Such macrodiols can be used as comonomers allowing the preparation of unique triblock copolymers.

Guillaume and coworkers used either borohydride complexes or bi-component catalytic systems for the ROP of TMC in a controlled/'living' manner affording linear PTMCs with functional end-groups.[190,235,263]

Zhou *et al.*[264] prepared a series of amino acid end-capped aliphatic polycarbonates by ROP of 5,5-dimethyl-1,3-dioxan-2-one initiated by N-carbobenzyloxy-L-valine without metallic catalysts. The authors noticed that the crystallization and drug release properties of the resultant polycarbonates were related to the polymer structure.

Grijpma's group[265,266] developed photo-cross-linkable PTMC macromonomers end-functionalized with methacrylate moieties obtained by ROP of TMC catalyzed by $Sn(Oct)_2$. Such macromonomers were used in stereolithography to prepare designed three-dimensional porous

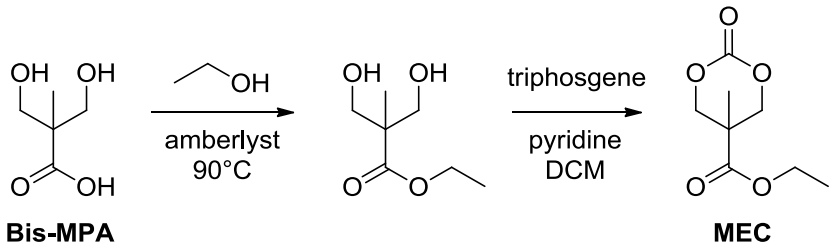
and non-porous structures. These materials have been applied as scaffolds for cartilage tissue engineering.

Moreover, Kakuchi *et al.* applied diphenyl phosphate as an efficient acidic organocatalyst for controlled/'living' ROP of TMC using different initiators.[150]

Recent advances on the synthesis of telechelic polycarbonates have been reviewed by Guillaume.[267]

4.1.2. Polycarbonates bearing alkyl functionalities

Knowing that alkyl groups don't affect the polymerizability of cyclic carbonate monomers, these moieties are often used to protect functional groups such as hydroxyl and carboxylic acid groups, which may be incompatible in a ROP process. A simple alkyl-functional monomer such as 5,5-dimethyl-1,3-dioxan-2-one (DTC) is also frequently used replacing TMC as comonomer.[268–276] Homopolymerization of DTC has been reported using various catalysts such as methyl triflate,[272] methyl iodide,[273] tin octanoate,[268,274] rare earth systems[269,271] and enzymes.[275,276] Poly(DTC) is a hydrophobic, semi-crystalline material with a melting point around 100°C which consequently leads to decreased degradation rates of the homopolymer and copolymers compared to PTMC.



Scheme 32: Synthesis of functional cyclic carbonate (MEC)[277]

Another well-known cyclic carbonate bearing an alkyl moiety is derived from the 2,2-bishydroxy(methyl)propionic acid (bis-MPA) (Scheme 32). Hedrick and coworkers have reported the copolymerization of the corresponding cyclic carbonate 5-methyl-5-ethyloxycarbonyl-1,3-dioxan-2-one (MEC) with other cyclic carbonates.[216,277–283] However, only two examples of MEC homopolymerizations have been reported in the literature.[216,279]

The ROP of carbonates bearing a group at the alpha position on the carbonate ring (Figure 7) have been investigated. **2** was polymerized through a cationic process affording the

corresponding polycarbonate without ether linkages.[158] Endo and coworkers reported the cationic homopolymerization of **1**; however only very low monomer conversions were observed and the resulting polymer was not isolated.[273] Higher monomer conversions have been reported using rare earth initiators, aluminum triflate, β-diiminate zinc complexes and organic bases.[187,230] The dissymmetry of **1** raises the question of catalyst selectivity in the ROP process. Microstructural analyses of the poly(**1**) revealed that the ring-opening is more favourable at the most hindered oxygen-acyl bond when zinc-based system was used. However, the authors noticed the absence of regioselectivity of the aluminum or guanidine catalyst systems. The difference in regioselectivity was caused by the bulky nature of the β-diiminate ligand present in the zinc-catalyzed reactions, but not in those catalyzed by aluminum triflate or organic bases.

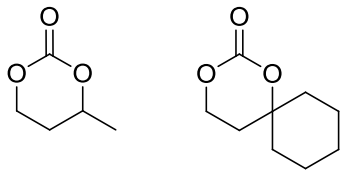


Figure 7: Functional 6CCs bearing an alkyl group at the alpha position on the carbonate ring

Finally, ring-opening of the cyclic carbonate from dihydroxyacetone ($TMC(OMe)_2$) using a range of metal-based and organic catalysts has recently received a lot of attention.[190,284] Poly($TMC(OMe)_2$) is a rigid, brittle, amorphous material with a glass transition temperature of 39–45°C.

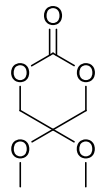


Figure 8: Functional 6CC from dihydroxyacetone

4.1.3. Polycarbonates bearing aryl functionalities

Most of aryl-functional monomers and their respective polymers contain a benzyl group. The protecting benzyl group can be subsequently removed by catalytic hydrogenation to give a polycarbonate containing either pendent hydroxyl groups or carboxyl groups offering a wide range of opportunities for further modification and functionalization. For these reasons, benzyl-functional monomers have been used extensively in the preparation of functional aliphatic poly(carbonate)s and poly(ester carbonate)s. The three most common carbonate structures bearing an aryl group are depicted in Figure 9.

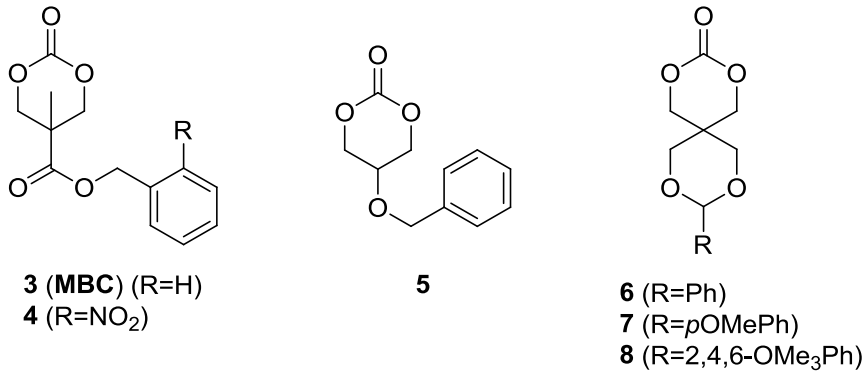


Figure 9: Functional cyclic carbonates bearing an aryl group

MBC (**3**) and 5-benzyloxy-trimethylene carbonate (**5**) have particularly received much attention. Homopolymerization of **MBC** was first reported by Bisht and coworkers in 1999 using an enzymatic route.[285] The purpose of this study was to prepare water-soluble polycarbonate having pendent carboxyl groups on the polymer backbone. Although polymer molar masses remained low due to a competitive initiation from water, higher molar masses could be obtained when the lipase was dried extensively. Additionally, the same group managed to control the degree of functionality in the polymer structure by copolymerizing **MBC** with TMC under the same conditions.[286] **MBC** was also homopolymerized using an organocatalyst such as DBU, resulting in well-defined homopolymers with controlled molar mass distributions.[287] Other research groups studied the copolymerization of **MBC** with lactide either using tin- and zinc-based catalysts[288–290] or using organocatalysts.[282,291]

Another frequently reported benzyl functional monomer is 5-benzyloxy-trimethylene carbonate (**5**). The latter can be polymerized in bulk at high temperatures using metal-based catalysts,

organic catalysts or immobilized enzymes and under reduced pressure without the use of catalyst.[188,276,292–296] Poly(**5**) homopolymers displayed medium to large dispersities (Đ = 1.41–1.92) and lower polymer molar masses than targeted (M_n=8 800-22 400 g.mol^{-1}) with [M]/[I] = 1000. The resultant materials are rubbery at room temperature with T_g around 0°C.

Nitrobenzyl-functional monomer (**4**) and methoxy functional monomers (**7** and **8**) have been used in the synthesis of PEO block copolymers prepared by the homopolymerization of the monomers or copolymerization with lactide from macroinitiators.[297–299]

4.1.4. Polycarbonates bearing alkene and alkyne functionalities

Alkene and alkyne functional groups are involved in many organic reactions such as Michael addition, thiol-ene coupling, Huisgen 1,3-dipolar cyclo-addition, epoxidation and UV cross-linking. Thus, the incorporation of such functionalities to the polycarbonate backbone makes the resulting polymers ready for further post-polymerization modifications.[300–305]

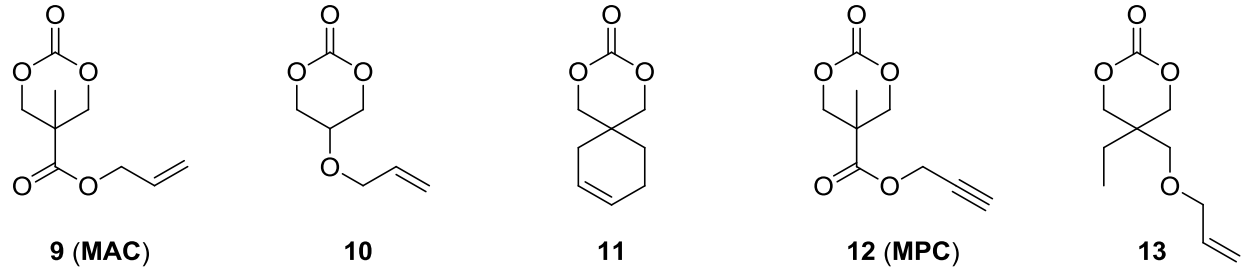


Figure 10: Functional cyclic carbonates bearing alkene or alkyne functionality

The most frequently used cyclic carbonates with alkene or alkyne functional groups are illustrated in Figure 10. The allyl ester-functional cyclic carbonate 5-methyl-5-allyloxycarbonyl-1,3-dioxan-2-one (**MAC**, **9**), has been widely employed in the preparation of a range of (co)polymers over the recent years.[206,275,306–313] First homopolymerizations of **MAC** have been performed either without added catalyst or with metal-based catalysts at high temperature.[308,311] However, these systems did not afford controlled polymerizations. In contrast, Dove and co-workers demonstrated that the ROP of **MAC** using efficient organocatalysts such as sparteine/TU led to a high level of control over the resulting polymer.[206] The ROP of **MAC** has also been reported in the synthesis of 3-armed star polymers initiated from triethanolamine.[306] The

polymerization was living and immortal, affording allyl-functional poly(carbonate)s with tunable molar masses, narrow dispersities and high hydroxyl end-group fidelity.

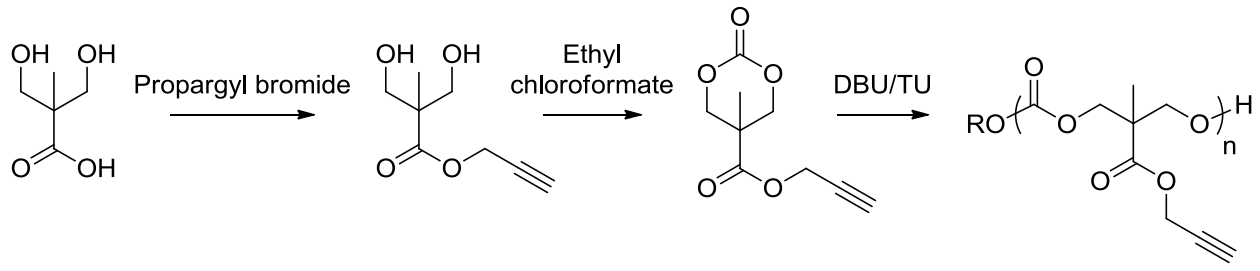
Other studies involving **MAC** have mostly focused on its copolymerization with other heterocyclic monomers. Indeed, **MAC** has been copolymerized with lactide[311] and poly(ethylene oxide)[309] yielding amphiphilic block copolymers which self-assemble as micelles.

The ROP of the related allyl-functional monomer 5-allyloxy-1,3-dioxan-2-one (**10**) has been reported by Parzuchowski[314] and He[315] affording the synthesis of a semi-crystalline poly(**10**) that was characterized by a melting temperature around room temperature and a low glass transition temperature (T_g= -40 °C).

In order to improve the thermal properties of the PCs, Gross and co-workers prepared the cyclohexene functional monomer (**11**).[316,317] Polycarbonates with more rigid backbone and higher glass transition temperature (T_g= 32°C) were obtained.

Recently, Dove and co-workers showed that the synthesis and subsequent ROP of **13** using a dual organocatalytic system provides a simple two-step method to present well-defined aliphatic polycarbonates bearing pendent allyl ether groups.[209]

Surprisingly, the only propargyl functional cyclic carbonate reported is 5-methyl-5-propargyloxycarbonyl-1,3-dioxan-2-one (**MPC**, **12**). The groups of Dubois and Dove investigated the homopolymerization of **12** using the dual catalyst system of TU and DBU (Scheme 33).[318] The resulting homopolymers showed low dispersities and high end-group fidelity.



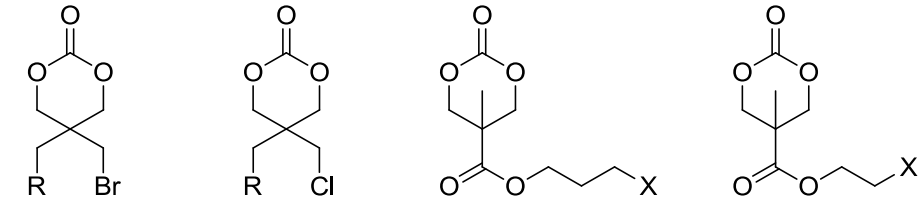
Scheme 33: Synthesis of ROP of propargyl functional cyclic carbonate

This monomer has only been copolymerized with lactide or trimethylene carbonate.[199,319–323] The resulting copolymers displayed **MPC** content in agreement with the feed and ranging from 7 to

20 mol.%. It was also found that **MPC** was incorporated preferentially to TMC at the beginning of the polymerization.

4.1.5. Polycarbonates bearing halide functionalities

Cyclic carbonates bearing halogen groups have been developed by several research groups since it allows subsequent nucleophilic substitution and introduction of novel functionalities even after polymerization. Mindemark *et al.* reported the synthesis and polymerization of four halide-containing monomers (**13-16**, Figure 11).[324] The resulting ROP using tin octanoate as catalyst yielded chloro- and bromo-functional polycarbonates with relatively high molar mass (up to 38 500 $g.mol^{-1}$). All polymers were semi-crystalline with similar melting points and glass transition temperatures (T_g around 15 °C and T_m around 120 °C). Interestingly, copolymerization of these monomers with TMC also resulted in semi-crystalline polycarbonates.



13 (R=H)
14 ($R=CH_3$)
15 (R=H)
16 ($R=CH_3$)
17 (X=Cl)
18 (X=Br)
18 (X=I)
19 ($X=CF_3$)

Figure 11: Functional cyclic carbonates containing halide functionality

Hedrick and co-workers reported the synthesis and the polymerization of several halogen-functional cyclic carbonates derived from bis-**MPA**.[199,278,279,281,324–326]

4.1.6. Polycarbonates bearing nitrogen-containing functionalities

Several functional groups are included in nitrogen-containing polycarbonates. First, cyclic carbonates with pendent amides are usually connected to protecting group such as carbamic acid benzyl ester groups (**20-21**, Figure 12)[166,327] and *tert*-butyl ester (Boc) groups (**22-25,** Figure 12).[166,199,279,328,329] After deprotection, this strategy enables the synthesis of primary amine functional polymers.

Starting from commercially available 2-amino-1,3-propane diols, Hedrick and co-workers prepared a variety of nitrogen-containing cyclic carbonate monomers through a general two-step strategy.[330] Such monomers were polymerized to produce well-defined homopolymers and copolymers ($Đ$ < 1.5) with controlled composition. By copolymerizing these monomers, the authors prepared pH-responsive diblock copolymers containing secondary and tertiary amines that have been demonstrated to be promising as delivery carriers for hydrophobic and hydrophilic drugs.[331]

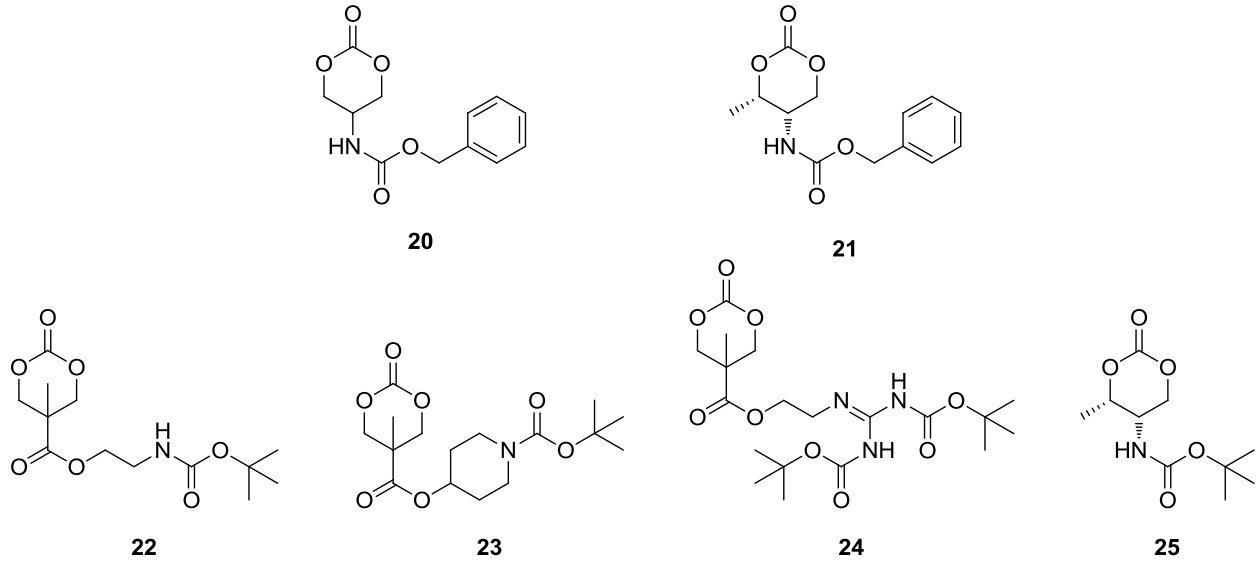
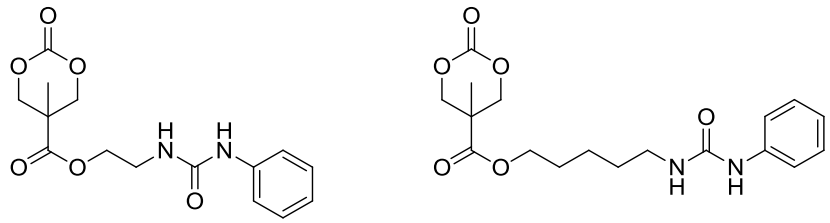


Figure 12: Functional cyclic carbonates containing amino protecting groups

Finally, polymerization of urea-functional monomers **26** and **27** were reported using the TU/(-)-sparteine catalytic system at room temperature in CH_2Cl_2.[196,280,282] The synthesis of block copolymers with a PEO block has also been reported using the same mild conditions. These block copolymers were used for the formation of micelles that displayed low CMC's. It has been also demonstrated that the hydrogen-bonding interactions between the urea groups increased the stability of drug-loaded micelles. Strong H-bonding interaction arising from the urea-groups was also highlighted in networks by a decrease of the overall degree of swelling.



26 **27**

Figure 13: Functional cyclic carbonates containing urea functional groups

4.1.7. Polycarbonates bearing other functionalities

Several other six-membered cyclic carbonate monomers have been reported. Few of them are illustrated in Figure 14. First, azide-containing cyclic carbonate monomers were reported by several groups (**28**-**30**).[332–336] The corresponding copolymers were used in hydrogel formation by subsequent "Click reaction" with alkyne moieties.

Other functional monomers reported include epoxide-functional cyclic carbonates (**31**-**32**).[207,337] Dove *et al.*[207] reported the organocatalytic ROP of the epoxy-functional cyclic carbonate **31** using TBD as catalyst, without opening the epoxy functionality. The pendent epoxide was then post-functionalized with primary amines. Endo *et al*.[337] converted the pendent epoxide to 5-membered cyclic carbonate for further cross-linking reactions.

Although hydroxyl-functional monomers **33** and **34** are incompatible for the ROP process as the hydroxyl functionality acts as an initiating group, the latter carbonates can be useful to prepare biodegradable, hydrophilic, hyper-branched aliphatic polycarbonates.[314,338,339] Parzuchowski reported that **35** did not polymerize, because an isomerization to an appropriate five-membered cyclic carbonate occurred.[295]

Mespouille *et al.* prepared morpholine-functionalized polycarbonate hydrogels for heavy metal ion sequestration.[340] A new six-membered cyclic carbonate **36** functionalized with 2-(morpholin-4-yl)ethyl was synthesized and copolymerized with a poly(ethylene oxide)-based cross-linker in a controlled, organo-catalyzed ROP process.

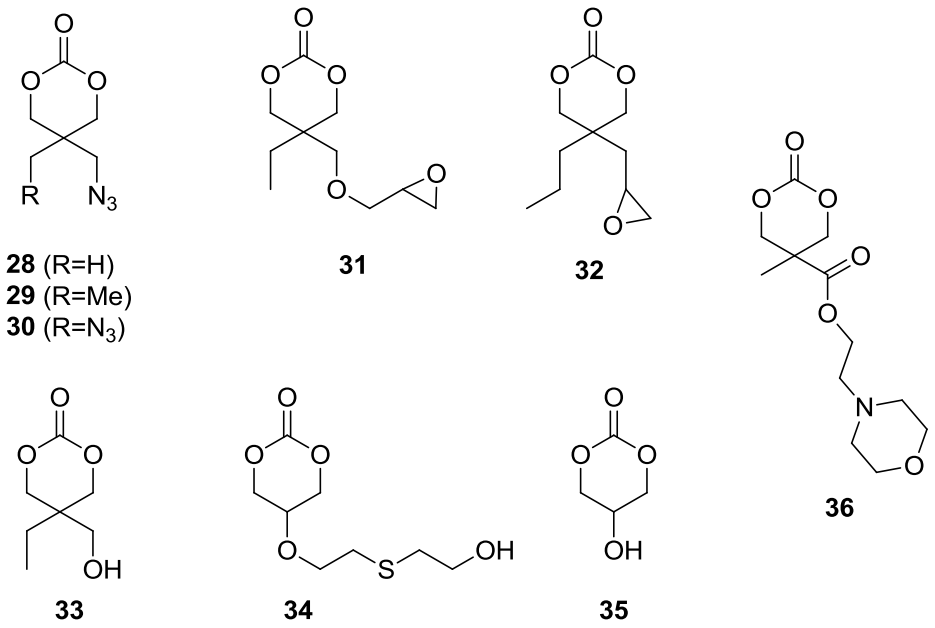


Figure 14: Miscellaneous functional cyclic carbonates

4.2. Post-polymerization modification of functional polycarbonates

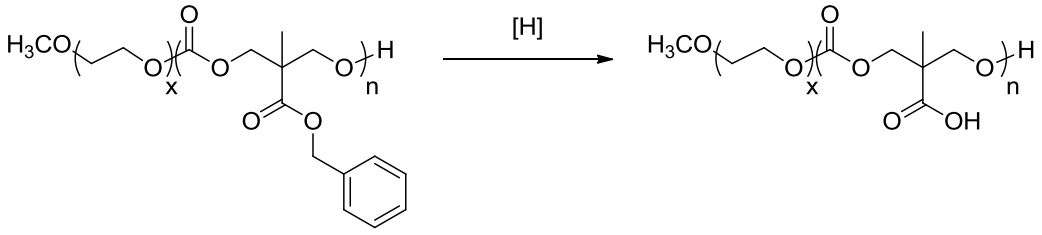
As described above, functional aliphatic polycarbonates have attracted significant attention as materials in recent years. Indeed, the incorporation of pendent functionality offers a facile method to modify materials after being polymerized, thus enabling the introduction into the polymer of functionalities not compatible with ring-opening polymerization. This part is dedicated to the most used post-polymerization modifications bringing new functionalities to polycarbonates.

4.2.1. Deprotection of aryl- and alkyl-functional polycarbonates

Alkyl- and aryl-functional groups are inert during most polymerization conditions and are therefore often used to protect functional groups such as hydroxyl and carboxylic acid groups, which can disturb ROP process. As described in Parts 4.1.2 and 4.1.3, aliphatic polycarbonates containing pendent hydroxyl and carboxylic acid functions, can be protected by alkyl- or aryl-protecting groups.

Deprotection of the benzyl groups of polycarbonates such as poly(**MBC**) and poly(**5**) has been extensively reported by catalytic hydrogenolysis over palladium or palladium hydroxide on carbon leading to carboxyl- and hydroxyl-functional polycarbonates (Scheme 34).[6,187,285–289,291–294,341–345] Protected polycarbonates are highly hydrophobic materials but the resulting hydroxyl

and carboxylic acid functional polymers exhibit hydrophilic properties. In addition, biocompatibility and hydrosolubility are enhanced compared to the benzyl-containing polymer. Thermal properties of homopolymers and copolymers of **MBC** are significantly modified after deprotection. For instance, T_g raises from 3°C to more than 45°C. Moreover, the polymer was isolated as a semi-crystalline white powder after deprotection. Remarquably, Poly(**5**) homopolymers displayed an impressive 64-fold increase in water absorption after debenzylation.



Scheme 34: Hydrogenolysis of protected copolycarbonate

Similarly, hydroxyl-functional polymers were obtained by removal of the benzylidene group in polymers prepared from **6**. In contrast to poly(**5**), poly(**6**) reveals two hydroxyl groups per repeating unit due to the double hydroxyl protection of the benzylidene group. These polymers were employed for the encapsulation of anti-cancer drugs and their subsequent pH-controlled release.[299,346,347]

Jing *et al*.[297,298] reported recently that the nitrobenzyl lateral groups in PEO-b-Poly(**4**) block copolymers could be deprotected under UV irradiation at 365 nm to convert the poly(carbonate) block from a hydrophobic block to a hydrophilic carboxylic acid-functional block. Micelles prepared from these PEO-b-Poly(**4**) block copolymers were shown to dissociate readily when irradiated due to the conversion of the amphiphilic block copolymers into hydrophilic copolymers.

4.2.2. Post-polymerization modifications of alkene-functional polycarbonates

Polycarbonates bearing alkene functional groups have generated considerable interest as their synthesis is easy and the latter do not require protection/deprotection steps to yield the functional polymer. Additionally, various functional groups can be grafted on the polymer backbone through simple post-polymerization modifications on the carbon-carbon double bond such as

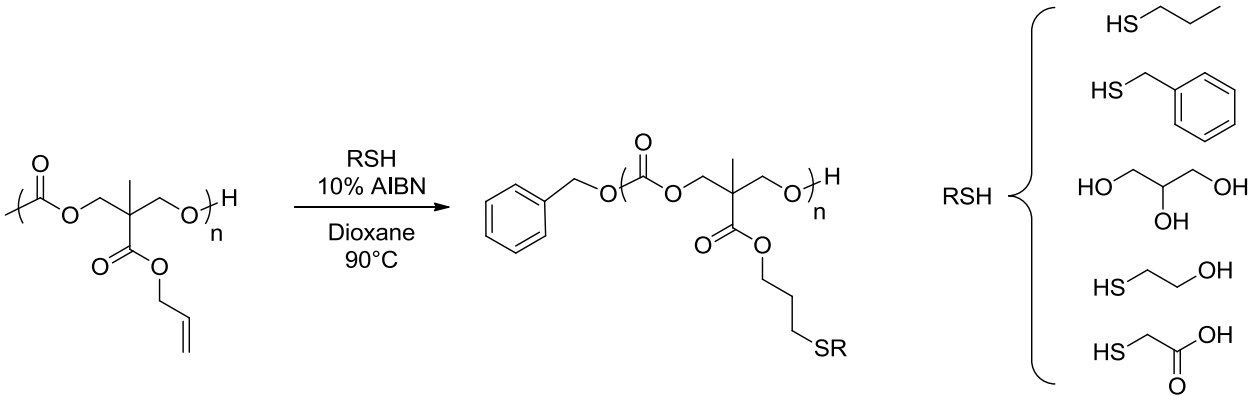
addition of functional thiol *via* the radical thiol-ene addition or Michael addition and epoxidation reactions. Thomas and Dove reviewed recently these post-polymerization modification of alkene-functional polycarbonates for the development of advanced biomaterials.[305] Terminal alkene functional polycarbonates can be also used in cross-linking reactions.

This part will detail notable examples of post-polymerization modifications of polycarbonates using the three main methods above described: thiol additions, epoxidations and free radical cross-linking.

Thiol additions

The reaction of thiols and alkenes ('thiol-ene') has been utilized extensively as an efficient method in the preparation of functional polymers. Reactions proceed either *via* the free radical addition of thiols to carbon-carbon double bonds or *via* the Michael-addition of thiols to electron-deficient carbon-carbon double bonds.[304]

Thermally initiated radical thiol-ene chemistry has been utilized by Tempelaar *et al*. to attach several different thiols to a polycarbonate backbone (Scheme 35).[206] The new functionality brought by the thiol-ene reaction has also an effect on thermal properties of the resulting polycarbonates. Indeed, the mercaptoacetic acid functionalized polycarbonate displayed a glass transition temperature of -33 °C whereas T_g of -5.1 °C was observed for the polycarbonate functionalized with benzyl mercaptan.



Scheme 35: Post-polymerization modification of PMAC with mercaptans via radical thiol-ene addition

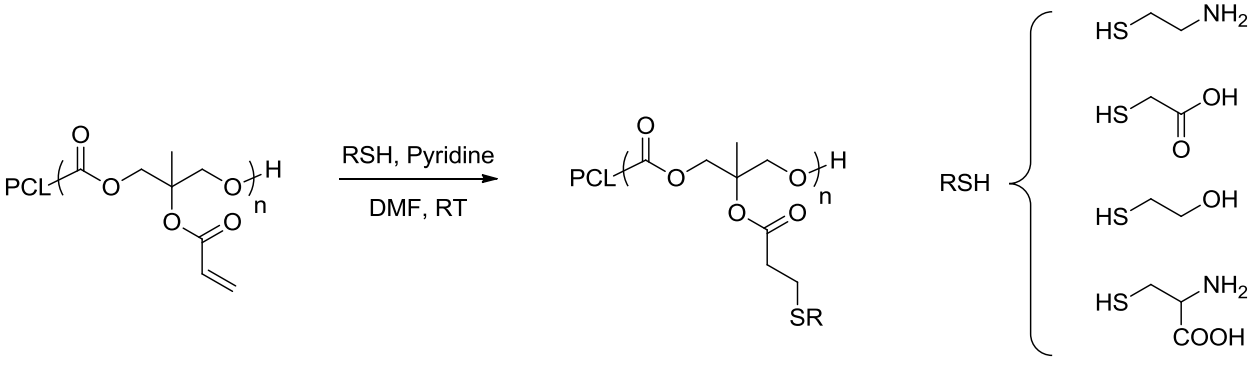
PMAC was also functionalized with DOPA-thiol using UV light to trigger a photo-initiated radical thiol-ene addition, generating polycarbonates with pendent catechol groups.[313] Gels were

formed by addition of Fe^{3+}, as a result of the high affinity of the catechol functionality for these ions. The authors showed that such polymers are capable of self-healing following damage resulting from the application of excess strain.

Olsén *et al.*[206] have revealed that the thiol-ene reaction can be applied to poly(**14**). The functionalization was shown to proceed with good control, with a linear relation between conversion of allyl groups and increasing polymer molar mass maintaining the structure of the final polymer. In a similar manner, Dove *et al.*[209] used the versatile photo-initiated radical thiol-ene coupling chemistry to provide a range of polycarbonates for potential drug-delivery applications with tunable thermal properties.

Radical thiol-ene addition has also been employed for the cross-linking of functional polymers. For instance, Stevens *et al.* have exploited the thiol-ene reaction for the formation of nanosponges, through cross-linking copolymers.[348] Truong *et al.*[349] and Stevens *et al.*[350] prepared hydrogels with tunable properties including water uptake content, mechanical strength, and degradation time by cross-linking **PMAC** with a range of PEG-thiols. Finally, Barker *et al.*[351] have used photo-initiated radical thiol-ene chemistry to produce 3D-printed structures based on polycarbonates via microstereolithography, as an alternative to potentially toxic acrylate-based printing systems.

As with radical thiol-ene addition, Michael addition reactions can be used to bring additional functionality to alkene-functional polycarbonates by addition of mercaptans to the alkene moiety (Scheme 36).[352] Yu *et al.*[353] also used Michael additions to prepare injectable hydrogels based on the acrylate-functional polymer poly(acryloyl carbonate).



Scheme 36: Post-polymerization modification of PMAC with mercaptans via Michael-type additions

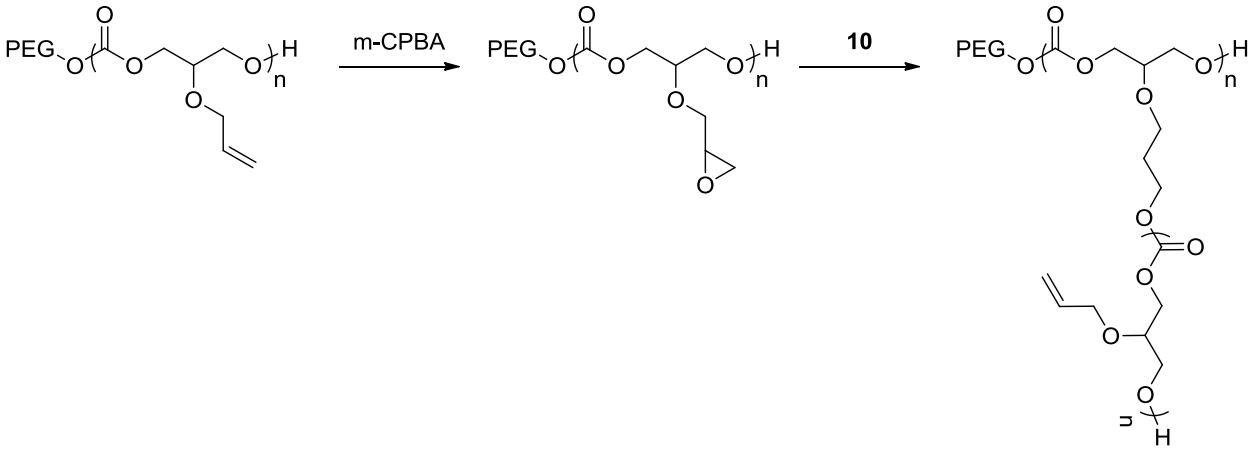
Interestingly, Uysal *et al.*[354] demonstrated that different mechanisms of Michael addition and radical thiol-ene addition can be exploited for orthogonal modification of copolymers containing two different allyl functionalities. This metal-free click chemistry methodology affords the synthesis of biocompatible PC copolymer with multifunctional groups.

Epoxidation

Alkene functional polycarbonates could also be epoxidized using meta-chloroperoxybenzoic acid (m-CPBA). Epoxidation of functional aliphatic poly(carbonate)s was reported for pendent allyl groups and pendent cyclohexenyl groups with efficiencies ranging from 35 to 99%.

For instance, He and co-workers[275,307] employed epoxidized polycarbonates to graft polyethyleneimine on the polymer structure. These materials have been used as biodegradable polycations for potential application as gene delivery carriers.

Besides using dithiols to prepare nanosponge from **PMAC**, Stevens *et al.*[348] have also utilized the epoxidation of pendent allyl groups for cross-linking using an ethylene oxide-based diamine as cross-linker. In terms of particle sizes, the results are similar regardless of the cross-linking method.



Scheme 37: Epoxidation of P(10) and subsequent ROP of 10, using epoxide functionality as initiator

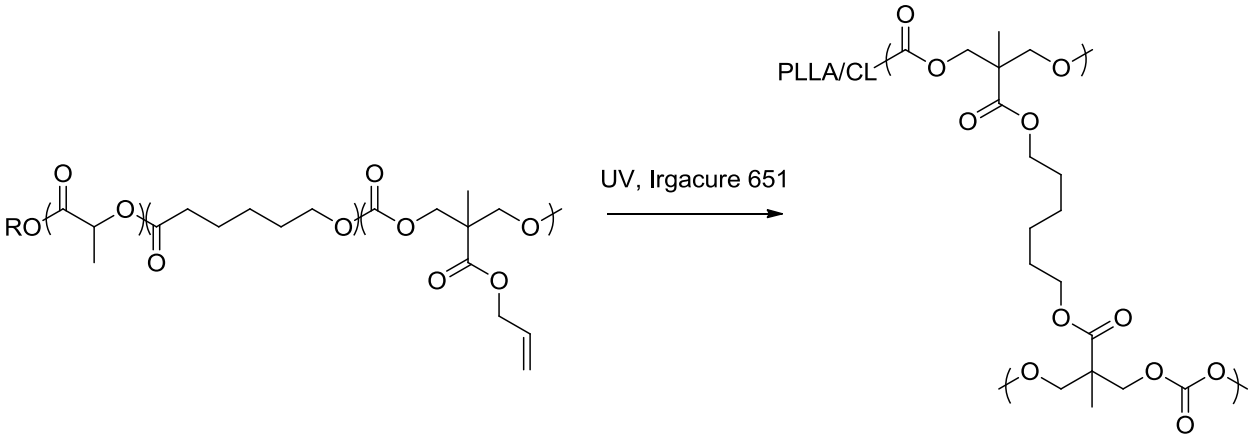
In 2014, Jiang *et al.*[355] synthesized block copolymers PEG-b-P(**10**) by enzymatic methods for controlled release of doxorubicin (Scheme 37). The grafted polymer demonstrated greater drug loading capacity and encapsulation efficiency, along with more sustained drug release behavior *in vitro* when compared to the linear diblock copolymer.

Free-radical cross-linking

The ability of alkene-functional polycarbonates to undergo photoinitiated radical cross-linking in the absence of additional cross-linkers has also been demonstrated and utilized for practical applications.

Several groups have investigated the cross-linking of the hydrophobic core of micelles prepared from block copolymers.[356–359] Such core cross-linked micelles exhibited improved properties such as increased thermal stability and reduced aggregation. Moreover, they have a greater resistance to water expansion and organic solvents in comparison to non-cross-linked micelles.

Besides, the group of Amsden has used the direct cross-linking method to generate fibrous materials with properties similar to human anterior cruciate ligament (ACL) tissue.[360] The authors revealed that cross-linking the fibers resulted in an elastic modulus increase of the dry fibers from 86 to 222 MPa. In 2016, the same research group demonstrated that the cross-linking reaction could be employed to cross-link fibers deposited by melt electrospinning writing, a method of 3D-printing (Scheme 38).[361] The modulus of the hydrated scaffold was greatly improved by cross-linking, making the scaffold highly resistant to dynamic loading.



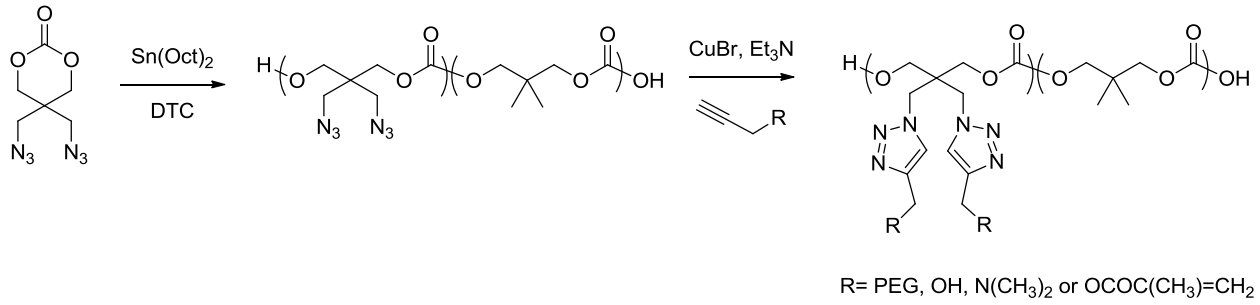
Scheme 38: Cross-linking of P(LLA-*co*-CL-*co*-MAC) with UV and no additional cross-linker

Finally, Mindemark *et al.* have recently reported the preparation of allyl ether-functional polycarbonate electrolytes.[362] UV-cross-linking of the allyl side groups provided mechanically stable electrolytes with improved molecular flexibility and higher ionic conductivity due to the plasticizing properties of the allyl ether side groups.

4.2.3. Post-polymerization modifications of polycarbonates via dipolar cycloadditions

Alkyne- and azide-functional polycarbonates or poly(ester-carbonate)s were successfully functionalized via 1,3-dipolar cyclo-addition reactions.

As an example, modifications of polycarbonates obtained from copolymerization of **MPC** with lactide were functionalized with azido-containing molecules using copper(II) sulfate pentahydrate and sodium ascorbate in water–DMSO mixtures.[320] Lu *et al.* investigated photo-induced reversible amphiphilic copolymer which was click-conjugated by connecting amphiphilic modified polycarbonates and an azide-functional molecule.[363] The resulting copolymer self-assembled into spherical micelles with a hydrophobic azo core stabilized by a hydrophilic PEG crown in aqueous solution.



Scheme 39: Synthesis of azido copolycarbonates Poly(30)-co-PDTC and their functionalization via the the click reaction

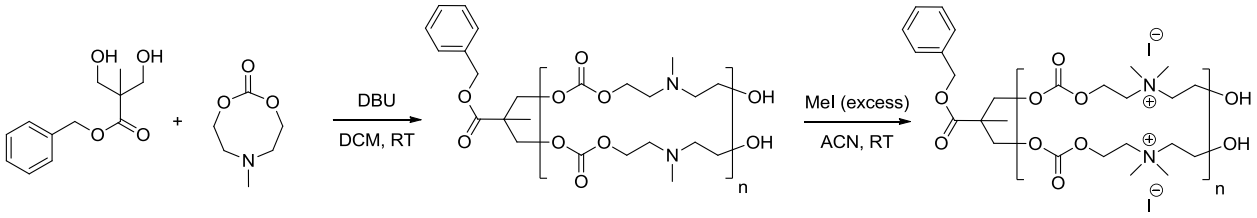
In contrast, Zhuo *et al.* prepared polycarbonates with pendent azido groups for their functionalization *via* click chemistry (Scheme 39).[334] This strategy provides a platform for the preparation of various functionalized polycarbonates.

4.2.4. Quaternization of halogen-functional polycarbonates

A range of polymers containing quaternary ammonium groups have shown to exhibit antimicrobial activity. However, these polymers are often not degradable which limits their use. The quaternization of amines was proceeded by the reaction of copolycarbonates bearing pendent halogen functionalities with tertiary amines such as trimethylamine or N,N,N',N'-tetra-methylethylenediamine (TMEDA).[278,281,325,364]

Very recently, Sardon's group revealed that the modification of the counter-anion of the antimicrobial polymer dramatically influences its antimicrobial and hemolytic activities.[365] The authors found that trifluoroacetate and benzoate afforded the most efficient antimicrobial polymers among the investigated different anions tested.

Similar strategy was applied by several research groups for obtaining antimicrobial and antifouling cationic aminated polycarbonates (Scheme 40).[366–368]



Scheme 40: Synthesis of antimicrobial cationic polycarbonate

The group of Endo developed a series of tertiary amine-modified polycarbonate films which were also used as antimicrobial agents after protonation with HCl or quaternization with benzyl bromide.[369]

Nimmagadda reported recently the design and synthesis of amphiphilic polycarbonates containing primary amino groups.[370] Interestingly, these polymers exhibited potent antimicrobial activity and excellent selectivity to Gram-positive bacteria.

Conclusion

This chapter reviewed the literature towards functional aliphatic polycarbonates obtained through a ring-opening process. The main different routes to cyclic carbonates synthesis have been first mentioned. Among them, oxiranes and 1,3-diols appear as the most convenient precursors for the synthesis of 5-membered and 6-membered cyclic carbonates respectively. Over the past decade, academic researchers have developed advanced catalytic systems affording cyclic carbonates with very high yields and selectivities.

In a second part, ROP of 5-, 6- and 7-membered cyclic carbonates were discussed in terms of mechanism, polymerization control and polymer composition. In comparison to most of the cyclic monomers, 5CCs behave very specifically. Indeed, due to thermodynamic limitations, the synthesis of true polycarbonates from 5CCs is impossible. The only way to produce pure polycarbonates from 5CCs is to copolymerize them with other heterocyclic monomers, such as lactone or lactide. However, 6-membered cyclic carbonates were easily polymerized to obtain PCs. Anionic polymerization of such monomers seems to be the most suitable methodology in order to proceed the polymerization in a controlled manner.

Finally, an extensive report on the synthesis of aliphatic polycarbonates bearing functional groups has been realized. Properties of such polymers and their potential applications have been also detailed.

However, as far as we know, most of the CC monomers are petro-sourced. Nonetheless, in the view of fossil fuel depletion, more and more raw materials from biomass are used to produce green monomers. In this context, the purpose of this PhD thesis is to synthesize new polycarbonates from fatty acid derivatives. The most straightforward route to access such polymers appears to be the ROP of fatty acid-based 5CCs obtained from epoxidized unsaturated fatty acids. However, as above-mentioned such monomers are not the best candidates to produce true polycarbonates. Therefore, the synthesis and subsequent ROP of fatty acid-based 6CCs will be investigated from lipidic 1,3-diols.

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Chapter 2

Copolymerization of ethylene carbonate (EC) and trimethylene carbonate (TMC)

Keywords: Ethylene carbonate, trimethylene carbonate, ring-opening polymerization, aliphatic polycarbonates

Mots-clés: Carbonate d'éthylène, carbonate de triméthylène, polymérisation par ouverture de cycle, polycarbonates aliphatiques

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Introduction

As detailed in Chapter 1, aliphatic polycarbonates (APCs) are mostly used for biomedical applications due to their biocompatibility, biodegradability, low toxicity and better mechanical properties as compared with similar polyesters.

Among all the methods dealing with the preparation of APCs, the most efficient one is the ring-opening polymerization (ROP) of cyclic carbonate monomers. With respect to the monomers, two types of cyclic carbonates behave very differently in ROP.

Six-membered ring cyclic carbonates (6CCs) and more specifically trimethylene carbonate (TMC) easily polymerize to obtain APCs. Their ring-opening (co)polymerization has been well studied using cationic, anionic, coordination-insertion and enzyme-catalyst routes.[1]

However, despite their straightforward synthesis especially from fatty acids,[2,3] 5-membered cyclic carbonates (5CCs) do not afford true APCs by ROP because of unfavourable thermodynamic features. The homopolymerization of 5CCs is thus rarely controlled and remains difficult to optimize.[4,5] Nevertheless, the latter can undergo copolymerization with more reactive cyclic monomers such as ε-caprolactone (ε-CL), δ-valerolactone (VL) or L-lactide (LLA).[6–12] Most of these copolymerizations proceed under mild conditions using ethylene carbonate (EC) as 5CC monomer. The amount of EC incorporated in these various EC copolymers remains in the range 4-31 mol.% thus affecting the thermo-mechanical properties of the copolymers. The degradability of poly(EC-*co*-ε-CL) and poly(EC-*co*-VL) was shown to be improved upon incorporation of EC units along the polyester backbone.[9]

However, except the work of Shen,[13] very few studies report on the copolymerization of 5CCs and 6CCs. This chapter is thus devoted to the copolymerization of 5CCs with 6CCs. The optimization of the experimental conditions with model molecules (EC and TMC) is first discussed. In a second part, EC content in the feed and the initiator/monomer ratio will be varied in order to enhance EC incorporation in the PTMC backbone. Finally, the influence of EC content on the copolycarbonate properties will be studied.

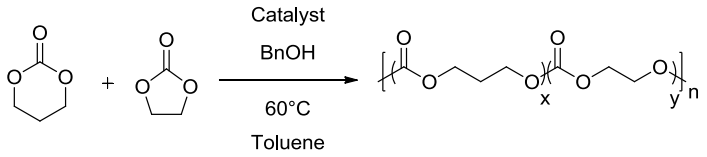
1. Preliminary investigations of experimental conditions

Taking into account that very few examples of copolymerization involve 5-membered cyclic carbonates and 6-membered ones, ethylene carbonate (EC) and trimethylene carbonate (TMC) were chosen as model molecules. As described in chapter 1, several methods can be applied to polymerize cyclic carbonates by ring-opening polymerization. Nevertheless, the most convenient route to prepare polycarbonates without undesired ether sequences remains the anionic method. In this study, a screening of anionic catalysts was performed and a mechanistic study was accomplished.

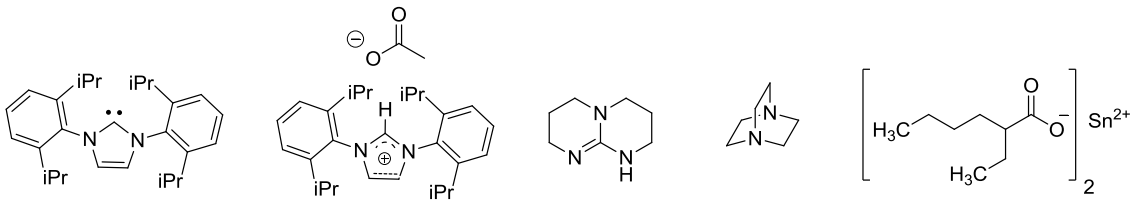
1.1 Catalyst screening

The random copolymerization of EC and TMC was first carried out in toluene at 60°C ($[EC]_0+[TMC]_0$ = 4 mol.L^{-1}) using several catalysts and benzyl alcohol as initiator with $[EC]_0/[TMC]_0/[Catalyst]_0/[BnOH]_0$ ratios of 50:150:2:2. Benzyl alcohol added as co-initiator accelerates the polymerization process and affords a better control of the molar mass by controlling the monomer/initiator ratio. Two organic bases (TBD and DABCO), two N-heterocyclic carbenes (**NHC-IPr** and **Ac-NHC-IPr**) and one tin-based compound ($Sn(Oct)_2$) were tested as catalysts. These catalytic systems were selected due to their ability to catalyze the ring-opening polymerization of a large scope of 6-membered cyclic carbonates.[14] It is worth mentioning that none of these catalytic systems enabled the homopolymerization of EC. In order to purify the copolymer obtained, free monomers were removed by precipitating the polymer in cold methanol. The polycarbonate molar masses were determined by SEC in THF (polystyrene standards were used for calibration). Theoretically, molar masses are predictable by the monomers to initiator ratio. In this case, the degree of polymerization (DP) should be 25 (50/2) for EC and 75 (150/2) for TMC. Based on this calculations and taking into account the molar mass of both monomers (M_{EC} = 88.2 g.mol^{-1} and M_{TMC} = 102.1 g.mol^{-1}), the targeted molar mass of the copolymer is $M_n = 88.2 \times 25 + 102.1 \times 75 \approx 9\,900$ g.mol^{-1}. All the data are indicated in Table 1.

Table 1: Catalyst screening for the copolymerization of EC and TMC in toluene at 60°C [a]



Catalyst:



Entry	Catalyst	EC content (mol.%)[b]	EC conversion (mol.%)[b]	M_n (g.mol^{-1})[c]	M_w/M_n [c]
P1	$Sn(Oct)_2$	no polymer	-	-	-
P2	NHC-IPr	7.1	18.5	8 000	2.1
P3	DBU	4.1	14.5	6 700	1.6
P4	TBD	2.4	15.9	1 500	1.6
P5	Ac-NHC-IPr	3.4	11.5	2 400	1.5

[a]: reaction conditions: $[EC]_0/[TMC]_0/[Catalyst]_0/[BnOH]_0$ ratio = 50:150:2:2, 2 hours, $[EC]_0+[TMC]_0$ =4 mol.L^{-1} [b]: calculated by ^{1}H NMR [c]: determined by SEC analysis in THF.

The EC unit content in the copolymer was calculated by means of ^{1}H NMR (Figure 1), from the integration of characteristic signals of both monomers units (Equation 1).

$$\boldsymbol{EC\ content} = \frac{\int \boldsymbol{H_{EC}}\ (H_1)}{\int \boldsymbol{H_{EC}}\ (H_1) + \int \boldsymbol{H_{TMC}}\ (H_2)}$$

Equation 1: Formula used for the calculation of EC unit integrated in the copolymer

Ethylene carbonate conversion was calculated from ^{1}H NMR spectra of the crude polymer samples by using the integration ratio $Int_{PEC}/[Int_{PEC} + Int_{EC}]$ of the methylene hydrogens (–O$\underline{CH_2CH_2}$O, δ_{PEC} 4.35 ppm, δ_{EC} 4.51 ppm) of EC.

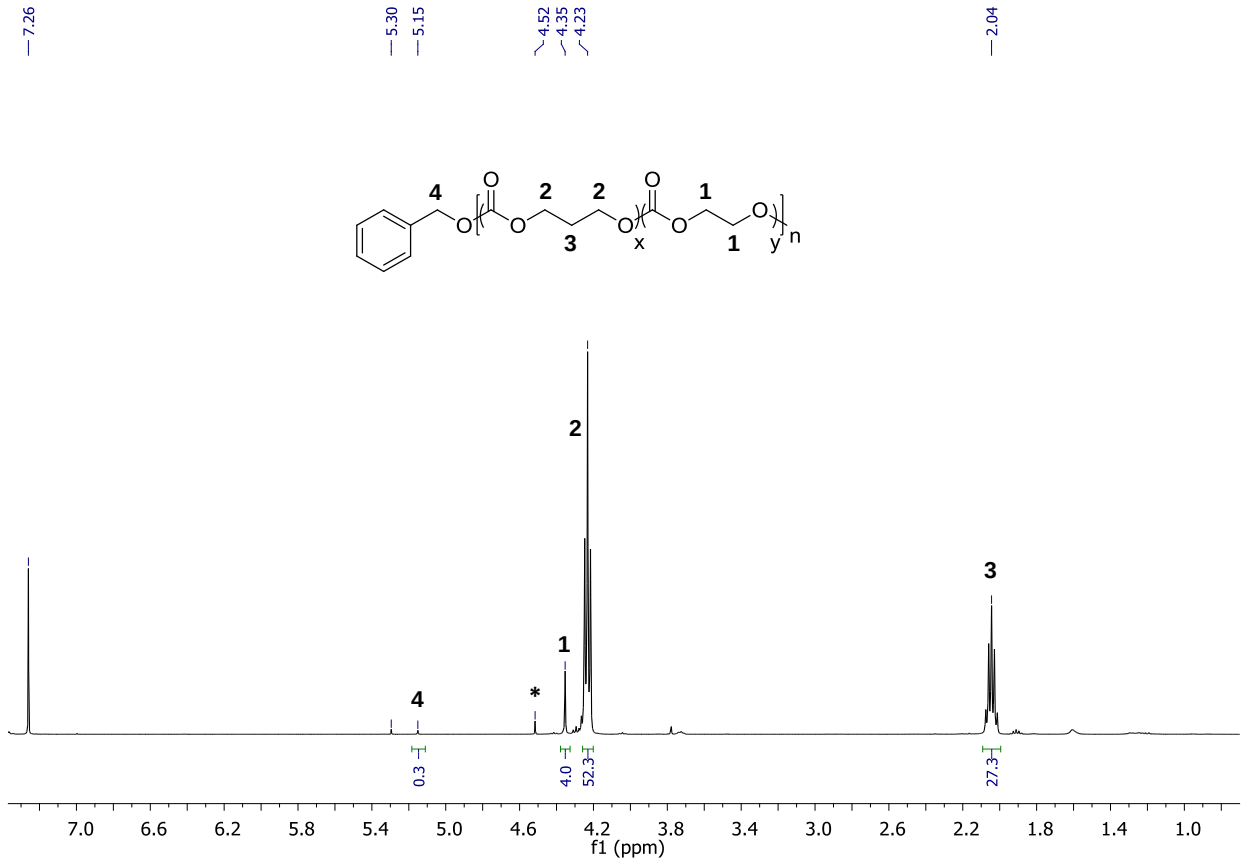


Figure 1: ^{1}H NMR spectrum of P(EC-*co*-TMC) (Table 1, entry 2) (*: EC residual monomer) in $CDCl_3$.

Despite its known efficiency,[15–17] $Sn(Oct)_2$ (Table 1, P1) did not afford any polymers in the conditions tested presumably due to the too low polymerization temperature. Contrarily to the Tin-based catalyst, organic catalysts enabled the synthesis of copolymer (Table 1, P2-P5).

Indeed, the copolymers synthesized with TBD and DBU as catalysts (Table 1, P3 and P4) produced polycarbonates with only 2.4 mol.% and 4.1 mol.% of EC content, respectively. Therefore, such organic bases afforded the copolymerization of EC and TMC but the EC content in the copolymers remains quite low. A better nucleophile (**NHC-IPr**) with respect to DBU and TBD was then used as catalyst in EC/TMC copolymerization in order to enhance EC incorporation.[18]

The high reactivity of N-heterocyclic carbenes (NHC) for transesterification reactions was manifested in their ability to catalyze the ROP of cyclic monomers. Since the first work in 2002 reporting the ability of NHC to catalyze the living ROP of lactones to generate polylactones,[19]

extensive work has been carried out to exploit the versatility of N-heterocyclic carbenes for the ROP of different monomers.

With respect to the mechanism, two possible routes can be envisaged: a chain-end-activated mechanism whereby the carbene activates an alcohol by hydrogen-bonding toward nucleophilic attack (Figure 2-(1)) and a monomer-activated mechanism mediated by the nucleophilic attack of the carbene on the cyclic carbonate (Figure 2-(2)).[20]

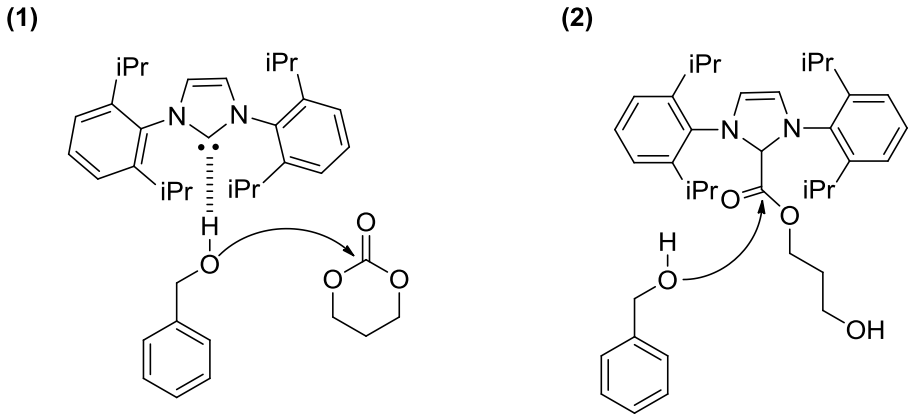


Figure 2: Possible initiation mechanisms in ROP of TMC

In our survey, the most significant result both in terms of EC incorporation and copolymer molar mass is obtained in the presence of the carbene 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**NHC-IPr**) used as catalyst (Table 1, entry P2) but a lack of control, as evidenced by the broad molecular weight distributions (2.1), is also noticed. In that case, 7.1 mol.% of EC units was incorporated into the PTMC backbone. This experiment (Table 1, P2) was performed in triplicate with satisfactory reproducibility (EC content = 7.1 ± 0.5 mol.%). The copolymer displayed a molar mass of 8 000 g.mol^{-1} by means of SEC in THF. Such value is only an estimation since the calibration of the measurement has been performed with polystyrene as standard polymer. The ^{1}H NMR spectra depicted in Figure 1 gives a better insight of the copolymer molar mass. Indeed, the DP of both monomers (and thus the copolymer molar mass) can be calculated by using integration ratio $\frac{\mathrm{Int}_{Monomer}}{4}/\frac{\mathrm{Int}_{BnOH}}{2}$ of the methylene hydrogens (-OCO$\underline{CH_2}CH_2\underline{CH_2}$O, δ_{PTMC} 4.23 ppm) of TMC, the methylene hydrogens (–O$\underline{CH_2}\underline{CH_2}$O, δ_{PEC} 4.35 ppm) of EC and the methylene hydrogens (Ph-$\underline{CH_2}$OCO, δ_{BnOH} 5.15 ppm) of BnOH. This method works only if all polymer chains are initiated by BnOH.

Thus, the calculated DP of EC by means of ^{1}H NMR is equal to $\frac{4}{4} / \frac{0.3}{2} \approx 7$ and DP of TMC is $\frac{52}{4} / \frac{0.3}{2} \approx 87$. Thus the global copolymer molar mass is 9 500 g.mol^{-1}. The latter value is close to the theoretical one (9 900 g.mol^{-1}). However, the DP of EC is lower than the theoretical value due to the poor reactivity of such monomer in ROP. Besides, the DP of TMC is slightly higher than targeted meaning that the initiating step is not fully efficient.

As far as we know, the highest incorporation of EC unit in a polycarbonate backbone without ether sequences was 5.1 mol.% revealed by Shen in 2010.[13] Therefore 7.1 mol.% is already a significant value for the incorporation of ethylene carbonate in a polycarbonate backbone. Nevertheless, for all catalytic systems, the EC content in the copolymers remained quite low (only up to 7.1 mol.%) thus confirming the difficulty for this five-membered ring monomer to undergo ROP, as mentioned previously. Several parameters will be evaluated in the next parts with the objective to increase the EC content incorporated in the PTMC chains.

Nevertheless, one limitation with such carbene is its sensitivity against oxygen and water. In order to make the carbene less sensitive, Taton and coll.[21–23] developed different masked carbenes. In this work, an acetate counter-anion interacting with the proton in C2-position of the imidazolium ring was used as masked carbene (**Ac-NHC-IPr)**. Such catalyst was developed by Lambert *et al.* in 2016 for various organocatalyzed reactions.[24] The *in situ* generation of NHC units was driven by a simple intramolecular thermal activation, owing to the basic character of the acetate counter-anion that could deprotonate the imidazolium moieties in C2-position. **Ac-NHC-IPr** was then tested as catalyst in the EC/TMC copolymerization (Table 1, entry P5). In that case, EC content incorporated in the copolymer was similar to those obtained with TBD and DBU. Finally, **NHC-IPr** appeared to be the best catalyst for this copolymerization.

A kinetic study of the copolymerization was performed by means of ^{1}H NMR spectroscopy of the crude polymer samples at different reaction times (Figure 3). The kinetic profile of the monomer consumption is depicted in Figure 4 and highlights the difference of reactivity between the two monomers, EC and TMC.

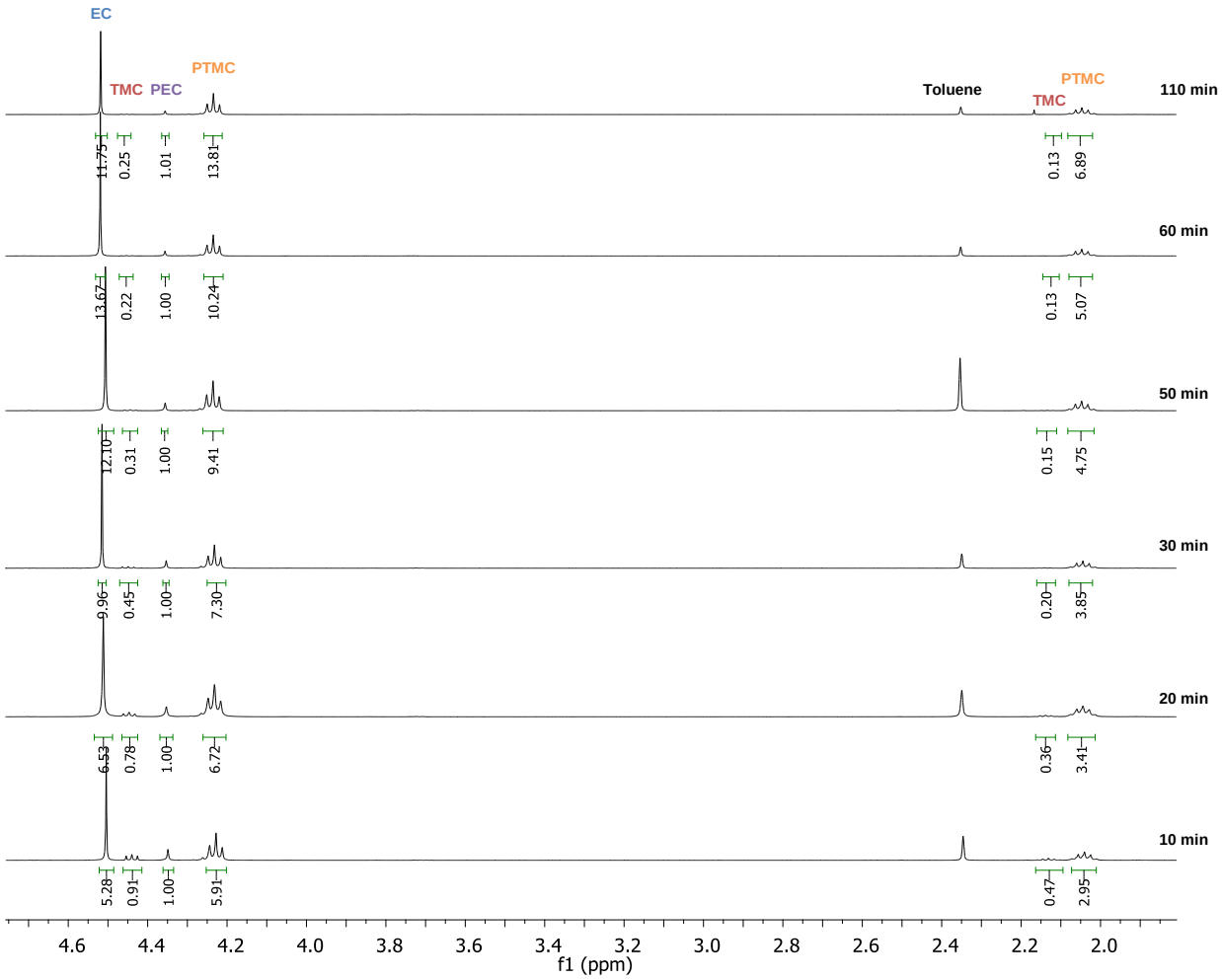


Figure 3: Stacked ^{1}H NMR spectra used for the kinetic study of the EC/TMC copolymerization in $CDCl_3$

EC content and EC conversion were calculated as above detailed and TMC conversion was calculated using the integration ratio $Int_{PTMC}/[Int_{PTMC} + Int_{TMC}]$ of the methylene hydrogens (-OCO$\underline{CH_2}CH_2\underline{CH_2}$O, δ_{PTMC} 4.23 ppm, δ_{EC} 4.44 ppm) of TMC. After 1h reaction, TMC is almost completely consumed while EC is only partially converted (maximum 18.5 mol.%, Table 1, P2). The kinetic profile also shows that the polymerization stops when all the TMC is consumed, thus explaining why EC/TMC reactions do not reach overall yields higher than 80 wt.%.

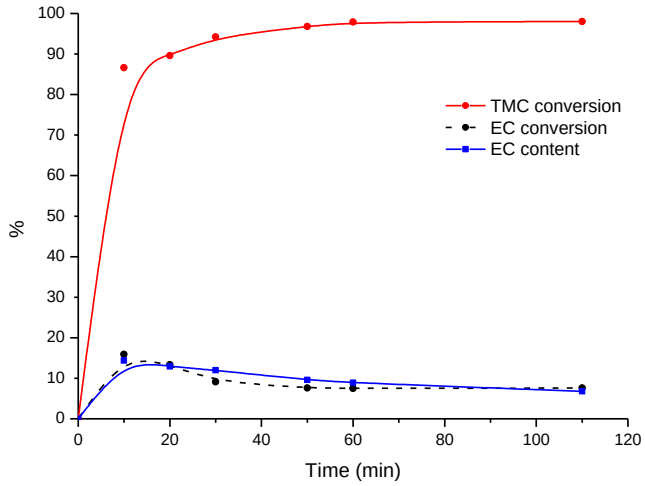
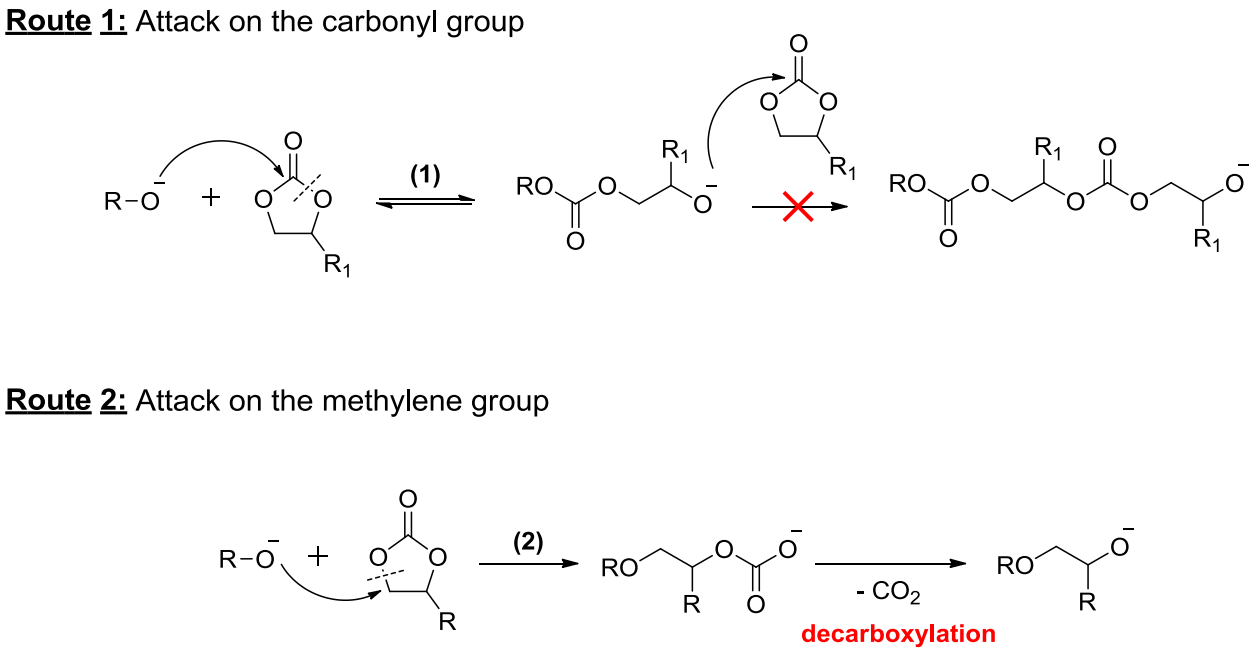


Figure 4: Kinetic profile of EC and TMC copolymerization (Table 1, P2)

As reviewed in chapter 1, due to the decarboxylation side reaction, polymerization of ethylene carbonate generally results in a copolymer comprising ethylene oxide (EO) units with a content of carbonate units lower than 50 mol.%. Because of thermodynamics, an ethylene carbonate monomer can be incorporated into a growing chain, but successive incorporation of ethylene carbonate monomers does not occur yielding to the formation of ether sequences as illustrated in Scheme 1.



Scheme 1: Formation of poly(ethylene ether-carbonate)s

In our cases, in agreement with the literature data,[5,11,25,26] no signals attributed to the ether linkages (3.7-3.3 ppm) were observed in ^{1}H NMR spectrum (Figure 1), indicating that no decarboxylation occurred in the ROP of TMC and EC.

1.2 Mechanistic study

In order to elucidate the copolymerization mechanism between the two EC and TMC monomers, different model reactions were performed. The NMR spectra of several reactions are depicted in Figure 5. All these reactions were performed in Young NMR tubes in CD_2Cl_2.

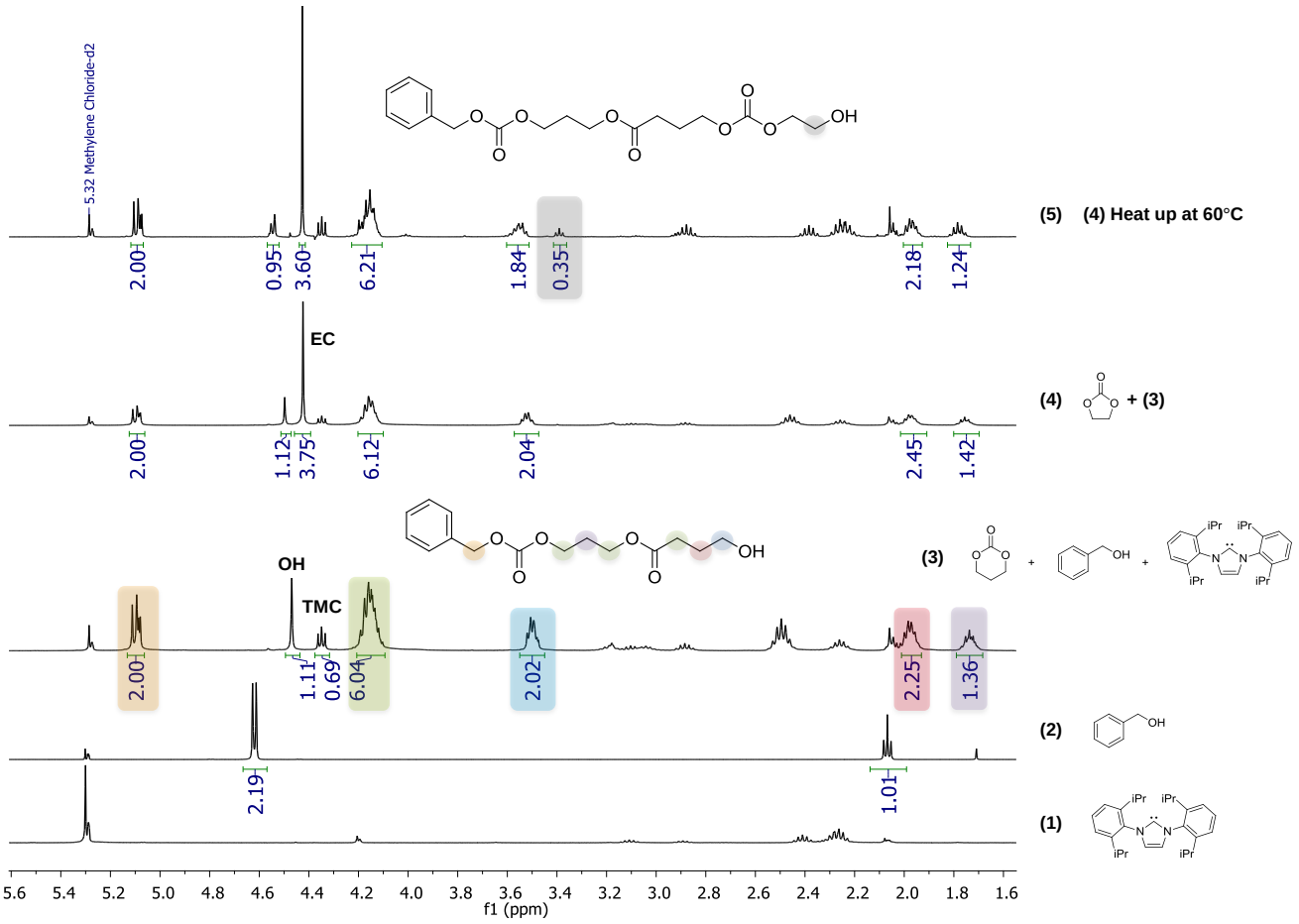
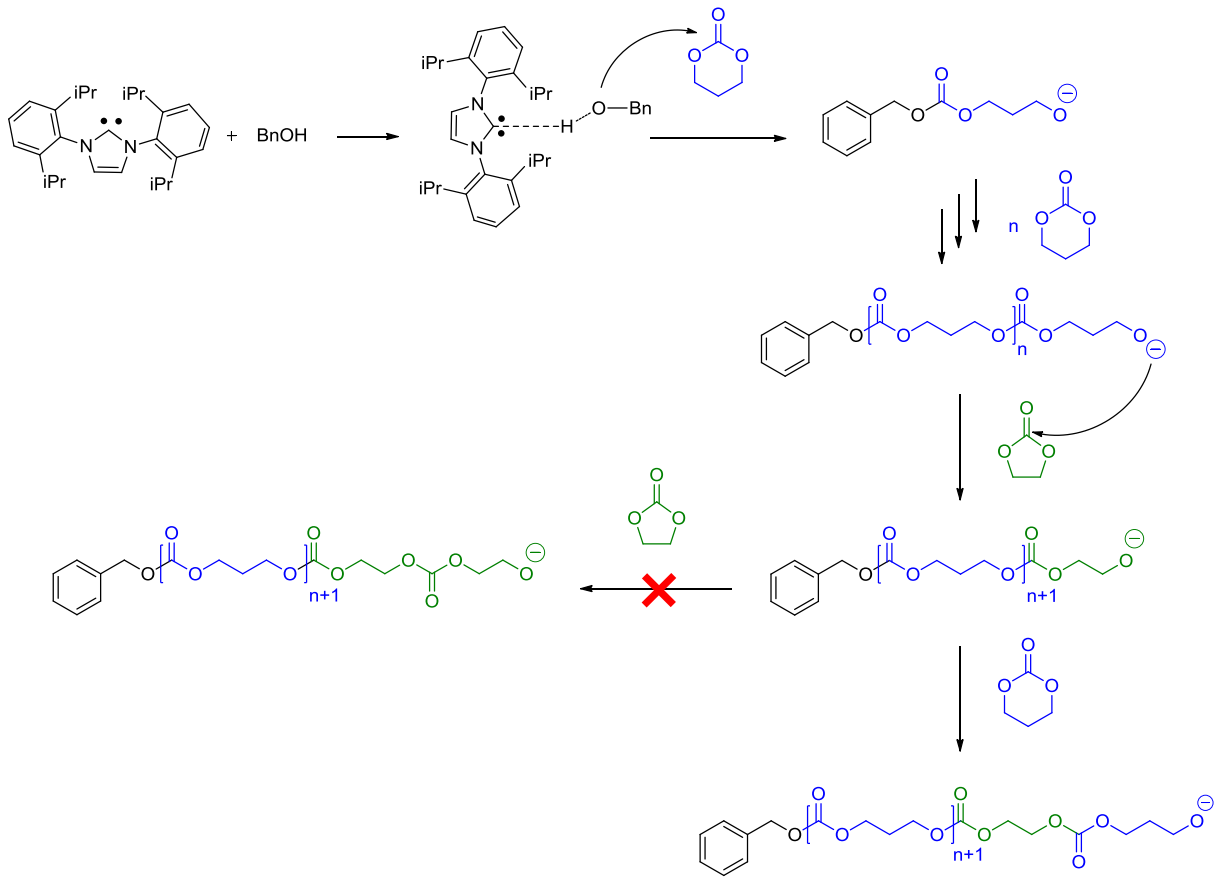


Figure 5: ^{1}H NMR spectra towards a better understanding of EC/TMC copolymerization in CD_2Cl_2

The catalyst (**NHC-IPr**) and the initiator (BnOH) were first analyzed to ascribe their characteristic peaks (^{1}H NMR spectra line (1) and (2)). Then two equivalents of TMC were added to one equivalent of benzyl alcohol and one equivalent of **NHC-IPr** (^{1}H NMR spectrum line (3)).

At room temperature, a shift (from 4.6 ppm to 5.1 ppm) of the characteristic signal of the benzyl alcohol was observed proving the ability of the initiator to open the 6-membered cyclic carbonate. The labile proton of the primary alcohol is represented by a singlet at 4.5 ppm. The other peaks were assigned and correspond to the opened form of TMC. As expected, this catalytic system is efficient to initiate the ring-opening polymerization of TMC. However, the same experiment was conducted with EC but no evidence of opened EC was observed. Therefore, such catalytic system doesn't afford the ring-opening of EC at room temperature.

Next, EC was added to the previous mixture (^{1}H NMR spectrum line (4)). Unfortunately, still no ring-opening of EC was observed (only the characteristic peak of EC at 4.4 ppm). However, when the reaction media was heated up at 60°C, a new triplet appeared at 3.4 ppm (^{1}H NMR spectrum line (5)). This triplet is more probably ascribed to EC protons next to the OH group. Moreover, the decrease of both the integration of the residual EC peak (from 3.75 to 3.60) and the integration of methylene protons of opened TMC next the OH group (from 2.02 to 1.84) confirms that few EC molecules reacted with opened TMC. The last evidence of this reaction is the splitting of the singlet corresponding to protons on OH groups confirming the presence of 2 end-groups (open EC and open TMC). Based on 2D NMR analysis and knowing that the reaction of open EC on itself is thermodynamically unfavourable, a mechanism was proposed for the copolymerization of EC and TMC (Scheme 2).



Scheme 2: Proposed mechanism for EC/TMC copolymerization in the presence of BnOH as initiator.

To conclude this part, several catalysts have been tested in the ROP of EC and TMC. Even though EC content incorporated in the PTMC backbone remains low and mostly isolated unit, all the copolymers do not contain ether units coming from the decarboxylation side reaction. The most promising catalyst in terms of EC incorporation and copolymer molar mass was **NHC-IPr**. In addition, mechanistic studies confirmed that one EC molecule could react with open TMC at 60°C. Based on this study, a mechanism (Scheme 2) was proposed for the ring-opening copolymerization of EC and TMC.

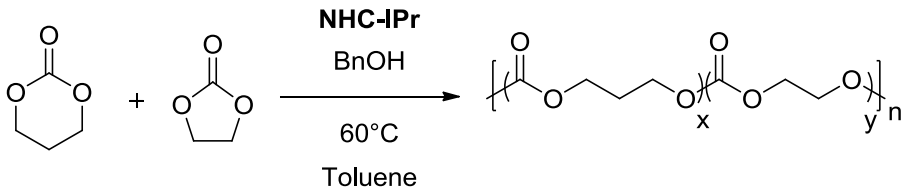
Consequently, **NHC-IPr** was chosen as catalyst for the optimization of the reaction conditions towards a higher incorporation of EC units. The monomer feed ratio and the initiator to monomer ratio will be adjusted with the aim of improving EC incorporation.

2. Towards higher EC unit incorporation

2.1 Influence of the $[EC]_0/[TMC]_0$ feed ratio

As a consequence of the above results, **NHC-IPr** was used as catalyst in the following part. Polymerizations were performed until full conversion of TMC (maximum 2 hours), in toluene at 60°C ($[EC]_0+[TMC]_0$ = 4 mol.L^{-1}) with BnOH as initiator ($[Catalyst]_0 = [BnOH]_0$ = 1 mol.% with respect to $[EC]_0+[TMC]_0$). Two main parameters were tuned in order to increase the EC content in the polycarbonate. The effect of $[EC]_0/[TMC]_0$ feed ratio was first studied on the copolymer composition. The results are summarized in Table 2.

Table 2: Effect of the $[EC]_0/[TMC]_0$ feed ratio on EC incorporation[a]



Entry	EC/TMC	[EC]/ [TMC]/ [BnOH]/[Cat.]	EC unit incorporation (%)[b]	EC conversion (%)[b]	Mn (g.mol^{-1})[c]	M_w/M_n[c]
P2	25/75	50/150/2/2	7.1	22.5	8 000	2.1
P6	50/50	100/100/2/2	6.9	7.4	7 500	1.74
P7	75/25	150/50/2/2	9.4	3	oligomers	-

a: reaction conditions: NHC -IPr used as catalyst, toluene, 60°C b: calculated by ^{1}H NMR c: determined by SEC in THF

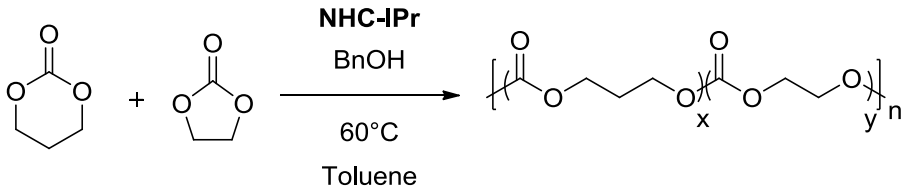
An increase of EC content in the feed (Table 2) enables to slightly increase the incorporation of EC in the copolymer. However, the EC content in the copolymer remains low (in between 7.1 mol.% and 9.4 mol.%). More importantly, it is associated with a decrease of the copolymer molar mass, explained by the very low reactivity of EC in ROP. Indeed, only oligomers are obtained for the $[EC]_0/[TMC]_0$ ratio = 75/25. This trend was also confirmed by Guillaume *et al.*[11] in the case of the copolymerization of EC with cyclic esters.

Consequently, as we observed that the polymerization stops when all the TMC is consumed, a methodology to incorporate more EC units in the PTMC backbone would be to target a higher degree of polymerization by varying the $[initiator]_0/[monomers]_0$ ratios, as discussed in the next section.

2.2 Effect of the initiator to monomer ratio

Several $[initiator]_0/[monomers]_0$ ratios were tested (Table 3) keeping the EC/TMC molar feed ratio of 1/1. Polymerizations were still performed until full conversion of TMC, in toluene at 60°C ($[EC]_0+[TMC]_0 = 4$ mol.L^{-1}) with **NHC-IPr** as catalyst and BnOH as initiator.

Table 3: Influence of the initiator loading on EC incorporation[a]



Entry	Initiator/monomers ratio (mol.%)	[EC]/[TMC]/ [BnOH]/[Cat.]	EC units incorporation (%)[b]	M_n (g.mol^{-1})[c]	M_w/M_n[c]
P6	1	100/100/2/2	6.9	7 500	1.74
P8	0,5	200/200/2/2	7.0	8 500	1.36
P9	0,25	400/400/2/2	8.9	10 800	1.42
P10	0,1	1000/1000/2/2	12.7	20 800	1.58
P11	0,05	2000/2000/2/2	15.0	30 400	1.40

a: reaction conditions: NHC- IPr used as catalyst, toluene, 60°C b: calculated by ^{1}H NMR c: determined by SEC analysis in THF.

As expected, the molar masses of the copolymer can be tuned by adjusting the quantity of initiator. The lower the $[initiator]_0/[monomers]_0$ ratio, the higher the copolymer molar mass (e.g. 20 800 g.mol^{-1} for $[initiator]_0/[monomers]_0$ ratio = 0.1). The molar masses varied from 7 500 g.mol^{-1} to 30 400 g.mol^{-1} with a dispersity around 1.5. These values are lower than theoretical ones -based on a living mechanism- because of the poor reactivity of EC in ROP. The SEC profiles of different EC/TMC copolymers prepared at various $[initiator]_0/[monomers]_0$ ratios are

presented in Figure 6. A shoulder is observed on SEC traces for low molar mass polymers. That may be due to the formation of homoPTMC since the incorporation of EC is relatively poor in such copolymers.

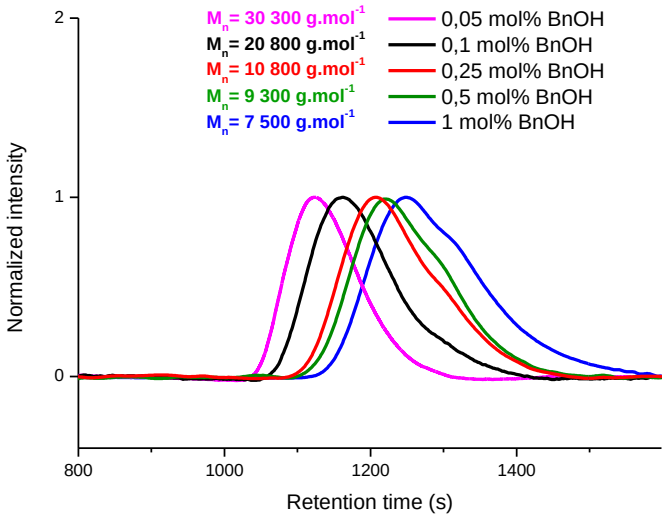


Figure 6: SEC traces of EC/TMC copolymers depending on $[initiator]_0$ / $[monomers]_0$ ratio

Surprisingly, a significant increase of EC content in the copolymer was observed when high molar masses were targeted, i.e. for low $[initiator]_0/[monomers]_0$ ratios. A value of 15.0 mol.% of incorporated EC was obtained (Table 3, entry P11) for M_n = 30 400 $g.mol^{-1}$. As far as we know, this represents the highest amount of EC units incorporated into a PTMC backbone. Therefore, targeting high copolymer molar mass appeared to be the best strategy to increase EC content in the copolymer.

3. Molecular characterization of the copolymers

The chemical structure of such copolymers was fully elucidated and confirmed thanks to ^{1}H, ^{13}C and 2D NMR spectroscopy as illustrated in Figure 7, Figure 8 and Figure 9.

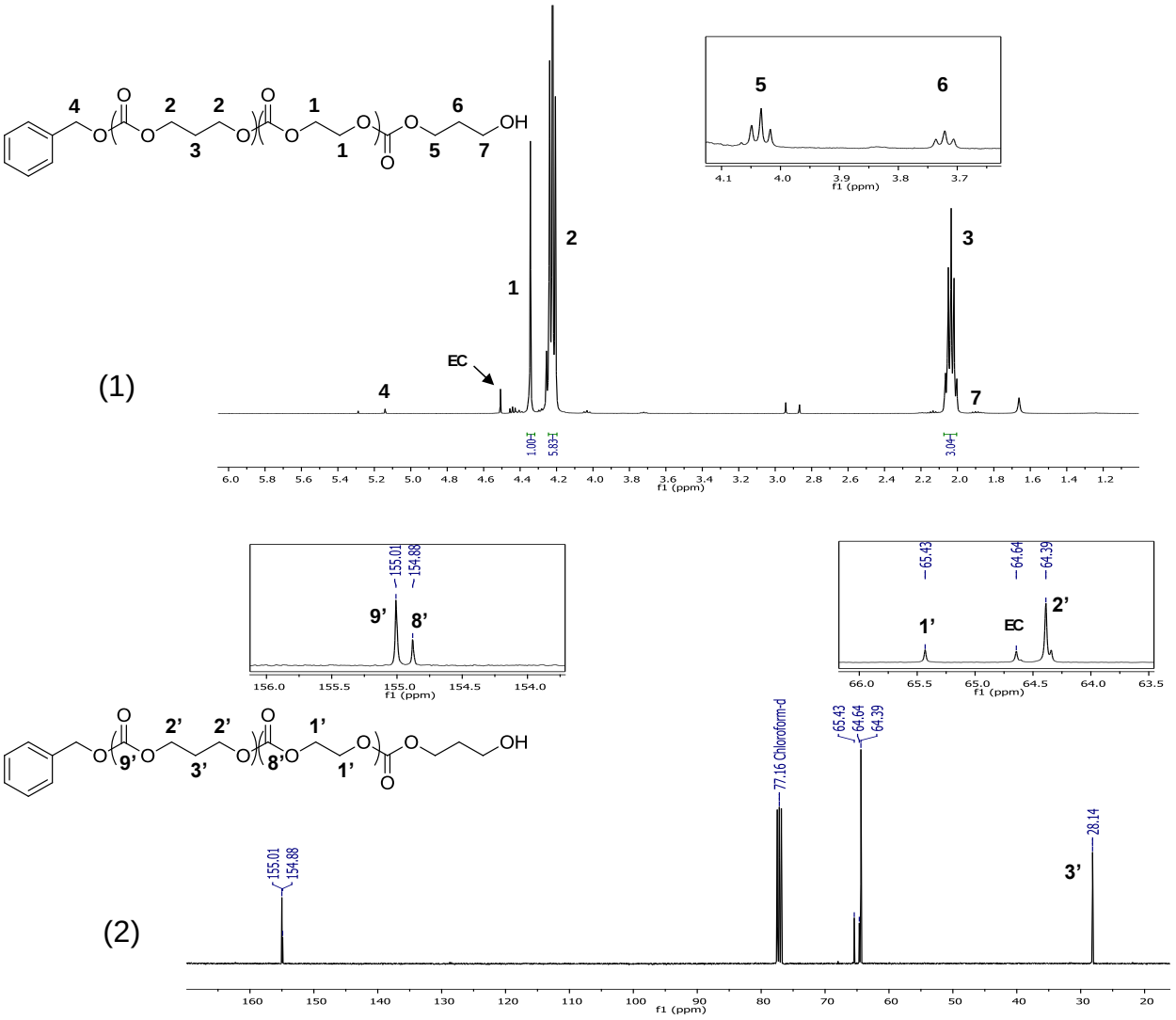


Figure 7: (1) ^{1}H and (2) ^{13}C NMR spectra of copolymer in $CDCl_3$ (Table 3, P11)

In the ^{1}H NMR spectrum (Figure 7-(1)), the appearance of the peaks at 2.02 to 2.10 ppm and 4.20 to 4.30 ppm were due to the main chain of the PTMC. In addition, the peak at 4.35 ppm is attributed to EC units incorporated into the PTMC backbone. This was confirmed by ^{1}H-^{1}H COSY NMR analysis (Figure 8) where the two signals are correlated. The peak of the initiator BnOH was observed at 5.15 ppm as shown in Figure 7-(1). It indicates that the ROP of TMC and EC was initiated by BnOH successfully. The chain-end was also identified by the peak at 4.04, 3.72 and 1.8 ppm. Even after several precipitations in methanol, residual EC monomer was observed in the ^{1}H NMR spectrum at 4.51 ppm. Weak signals were also observed at 5.3 ppm and

1.65 ppm, which were attributed to residual DCM and water respectively. Finally, traces of DMF were detected at 2.88 and 2.96 ppm.

Thanks to 2D HSQC NMR analysis (Figure 9), the peaks in the ^{13}C NMR spectrum at 155.0, 64.4 and 28.1 ppm were assigned to carbons on the PTMC skeleton (Figure 7-(2)). Moreover, the signal at 65.4 ppm represented the EC units integrated to the copolymer whereas the peak at 64.6 ppm was attributed to the EC monomer. Once again no ethylene oxide units were identified at 71.1–68.3 ppm. Importantly, only 2 signals were observed in the carbonyl region of the ^{13}C NMR spectrum (Figure 7-(2)). The most downfield carbonyl signal (δ = 154.9 ppm) was assigned to an isolated EC unit within several consecutive TMC units. Indeed, Agarwal *et al.*[25] reported that the absence of several signals assigned to the carbonyl of EC suggested its occurrence as isolated EC units.

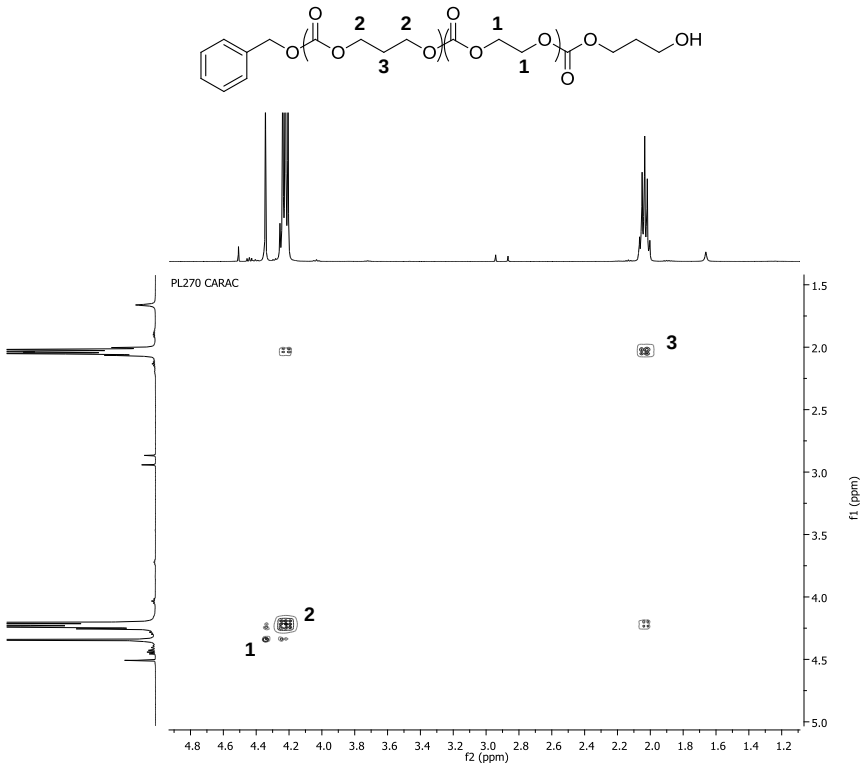


Figure 8: ^{1}H-^{1}H COSY NMR spectrum of P(EC-*co*-TMC)

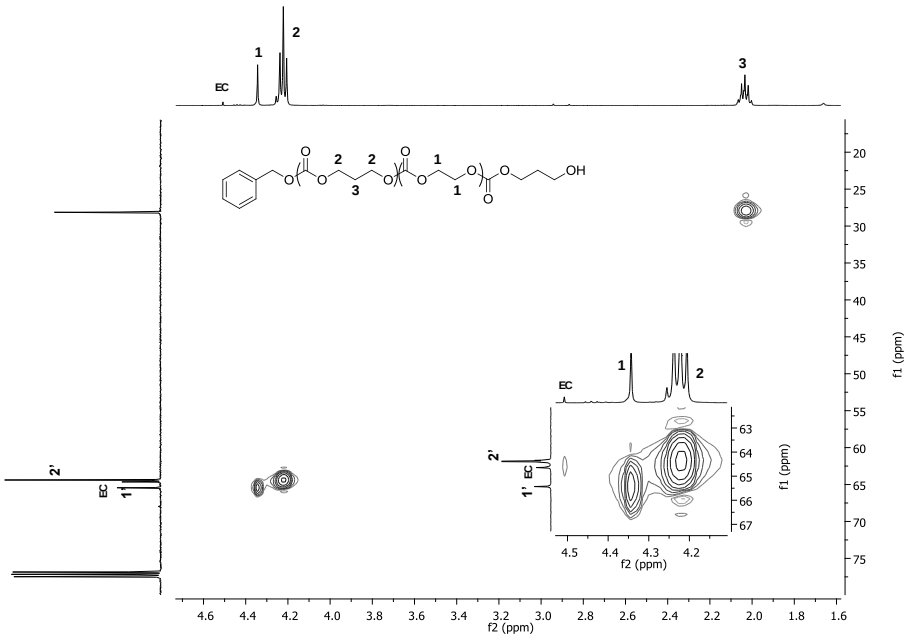


Figure 9: ^{1}H-^{13}C HSQC NMR spectrum of P(EC-*co*-TMC)

However, these techniques did not prove that both EC and TMC units belong to the same polymer chain. This is why copolymers have been characterized by Diffusion-Ordered SpectroscopY (DOSY) analysis. DOSY enables to separate the NMR signals of different species according to their diffusion coefficient. Therefore, if the NMR signals of both EC and TMC units have the same diffusion coefficient, they formed only one polymer chain.

The diffusion ordered NMR spectrum of the copolymer is depicted in Figure 10. It shows that EC units and TMC units have the same coefficient of diffusion ($D = 8.78.10^{-11}$ $m^2.s^{-1}$) so that they belong to the same polymer chain. However, residual EC monomer exhibits a different diffusion coefficient that proves that it is not linked to the polymer chain. This analysis confirms the formation of one copolymer and not of two homopolymers.

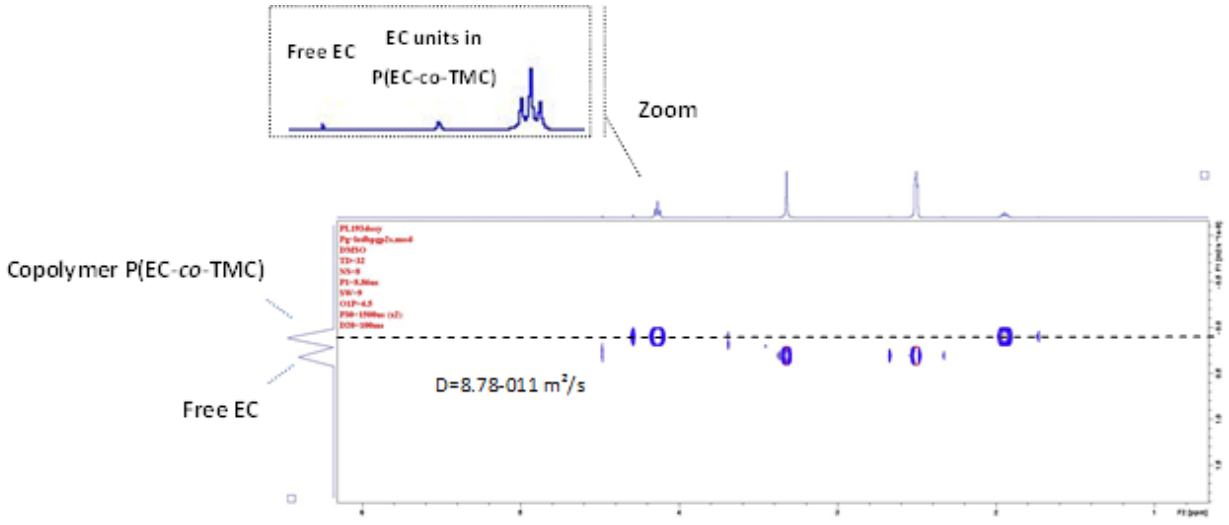


Figure 10: 400 MHz DOSY NMR spectrum obtained at 298K in DMSO-d_6

As a conclusion of this part, the characterization of the EC-TMC copolymer confirmed the absence of decarboxylation side reaction during the polymerization. It also proved that EC units were isolated in the PTMC backbone supporting the fact that an opened EC cannot react on another EC unit. Finally, DOSY experiment proved the formation of true random copolymers.

4. Influence of EC content on the copolymer thermal properties

With respect to the thermal properties, all the copolymers were characterized by DSC and TGA analyses. The copolymer characteristics are summarized in Table 4. As displayed in Figure 11, all the copolymers presented a rather low thermal stability with a significant weight loss (5 wt.%) occurring from 139.7°C (copolymer with 4.1 mol.% of EC) to 194.5°C (copolymer with 15.0 mol.% of EC). However, it is worth noting that increasing the content of EC in the copolymer enables to enhance the copolymer thermal stability. In addition, all these polycarbonates decompose quickly beyond the temperature of 200°C and lost almost their entire weight (> 99%) around 280°C under nitrogen. Nevertheless, it is also important to mention that the copolymers discussed in this study displayed different molar masses. Therefore, the thermal stability could be also impacted by a higher molar mass of the copolymer.

Table 4: Thermal properties of P(EC-*co*-TMC) with different EC content

Entry	EC content in the copolymer (mol.%)[a]	T_g (°C)[b]	T_d (°C)[c]
P3	4.1	-26.1	139.7
P6	6.9	-26.3	143.0
P9	8.9	-25.2	158.5
P10	12.7	-24.1	171.0
P11	15.0	-23.6	194.5

a: calculated by ^{1}H NMR b: determined by DSC analysis c:determined by TGA analysis after 5 wt% loss

The random copolymers prepared in this work, containing from 4.1 mol% to 15.0 mol% of EC units were analyzed by means of differential scanning calorimetry (DSC) after precipitation into methanol. DSC traces (second heating cycle) are presented in Figure 12. As can be seen, all the copolymers are amorphous with T_g values around -25°C. Since less than 20 mol.% of EC was incorporated into the PTMC backbone, the T_g of the different copolymers was roughly in the same range of temperature. Indeed, the incorporation of 15.0 mol% of EC only increased the copolymer T_g of around 6°C with respect to homoPTMC (T_g = -29°C).

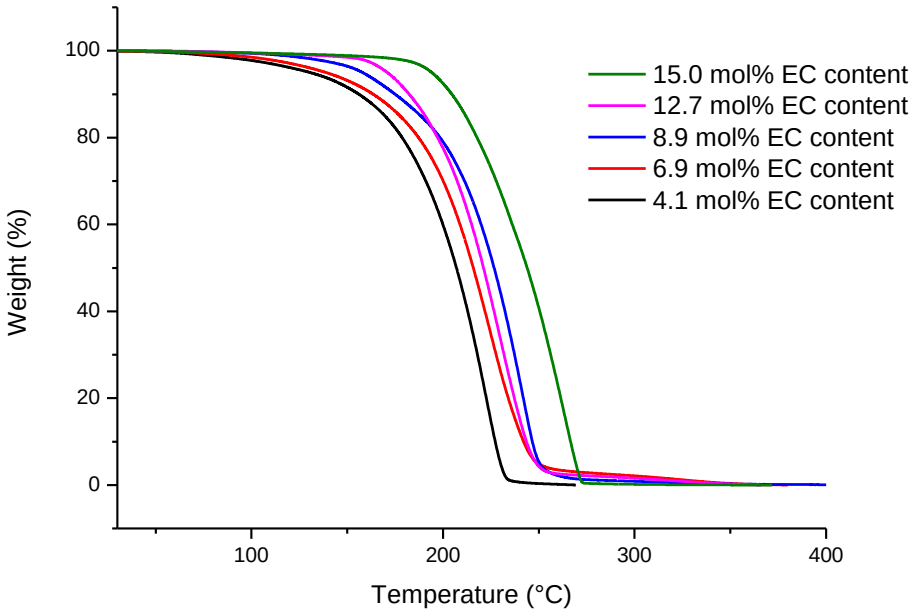


Figure 11: TGA curves of P(EC-*co*-TMC) with different EC content

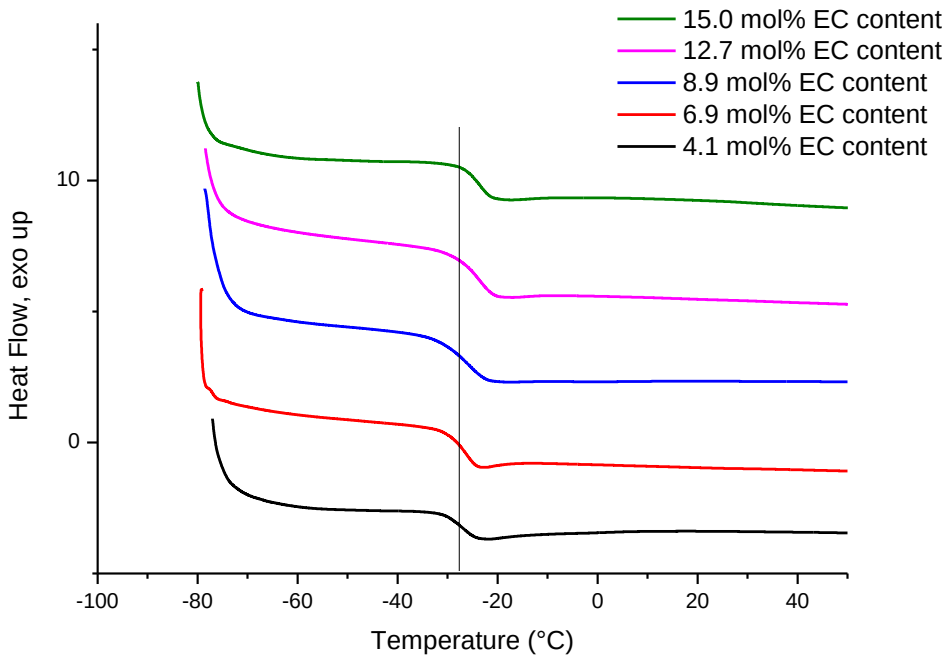


Figure 12: DSC traces of Poly(EC-*co*-TMC) with respect to EC content

A representation of $1/T_g$ vs w_2 according to the Fox relation (Equation 2), where w_1 and w_2 represent the weight fractions of TMC and EC respectively, and T_{g1} (- 29°C) and T_{g2} (13°C) the glass transition temperatures of the homopolymers poly(TMC) and poly(EC), reveals that the experimental values (cf. Figure 13, red line) are in good agreement with those predicted by the Fox equation (cf. Figure 13, dotted line).

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

Equation 2: Fox equation relating the T_g of the copolymer and of the two homopolymers

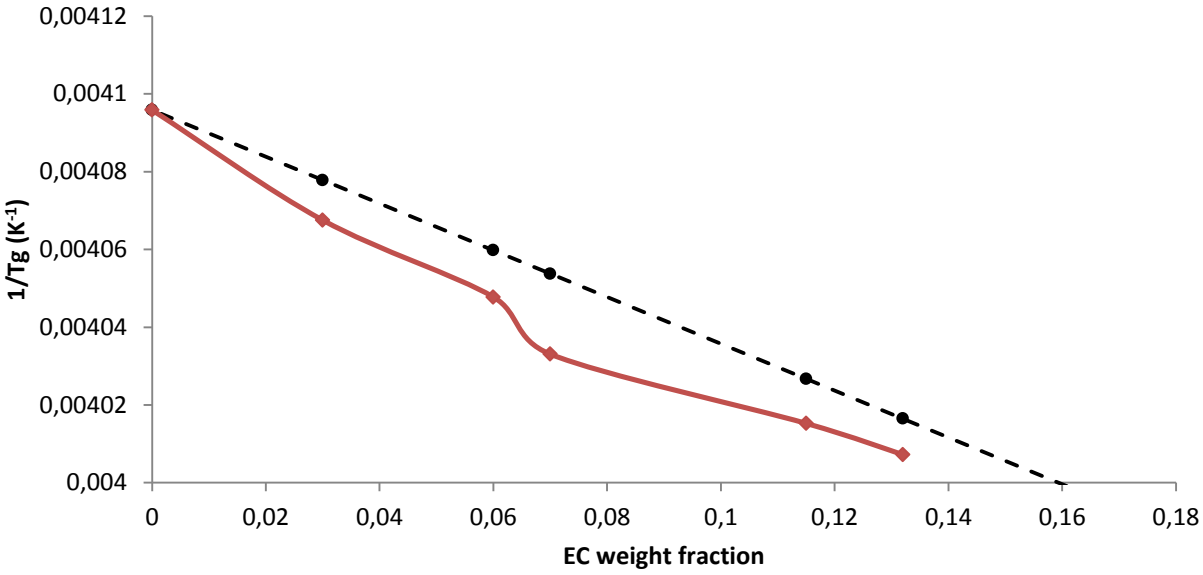


Figure 13: Glass transition temperature (T_g) of statistical P(EC-*co*-TMC) copolymers as a function of the copolymer composition, represented according to the Fox relation (Equation 2)

As a conclusion of this section, several copolymers with different EC content were characterized in terms of thermal properties. The incorporation of EC units improved the thermal stability and the T_g value of the copolymers.

Conclusion

This chapter highlights the problematic encountered with 5-membered ring cyclic carbonates. Indeed, although the latter can be easily prepared from fatty acids, their unfavourable characteristic in ring-opening polymerization, imparted by their inherent structure, is an obstacle to their homopolymerization. However, such cyclic carbonates can undergo ring-opening copolymerization with other heterocyclic monomers. Undescribed in the literature, the copolymerization of EC and TMC has been studied as a model reaction.

The influence of various parameters such as the nature of the catalyst, the EC feed content or the initiator to monomer ratio has been studied. The optimized process affords the incorporation of 15.0 mol.% of EC incorporated in a PTMC backbone. In addition, all the polymerizations occur without decarboxylation side-reaction, which is usual for the polymerization of 5CCs. Further characterizations of the obtained copolymers demonstrated that EC units were isolated in the PTMC backbone.

Then, the effect of EC incorporation on copolymer properties has been investigated. Interestingly, it reveals that an increase of EC content in the copolymer enhanced its thermal stability. Besides, the presence of EC units in the copolymers slightly increases their glass transition temperatures.

Finally, some copolymerizations of a series of lipidic 5CCs with TMC have been performed under the optimized conditions described above (in toluene at 60°C ($[EC]_0+[TMC]_0$ = 4 mol.L^{-1}, **NHC-IPr** as catalyst and BnOH as initiator with $[5CCs]_0/[TMC]_0/[Catalyst]_0/[BnOH]_0$ ratios of 2000:2000:2:2). Such lipidic monomers were developed by Lamarzelle *et al.* in the framework of another project dealing with the synthesis of poly(hydroxyurethane)s (Figure 14).[3]

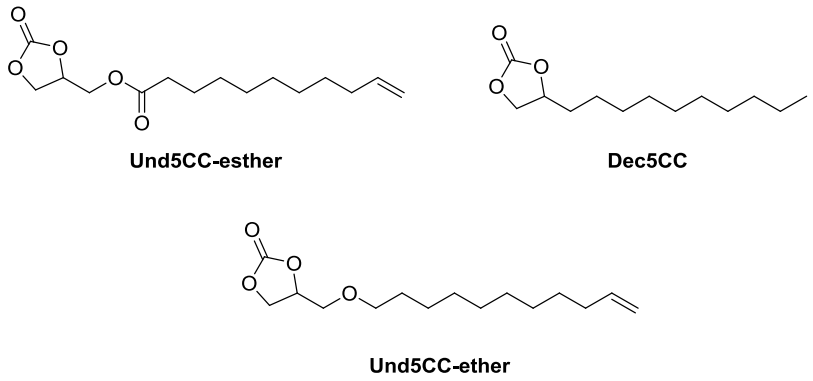


Figure 14: Activated lipidic 5-membered cyclic carbonates used in copolymerization with TMC

Unfortunately, these copolymerizations failed, affording only homoPTMC.

This work investigated the copolymerization of 5CCs and 6CCs with EC and TMC as models. Few others parameters could have been studied but we decided to move towards the synthesis of more reactive cyclic carbonates, i.e. 6-membered ring cyclic carbonates. Consequently, the next chapter will be focused on the synthesis of more reactive lipidic 6CCs. Their reactivity in ROP will be also discussed.

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Experimental methods

1. Synthesis of activated lipidic 5CCs

- Dec-5CC synthesis: The commercially available 1,2-epoxydodecane (3.02 g, 16.4 mmol) was first pre-mixed with TBABr (0.09 g, 0.28 mmol, 3 w.%) and 5 mL of acetone. Afterwards, the mixture was placed in a high-pressure autoclave and heated up at 80°C. Once the temperature got stabilized, CO_2 was slowly introduced into the reactor until 40 bars. After 3 days, the reactor was cooled down to RT and slowly depressurized to the atmospheric pressure. The ^{1}H NMR of the final mixture revealed a conversion of 98%. The **Dec-5CC** was purified by flash chromatography using a mixture of cyclohexane: ethyl acetate (100:0 to 88:12). The product was isolated as transparent viscous oil with a yield of 90%. ^{1}H NMR ($CDCl_3$, 25°C, 400 MHz), δ (ppm): 4.70 (m, 1H), 4.49 (t, 1H), 4.06 (t, 1H), 1.80 (m, 1H), 1.65 (1H), 1.40-1.26 (16H), 0.89(t, 3H). ^{13}C-NMR ($CDCl_3$, 25°C, 100 MHz), δ (ppm): 155.3 (OCOO), 77.4 (<u>C</u>H-OCOO), 69.5 (<u>C</u>H_2-OCOO), 34.0 (<u>C</u>H_2-CH-OCOO), 31.9-22.7 (CH_2), 14.2 (CH_3). IR (cm^{-1}): 2925, 2848, 1789

- UndCC-ether synthesis : **(i)** In a round-bottom flask, 10-undecen-1-ol (10 g, 58.7 mmol) was stirred with epichlorohydrin (54.35 g, 587 mmol, 10 eq.) and TBABr (1.89 g, 5.87 mmol, 0.1 eq.) at room temperature for 30 min. NaOH was added *via* a 50 w.% concentrated aqueous solution (70 mL, 0.88 mol, 15 eq.). After 24h of reaction at room temperature, the mixture reaction was diluted with 4 volumes of distilled water. The aqueous phase was extracted 3 times with 100 mL of ethyl acetate. The organic phase was then washed twice with 75 mL of water, dried over anhydrous magnesium sulfate, filtered and the remaining epichlorohydrin was removed on rotary evaporator. The ^{1}H NMR spectrum revealed a conversion of 72%. The compound **Und-epoxide** was purified by flash chromatography using a mixture of cyclohexane and ethyl acetate (100:0 to 88:12) and obtained as a viscous transparent liquid. Yield: 58%. ^{1}H NMR ($CDCl_3$, 25°C, 400 MHz), δ (ppm): 5.80 (m, 1H), 4.96 (m, 2H), 3.70 and 3.37 (dd, 2H), 3.49 (m, 2H), 3.14(m, 1H), 2.78 and 2.59 (t, 2H), 2.02 (m, 2H), 1.58-1.28 (m, 14H). ^{13}C NMR ($CDCl_3$, 25°C, 100 MHz), δ (ppm):137.9 (<u>C</u>H=CH_2), 113.2 (CH=<u>C</u>H_2), 70.7 (O<u>C</u>H_2-CH_2), 70.4 (<u>C</u>H_2O-CH_2CH_2), 49.9 (CH_2-<u>C</u>H-CH_2O), 43.4 (<u>C</u>H_2-CH-CH_2O), 32.7 (<u>C</u>H_2-CH=CH_2), 28.7-25.1 (CH_2). **(ii)** The **Und-epoxide** (7.72 g, 34.2 mmol) was first pre-mixed with the TBABr (0.24 g, 0.7 mmol, 3 w.%) in 5 mL of acetone. 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 bars. After 3 days, the reactor

was cooled down to RT and slowly depressurized to the atmospheric pressure. The mixture was reconcentrated on rotary evaporator. The ^{1}H NMR of the final mixture revealed a conversion of 98%. The **UndCC-ether** was purified by flash chromatography using a mixture of cyclohexane and ethyl acetate (100:0 to 81:19), and obtained as a viscous transparent liquid. Yield: 82%. ^{1}H NMR ($CDCl_3$, 25°C, 400 MHz), δ (ppm): 5.72 (m, 1H), 4.90 (m, 2H), 4.73 (m, 1H), 4.42-4.32 (t, 2H), 3.58 (m, 2H), 3.41 (t, 2H), 1.98 (dd, 2H), 1.48 (m, 2H), 1.21 (m, 14H). ^{13}C NMR ($CDCl_3$, 25°C, 100 MHz), δ (ppm): 155.3 (O<u>C</u>OO), 138.8 (<u>C</u>H=CH_2); 114.2 (CH=<u>C</u>H_2), 74.7 (CH_2-<u>C</u>H-CH_2O), 71.8 (CH_2O-<u>C</u>H_2-CH_2), 68.8 (CH-<u>C</u>H_2O-CH_2), 66.1 (<u>C</u>H_2-CH-CH_2O), 33.6 (<u>C</u>H_2-CH=CH_2), 28.7-26.2 (CH_2). IR (cm^{-1}): 3075, 2979, 2928, 2850, 1760

- UndCC-ester synthesis*:* **(i)** Into a round-bottom flask containing 1 eq. (250 g, 1.34 mol) of undecenoic acid, thionyl chloride (271.5 g, 2.28 mol) was added dropwise under inert atmosphere at 60°C and the formed SO_2 and HCl were trapped during the reaction (with gas traps containing aqueous sodium hydroxide solution). When the conversion (determined by GC) was quantitative (> 99%), the excess of thionyl chloride was distilled out and the product was stored at -18°C. Yield: 99%. **(ii)** In a round-bottom flask, 1 eq. (116.7 g, 0.99 mol) of glycerol carbonate and 1.3 eq. (130.2 g, 1.29 mol) of triethylamine were diluted in 500 mL of dry THF. 1 eq. (270 g, 0.99 mol) of undecenoyl chloride was added dropwise under inert atmosphere at 0°C. The mixture reaction was left 2h at room temperature and the conversion (determined by GC) reached 96%. **UndCC-ester** was then extracted with 250 mL of ethyl acetate and washed several times with 250 mL of water before solvent reconcentration. ITERG provided 20 g of the crude **UndCC-ester**, obtained as an oily white powder that could be purified by recrystallization in 100 mL of cold heptane. 73% yield was achieved after subsequent reconcentration of the recrystallization filtrate and recrystallization.^{1}H NMR ($CDCl_3$, 25°C, 400 MHz), δ (ppm): 5.82 (m, 1H), 5.00 (m, 2H), 4.91 (m, 1H), 4.55 (t, 1H), 4.31 (m, 3H), 2.36 (t, 2H), 2.02 (m, 2H), 1.59-1.29 (m, 14H). ^{13}C NMR ($CDCl_3$, 25°C, 100 MHz), δ (ppm): 173.6 (CH_2-O<u>C</u>O-CH_2), 154.2 (OCOO), 139.2 (<u>C</u>H=CH_2), 114.0 (CH=<u>C</u>H_2), 73.5 (<u>C</u>H-CH_2-OCO), 65.5 (<u>C</u>H_2-CH-CH_2-OCO), 62.7 (CH-<u>C</u>H_2-OCO), 34.4 (OCO-<u>C</u>H_2-CH_2), 33.9 (<u>C</u>H_2-CH=CH_2), 31.1-29.0 (CH_2), 24.9 (OCO-CH_2-<u>C</u>H_2). IR (cm^{-1}): 3081, 3000, 2920, 2853, 1781, 1733

2. Typical procedure for the copolymerization of EC and TMC:

All polymerizations were performed under inert atmosphere (nitrogen) in 20-mL ampules using standard Schlenk, vacuum line, and glovebox techniques. In a typical procedure (Table 2, entry P6), EC (113 mg, 1.29 mmol, 100 equiv.) and TMC (131 mg, 1.29 mmol, 100 equiv.) were added to a solution of **NHC-IPr** (10.0 mg, 26 μmol, 2 equiv.) and benzyl alcohol (2.6 μL, 26 μmol, 2 equiv.) in toluene (0.6 mL, $[EC]_0+[TMC]_0$ = 4 mol.L^{-1}). The mixture was then stirred at 60°C over the appropriate period of time (conversion of TMC monitored by ^{1}H NMR). After full conversion of TMC, the reaction mixture was concentrated to dryness under vacuum. The conversion of EC was determined from the crude reaction mixture. The crude polymer was next dissolved in CH_2Cl_2 and precipitated in cold methanol, filtered and dried under vacuum. Yield = 50-70%. The final P(EC-co-TMC) copolymers were then analyzed by NMR, SEC and DSC.

3. Characterization of copolymers

^{1}H and ^{13}C-NMR spectra were recorded on Bruker Avance III 400 spectrometer (400.20 MHz or 400.33 MHz and 100.63 MHz for 1H and 13C, respectively) by using $CDCl_3$ as a solvent at room temperature, except otherwise mentioned.

All DOSY (Diffusion Ordered Spectroscopy) measurements were performed at 298K on a Bruker Avance III 400 spectrometer operating at 400.33 MHz and equipped with a 5mm Bruker multinuclear z-gradient direct cryoprobe-head capable of producing gradients in the z direction with strength 53.5 G cm^{-1}. For each sample, 2 mg was dissolved in 0.4 ml of DMSO-d6 for internal lock and spinning was used to minimize convection effects. The dosy spectra were acquired with the *ledbpgp2s* pulse program from Bruker topspin software. The duration of the pulse gradients and the diffusion time were adjusted in order to obtain full attenuation of the signals at 95 % of maximum gradient strength. The values were 3.0 ms for the duration of the gradient pulses and 100 ms for the diffusion time. The gradients strength was linearly incremented in 32 steps from 5% to 95% of the maximum gradient strength. A delay of 3 s between echoes was used. The data were processed using 8192 points in the F2 dimension and 128 points in the F1 dimension with the Bruker topspin software. Field gradient calibration was accomplished at 25°C using the self-diffusion coefficient of H2O+D2O at 19.0 x 10^{-10} $m^2.s^{-1}$

Differential scanning calorimetry (DSC) measurements of polymer samples (~5 mg) were performed using a Q 100-RCS apparatus from TA Instruments over temperature range from 0 to 230°C, in a heating cooling mode of 10°C min^{-1}. The analyses were carried out in a nitrogen atmosphere with aluminum pans.

Polymer molar masses were determined by size exclusion chromatography (SEC) using tetrahydrofuran (THF with 250ppm of BHT as inhibitor) as the eluent. Measurements in THF were performed on a PL GPC 50 from Agilent equipped with RI and UV detector. The separation is achieved on three Tosoh TSK HXL gel columns (300 × 7.5mm) G4000, G3000 and G2000 with an exclusion limits from 200 to 400 000 Da, at flow rate of 1 mL/min. The injected volume was 20µL. Columns' temperature was held at 40 °C.

Chapter 3

Synthesis and polymerization of new fatty acid-based six-membered ring cyclic carbonates

Keywords: Fatty acids, six-membered cyclic carbonates, ring-opening polymerization, thermoplastics

Mots-clés: Acides gras, carbonates cycliques à 6 centres, polymérisation par ouverture de cycle, thermoplastiques.

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Introduction

Aliphatic polycarbonates are well known for their specific features such as low T_g, resistance towards hydrolysis, biocompatibility and biodegradability. Their synthesis can be achieved *via* different routes but they are mainly synthesized through ring-opening polymerization (ROP) of cyclic carbonate monomers.[1] Indeed, under suitable conditions, the ROP of cyclic carbonates affords the polymer in a controlled manner. In addition to the polymer size and dispersity, the polymer microstructure and the nature of end-groups can be controlled.

The advantage of functional polycarbonates over the traditional PTMC is the possibility to modulate the polymer physico-chemical properties to specific needs, thereby broadening and improving their performance characteristics. Such functional polymers can be synthesized either upon direct polymerization of the functionalized monomer or upon chemical modification post-polymerization. This chapter will be focusing on the design of functional 6-membered cyclic carbonates and their direct polymerization.

Moreover, because of environmental concerns and also in view of fossil fuel depletion, the use of building blocks from renewable resources such as vegetable oils is of great interest.[2] With this philosophy, we aimed at synthesizing a platform of fatty acid-based cyclic carbonates as precursors of original aliphatic bio-based polycarbonates. With the objective to develop new bio-based poly(hydroxyurethane)s, our research group recently investigated the design of vegetable oil-based 6-membered cyclic carbonates (6CCs) from bio-sourced methyl undecenoate.[3,4] In this context, the first part of this chapter covers the synthesis of a first series of bio-based 6CCs through the formation of a malonate intermediate. However, the latter route towards functional cyclic carbonates implies several synthetic steps leading to a rather low overall yield. To overcome this issue and based on the work of Venkataraman *et al.*,[5] a second strategy was investigated. This second route involves a coupling reaction between a fatty-acid derivative and 2-amino-1,3-propanediol yielding, after cyclization, a second generation of bio-based cyclic carbonates.

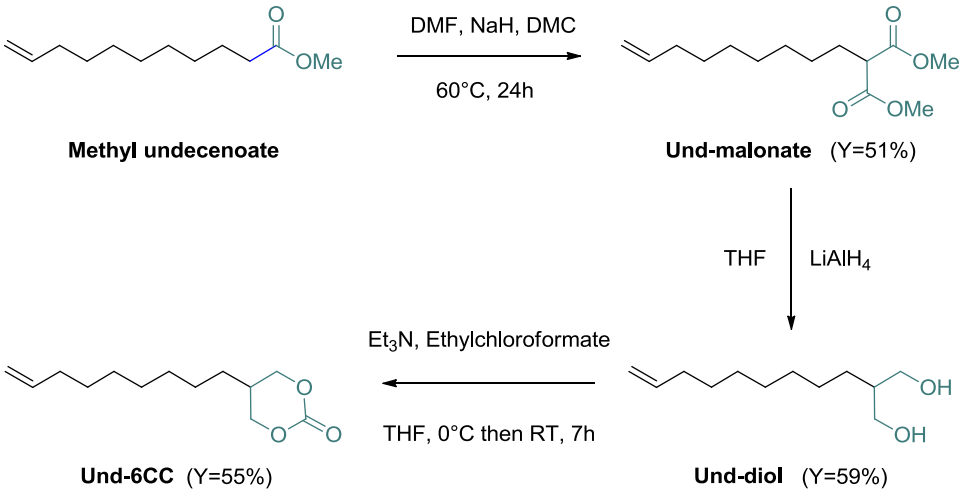
In a second part, optimized conditions were investigated to polymerize the two cyclic carbonate platforms. We find out that harsh conditions were needed to polymerize the first generation of lipidic cyclic carbonates. However, the second generation was polymerized under milder

conditions using an organo-catalytic system. These functional aliphatic polycarbonates were then fully characterized by NMR, SEC, DSC and TGA and the influence of several parameters on the polymer properties was also investigated.

1. Synthesis of bio-based 6-membered cyclic carbonates

1.1. First platform of 6CCs *via* the malonate route

As illustrated in Scheme 1, a 6-membered ring cyclic carbonate bearing an unsaturation moiety was prepared from fatty-acid derivatives using a three-step procedure.[3] Figure 1 presents the stacked ^{1}H NMR spectra of the different intermediates starting from methyl undecenoate.



Scheme 1: Synthetic route to functional 6-membered cyclic carbonate from methyl undecenoate[3]

The first step consisted in the malonate synthesis at 60°C for 24 hours from methyl undecenoate using 40 equivalents (equiv.) of dimethyl carbonate (DMC, acting also as a solvent), 2.5 equiv. of NaH and 1 equiv. of DMF. This approach using the non-toxic DMC rather than phosgene and its derivatives was developed by Kolb *et al.*.[6,7] The authors proved that a large excess of DMC prevents the Claisen-condensation side product. This method has been optimized by Maisonneuve *et al.*[3] who performed the synthesis of **Und-6CC** for the synthesis of poly(hydroxyurethane)s. Additionally, anhydrous DMF can accelerate considerably the deprotonation in α-position of the ester by increasing the solvation of the reactants and/or the

intermediates. The conversion of methyl undecenoate into **Und-malonate** was determined by ^{1}H NMR spectroscopy. The signal at 3.66 ppm of the methylene protons nearby the ester linkage of methyl undecenoate has disappeared (See Figure 1-(1)). In addition, a triplet at 3.35 ppm and a multiplet at 1.88 ppm, corresponding to the malonate group protons, confirmed the synthesis of **Und-malonate.**

In a second step, the reduction of **Und-malonate** was carried out using 4.1 equiv. of $LiAlH_4$ as reducing agent. The synthesis of the corresponding diol (**Und-1,3-diol**) was confirmed by ^{1}H NMR (See Figure 1-(3)) with the disappearance of the singlet and the triplet at 3.73 ppm and 3.35 ppm respectively, combined with the appearance of the two multiplets at 3.78 ppm and 3.63 ppm assigned to the methylene protons nearby the hydroxyl groups.

In the literature, various methods have been developed to cyclize 1,3-diols to form 6-membered cyclic carbonates.[8–16] One of these methods involves the use of ethyl chloroformate and triethylamine (TEA). To obtain **Und-6CC** from the cyclization of **Und-1,3-diol**, this method was preferred over non phosgene route due to the compared high conversion obtained. The structure of the 6-membered cyclic carbonate was confirmed by ^{1}H NMR (See Figure 1-(4)). The spectrum clearly shows the disappearance of the two multiplets corresponding to the methylene protons nearby the hydroxyl groups and the appearance of the two multiplets at 4.10 ppm and 4.35 ppm assigned to the cyclic carbonate protons. However, due to the multiple steps, the overall yield of this synthesis was approximately equal to 13 % with methyl undecenoate as starting reagent.

Using the same procedure, a series of bio-based cyclic carbonates was synthesized from other fatty acid derivatives. The latter are depicted in Figure 2 and their detailed syntheses are given in the experimental part. The yields of these syntheses were similar than the one for the synthesis of **Und-6CC**.

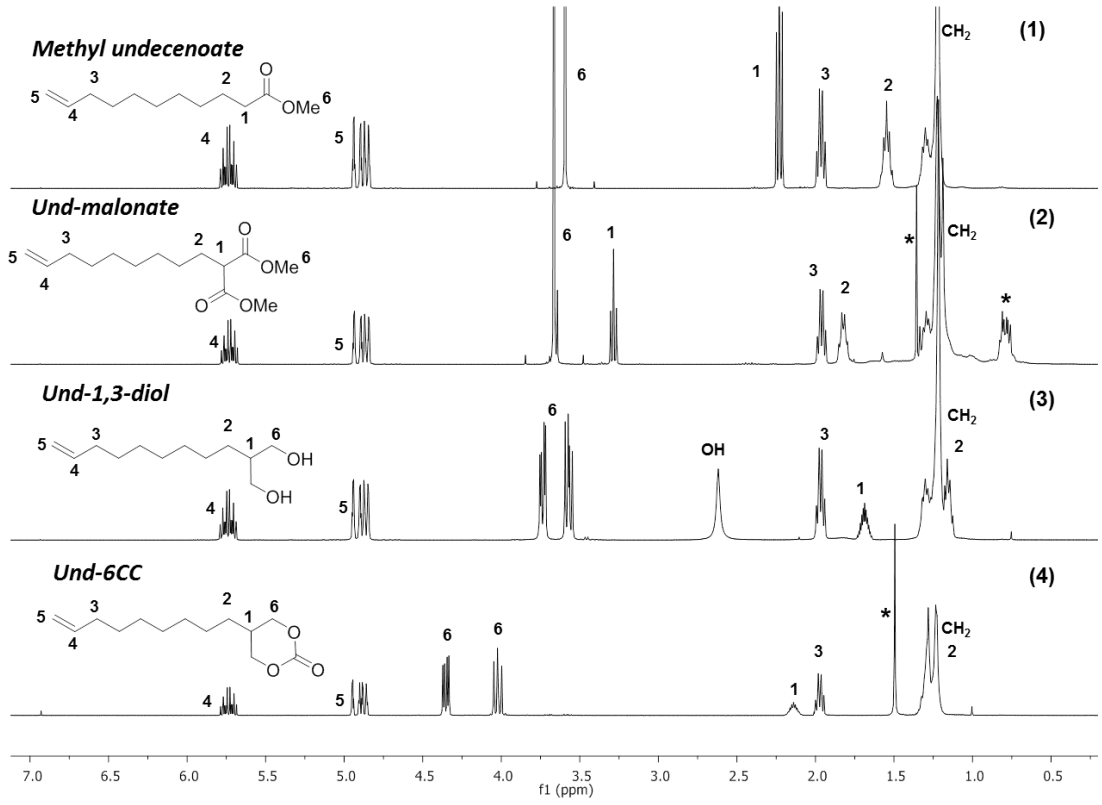


Figure 1: Stacked ^{1}H NMR spectra of (1) methyl undecenoate, (2) Und-malonate, (3) Und-1,3-diol and (4) Und-6CC. (All analyses were performed in $CDCl_3$) (* : residual solvents)

This first platform (Figure 2) allowed us to study the effect of different parameters on the polymerization. The influence of the chain length as well as of the number of unsaturations was investigated by synthesizing **Ole-6CC** from methyl oleate and **Lin-6CC** from methyl linoleate, respectively. Lastly, **Ric-6CC** from methyl ricinoleate was prepared in order to evaluate the effect of the polar hydroxyl group. Based on several studies,[17–19] an hydroxyl group was introduced on the cyclic carbonate side chain to bring polarity (**Ric-6CC**). The synthesis is detailed in the experimental part. The hydroxyl group could be useful for further post-modification reactions even though it requires protection prior to the polymerization due to its incompatibility with the ring-opening process. Hydroxyl functional groups have been commonly introduced into biodegradable polymers *via* homopolymerization of benzyloxy[20–22] or acetal[23–26] protected cyclic carbonate followed by deprotection with Pd/C or hydrolysis in mild acidic conditions.

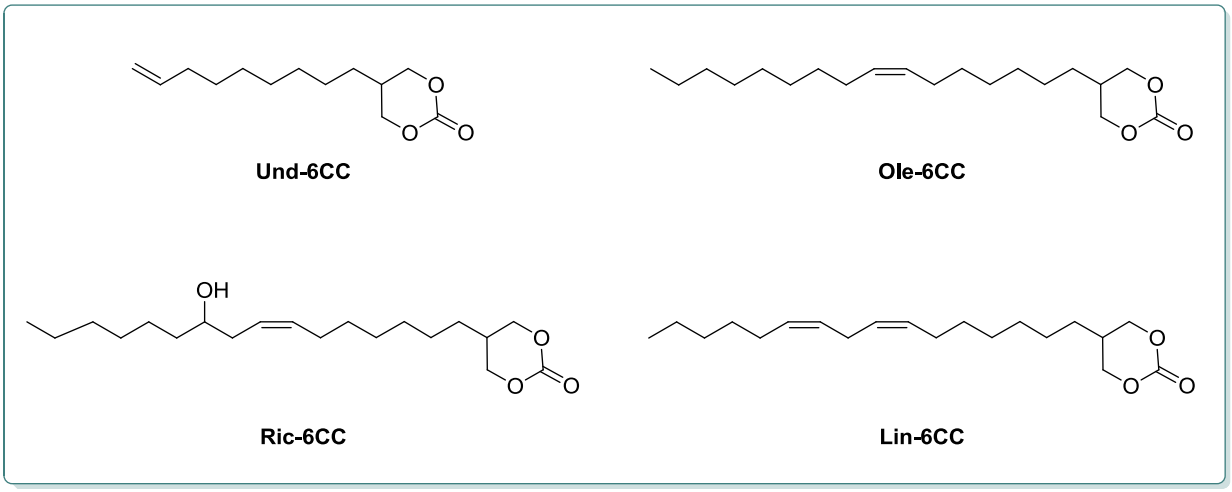
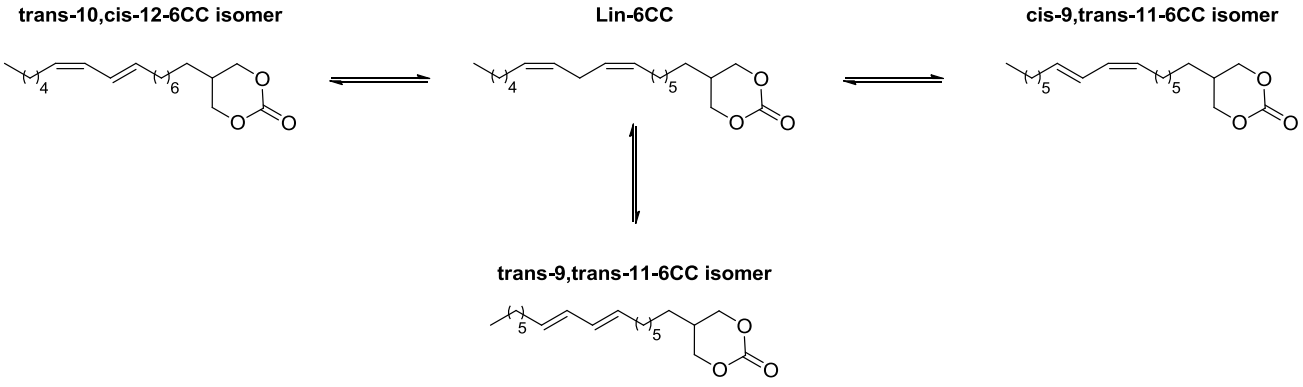


Figure 2: First platform of fatty acid-based 6-membered cyclic carbonates

All these structures were confirmed by ^{1}H NMR analyses (See Figure 1 and Figure 3). For **Ole-6CC**, a unique signal in the vinylic region at 5.33 ppm confirmed the presence of an internal double bond. Concerning **Lin-6CC**, ^{1}H NMR spectrum shows weak signals at 6.26 ppm, 5.95 ppm and 5.63 ppm, respectively. These signals are assigned to hydrogens belonging to isomerized methyl linoleate derivatives. Indeed, Jie *et al.*[27,28] highlights the isomerization of linoleic acid into *trans*-9,*trans*-11-conjugated linoleic acid (CLA), *trans*-10,*cis*-12-CLA and *cis*-9,*trans*-11-CLA as illustrated in Scheme 2. Moreover, Gunstone and Said[29] noted that the presence of DBU in a reaction media appeared to be very suitable for the preparation of the *cis*-9,*trans*-11-CLA isomer. Unsurprisingly, characteristic signals of this latter isomer observed by ^{1}H NMR fit with the unassigned signals in the **Lin-6CC** ^{1}H NMR spectrum. This study thus confirmed the formation of the *cis*-9,*trans*-11-CLA isomer.



Scheme 2: Isomerization reactions of Lin-6CC

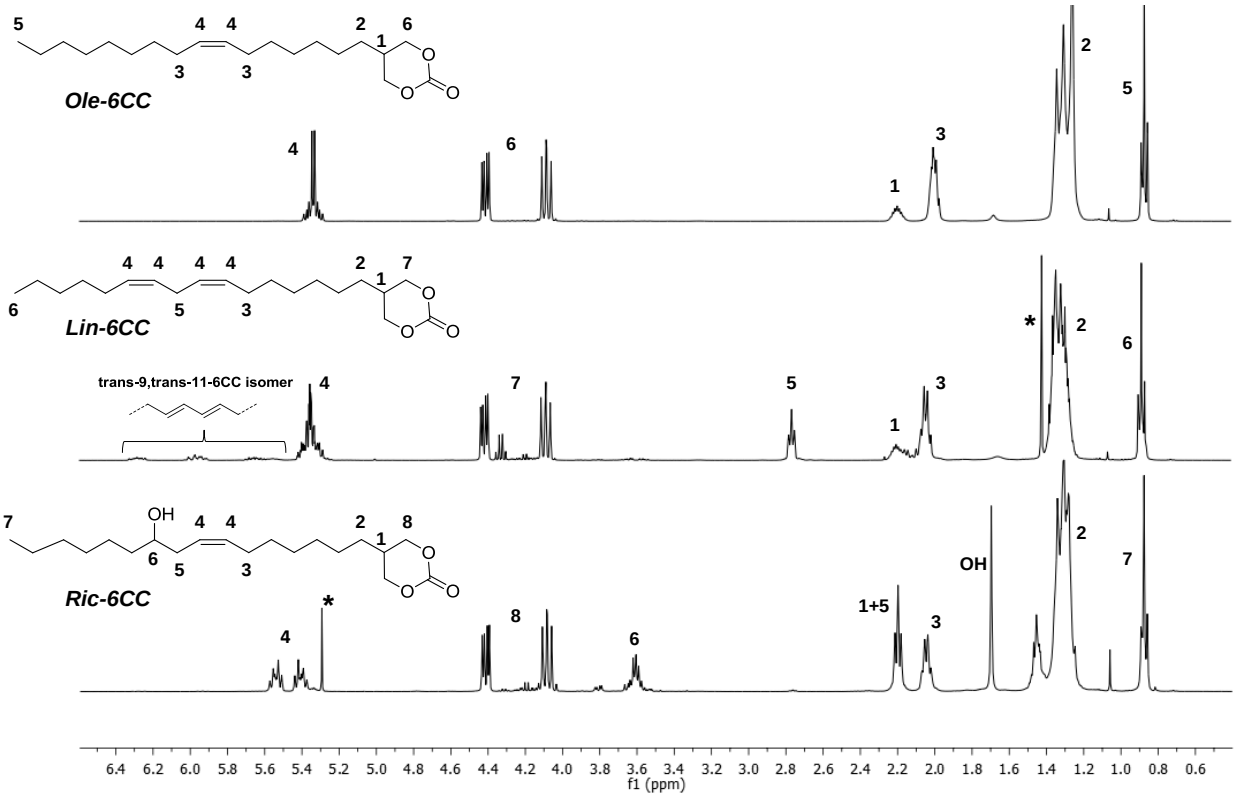


Figure 3: Stacked ^{1}H NMR of Ole-6CC, Lin-6CC and Ric-6CC in $CDCl_3$

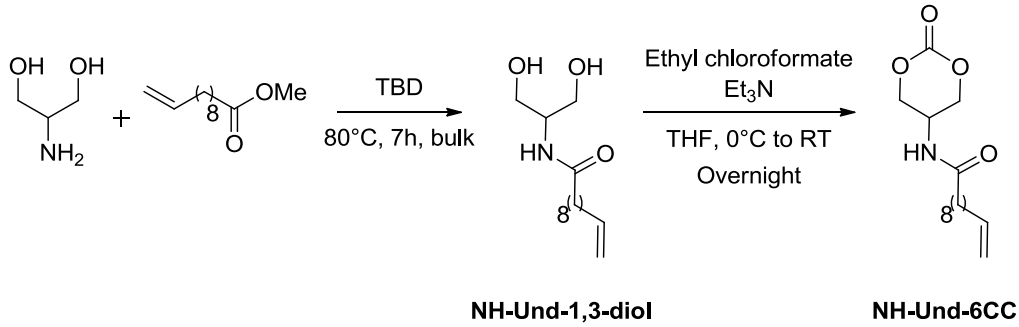
To conclude this part, four different fatty acid-based 6CCs were synthesized using the malonate route. All these cyclic carbonates were liquid but highly viscous at room temperature, which is not very convenient for polymerization purposes. The 6CC syntheses were scaled-up to maximum 3 grams starting from 20 grams of fatty acid. This synthetic pathway to 6CCs shows some limitations such as a rather overall low yield (around 10%) and a tedious work-up, for instance, with the treatment of large quantities of sensitive reactants such as NaH and $LiAlH_4$. Consequently, an alternative route has been investigated to overcome these limitations.

1.2. Second platform of 6CCs via 2-amino-1,3-propanediol coupling

As described above, the low yield of synthesis of the first lipidic 6CCs platform led us to investigate another pathway yielding a new family of bio-based 6-membered cyclic carbonates. Inspired by Endo's work[30] who employed amino acids as starting materials to cyclic carbonates, Yang and Hedrick developed a simple two-step strategy to access a large variety of functional cyclic carbonate monomers.[5] This strategy involves first a coupling reaction between 2-amino-

1,3-propanediol and different electrophiles yielding functional 1,3-diol intermediates. The latter are then cyclized intramolecularly to generate functional six-membered cyclic carbonate monomers. One of the main advantages of this method is the chemo-selectivity of the coupling due to the differences in reactivity of primary amine and alcohol towards an electrophile. Thus no protection/deprotection steps are necessary contrarily to most of the strategies described in the literature.[31–42]

Based on these studies, we thus investigated the synthesis of bio-based 6-membered cyclic carbonates with 2-aminopropane-1,3-diol and fatty acid derivatives as precursors. Scheme 3 illustrates the strategy to access the 6CC monomer from methyl undecenoate.



Scheme 3: Synthesis of 6-membered cyclic carbonate from 2-amino-1,3-propanediol and methyl undecenoate

The first step consists in the coupling between the methyl undecenoate and 2-amino-1,3-propanediol yielding the formation of the corresponding functionalized amide. This amidation is performed at 80°C, under bubbling nitrogen to remove the methanol by-product, in the presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as an organo-catalyst. This step was scaled-up to about 100 g of desired product. The second step is the intramolecular cyclization giving the corresponding 6-membered ring cyclic carbonate by using ethylchloroformate in THF in the presence of triethylamine as a base. After removal of trimethylamine salts, **NH-Und-6CC** was purified by flash chromatography. The purity and the formation of the cyclic carbonate was verified by ^{1}H NMR analysis (Figure 4). The spectrum clearly indicates the presence of the cyclic carbonate by the disappearance of both methylene hydrogens in alpha and beta positions of the diol (δ = 3.8 ppm and 3.9 ppm for protons in alpha and δ = 4.0 ppm for proton in beta) and the appearance of the characteristic methylene hydrogens of the cyclic carbonate (δ = 4.4 ppm and 4.6 ppm).

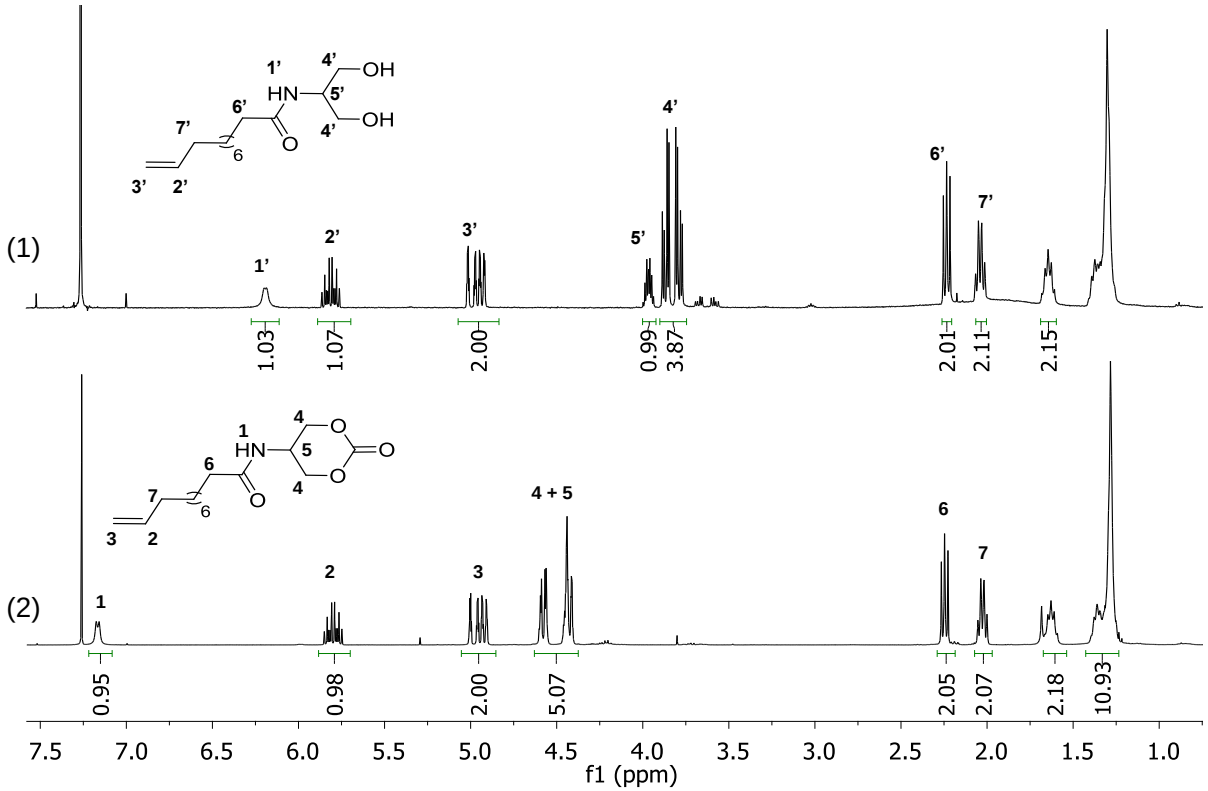


Figure 4: Stacked ^{1}H NMR spectrum of (1) NH-Und-1,3-diol and (2) NH-Und-6CC in $CDCl_3$

The above-mentioned strategy was then extended to other fatty acid derivatives such as methyl oleate (C18:1) and methyl erucate (C22:1) leading to corresponding cyclic carbonates (See Figure 5). The detailed syntheses are given in the experimental part.

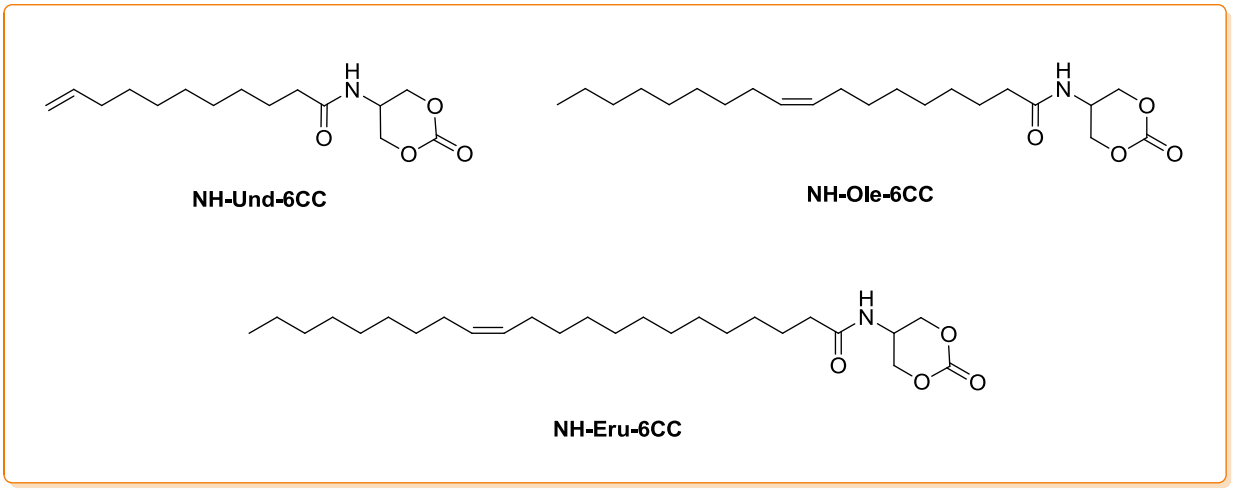


Figure 5: Second platform of fatty acid-based 6-membered cyclic carbonates

In summary, this second route afforded the synthesis of functional bio-based 6-membered cyclic carbonates. All these lipidic 6CC were obtained as white solids (soluble in THF or DCM except **NH-Eru-6CC**), which is an advantage for further manipulations. The latter were synthesized in a multi-gram scale with a global yield around 40 %. For instance, 11 grams of lipidic cyclic carbonate were obtained from 20 grams of methyl undecenoate. Moreover, the scale-up is easily feasible due to straightforward syntheses and work-up combined to the absence of hazardous components. In view of further polymerizations and post-functionalization reactions, this is a significant advantage compared to the first method. Figure 6 summarizes the two approaches used to access bio-based 6CC.

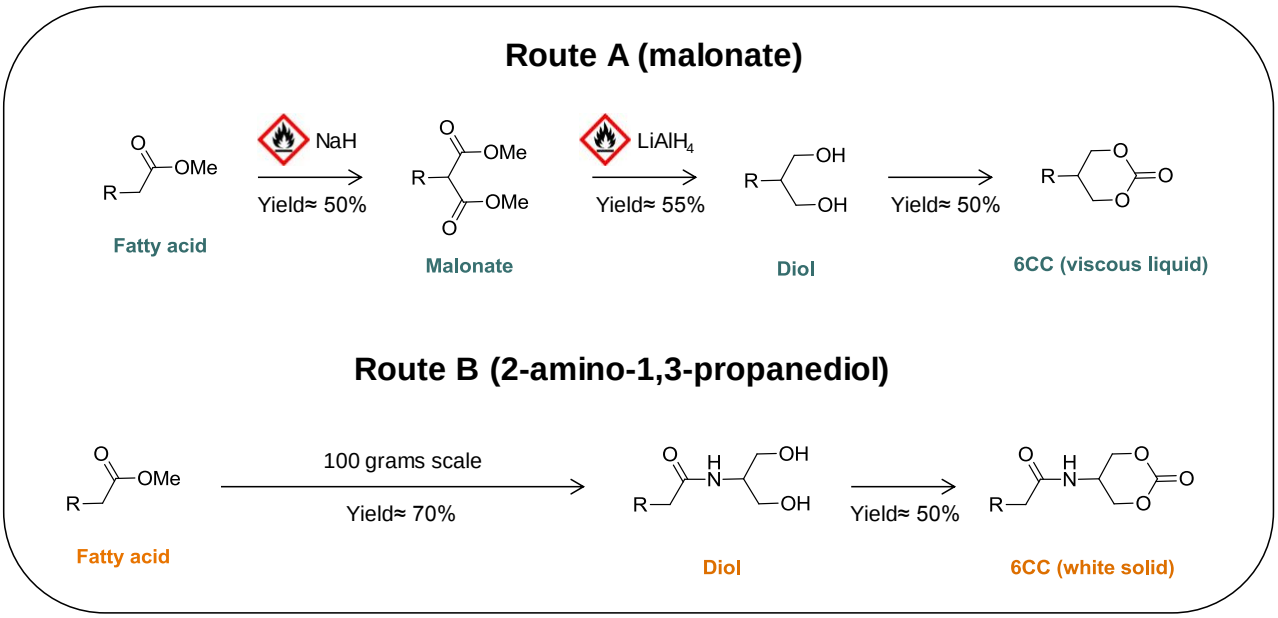


Figure 6: Comparison between the two routes affording bio-based 6CC synthesis

2. Ring-opening polymerization of the bio-based 6CC

As reported in Chapter 1, a wide variety of methods are available for the polymerization of six-membered cyclic carbonates. Two methodologies will be discussed in this chapter. The first approach involves the use of an organometallic weak Lewis acid catalyst, $Sn(Oct)_2$, known to be an active complexation catalyst for the polymerization of cyclic carbonates.[20–22,25,34–36,38,43–51] $Sn(Oct)_2$ is a widely used catalyst for the synthesis of polyesters and polycarbonates for

biomedical applications due to its acceptance by the United States Food and Drug Administration as a food additive. The second route to polycarbonates deals with the organo-catalyzed ROP of 6CCs. Indeed, organo-catalysts have been widely investigated towards the polymerization of cyclic monomers such as carbonates and lactones.[52,53] This type of catalysis present the advantage not to use toxic heavy metals, which are most of the time difficult to completely remove from the polymers. Among the catalytic systems, the amidine 1,8-diazabicycloundec-7-ene (DBU) associated with a thiourea has been extensively used for the polymerization of cyclic carbonates (**MAC**, **MBC**, **MPC**,… see Chapter 1)[5,41,47,54–71] enabling a control over molar masses, dispersity and functional end-groups of the resulting polymers.

2.1. Aliphatic polycarbonates from the first generation of 6CC

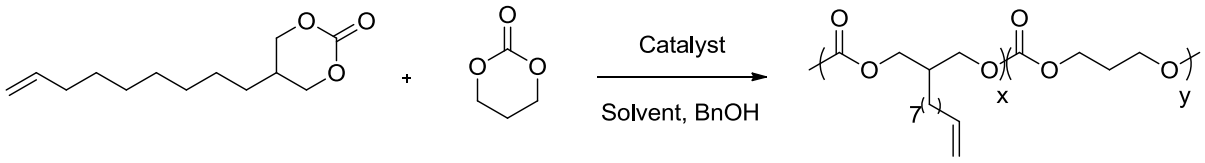
Bio-based cyclic carbonates from the first series (see Figure 2) were first copolymerized with TMC, as illustrated in Table 1. Different parameters were investigated such as the nature of the catalyst, the influence of the monomer ratios and the effect of the copolymer composition on the thermal properties.

2.1.1. Catalyst screening

The random copolymerizations of **Und-6CC** and TMC were first carried out in toluene at 120°C or in THF at 60°C ($[\mathbf{Und\text{-}6CC}]_0+[TMC]_0 = 4$ mol.L^{-1}) using several catalysts and benzyl alcohol as initiator with $[\mathbf{Und\text{-}6CC}]_0/[TMC]_0/[Catalyst]_0/[BnOH]_0$ ratios of 10:90:1:1.

Benzyl alcohol added as co-initiator accelerated the polymerization process and afforded a better control of the molar mass by monitoring the monomer/co-initiator ratio. The **Und-6CC** to TMC ratio was kept equal to 10/90 because **Und-6CC** was suspected to be less reactive in ROP due to its long pendant alkyl chain. The polymerizations were performed in gram scale until full conversion of TMC. Free monomers were removed by precipitating out the polymer in cold methanol (Yield = 80-85 % calculated with the ratio: g of precipitated copolymer/g of the monomers). All the results are summarized in Table 1.

Table 1: Catalysts screening for the copolymerization of Und-6CC and TMC[a]



Entry	Catalyst (1 mol.%)	Solvent/T	Und-6CC content (%)[b]	Reaction duration to full conversion of TMC (hours)	M_n[c] (g.mol^{-1})	Đ[c]
1	TBD	THF/60°C	8.2	72	4 200	1.41
2	DBU	THF/60°C	9.0	144	3 200	1.35
3	NHC-IPr	THF/60°C	0	2	12 000	1.95
4	$Sn(Oct)_2$	Toluene/120°C	9.1	`5	5 400	1.49

[a]:reaction conditions: 10 equiv. of Und-6CC, 90 equiv. of TMC, 1 equiv. of BnOH, 1 equiv. of catalyst; [b] :Calculated from [1]H NMR spectra; [c] :Determined by SEC with polystyrene standards

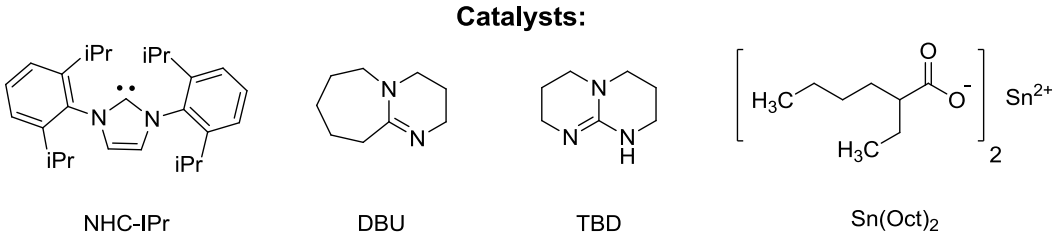


Figure 7: Catalysts used during the copolymerization of Und-6CC and TMC

Und-6CC unit content was calculated from the integration of characteristic signals of both monomer units (Equation 1).

$$\boldsymbol{Und-6CC\ content}\ (\%) = \frac{\int \boldsymbol{H_{Und-6CC}}\ (H_2)}{\int \boldsymbol{H_{und-6CC}}\ (H_2) + \int \boldsymbol{H_{TMC}}\ (H_6)}$$

Equation 1: Formula used for the calculation of Und-6CC units incorporated in the copolymer

For all experiments, ^{1}H NMR showed that characteristic signals of both TMC units (δ= 4.17 and 1.98 ppm) and **Und-6CC** units (δ= 5.75, 4.89 and 4.07 ppm) were clearly detected (Figure 8). The singlet at 5.09 ppm was assigned to the methylene protons on the benzyl alcohol acting as the polymerization initiator. It is important to note that no signals were observed between 3.3 and

3.7 ppm corresponding to ether signals. Thus, no decarboxylation side reaction occurred during the polymerization.

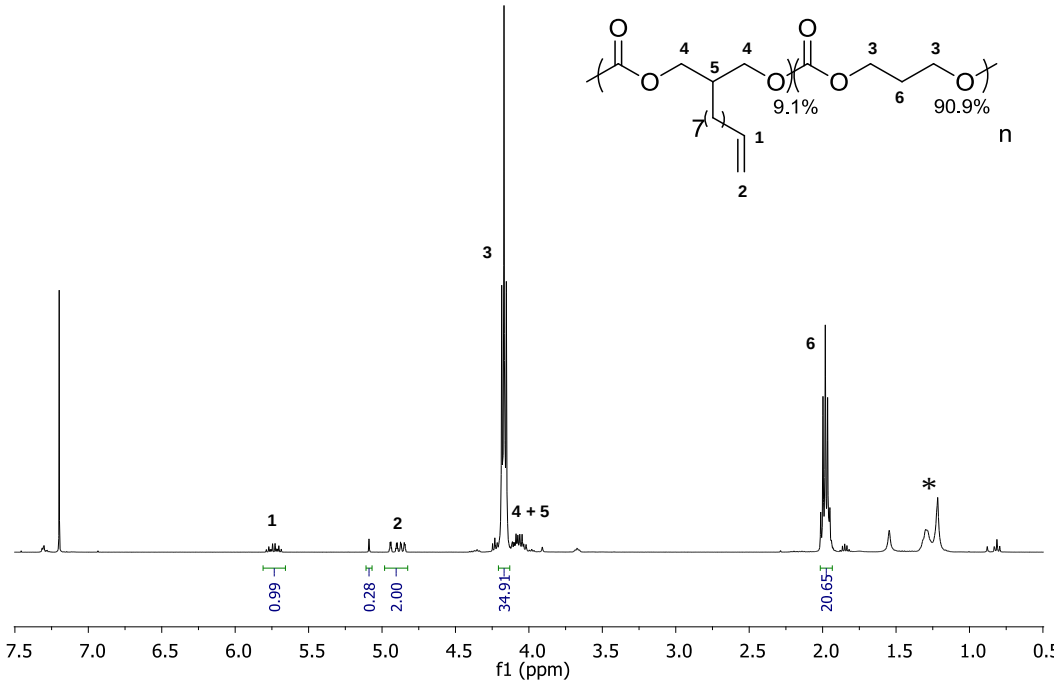


Figure 8: ^{1}H NMR spectrum of P(TMC-*co*-Und-6CC) (Table 1, entry 4)(*: CH_2 signals of Und-6CC units).

The highest incorporation of **Und-6CC** monomer was obtained with $Sn(Oct)_2$ (entry **4**), reaching 9.1%. As a general trend, the obtained copolymers exhibited moderate molar masses with unimodal distribution and a relative narrow dispersity (see Figure 9).

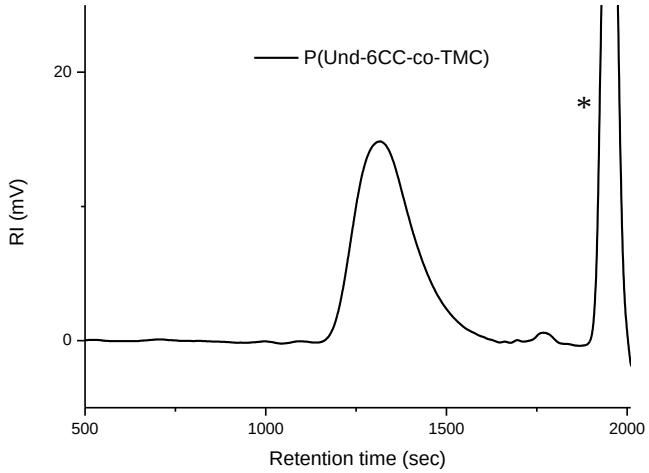
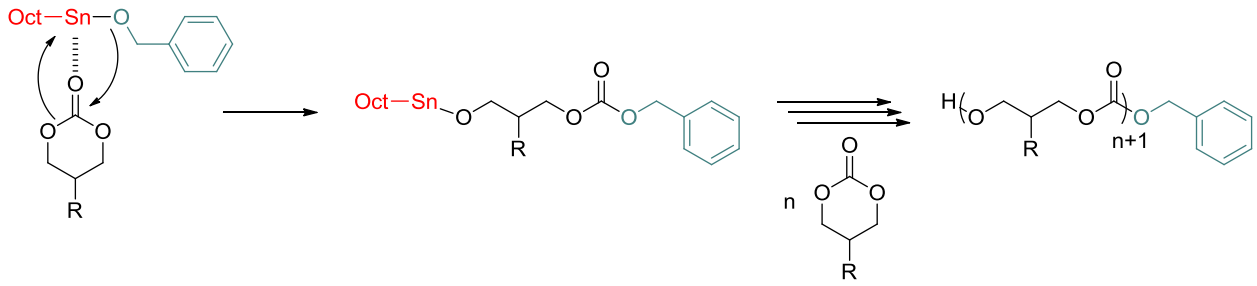


Figure 9: Typical SEC trace in THF of P(Und-6CC-*co*-TMC) (Table 1, entry 4) (*: Flow marker).

The ring-opening polymerization mechanism of TMC using $Sn(Oct)_2$ was investigated by Kricheldorf and coll..[46] Besides, benzyl alcohol undergoes a rapid complexation and equilibration reaction with $Sn(Oct)_2$. The authors demonstrated that below 120°C, the resulting tin benzyloxide group initiated the polymerization of TMC *via* the normal coordination/insertion mechanism (Scheme 4).



Scheme 4: ROP mechanism of cyclic carbonate initiated by benzyl alcohol and $Sn(Oct)_2$

Surprisingly, when the polymerization was performed with 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**NHC-IPr** in Table 1) as a catalyst, no incorporation of **Und-6CC** monomer was observed. This is presumably due to the too high activity of the carbene towards TMC in comparison to less reactive **Und-6CC**. Interestingly, in the presence of TBD or DBU as organo-catalysts (entry **1** and **2**), a relatively good control of the polymerization was

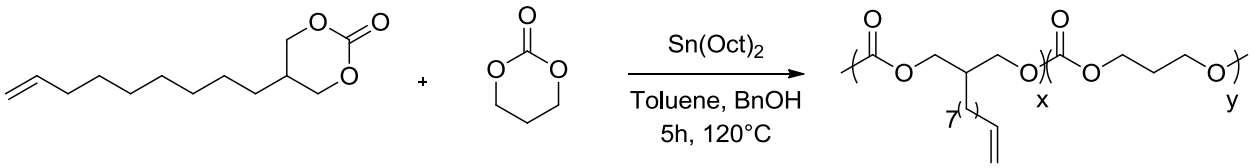
achieved. Indeed, 8.2 mol.% and 9.0 mol.% (out of 10mol.% maximum) of **Und-6CC** was respectively incorporated in the resulting polycarbonate, with reasonable dispersity (1.41 and 1.35 respectively). However, the inconvenience to work with these systems is the long reaction time. While the polymerization lasts for 5 hours using $Sn(Oct)_2$ as catalyst, it takes 3 days with TBD and 6 days with DBU. Finally, for all above-mentioned features, $Sn(Oct)_2$ was chosen as catalyst for further polymerizations.

2.1.2. Effect of the copolymer composition on thermal properties

In this part, the influence of the co-monomers ratio was investigated on the resulting copolymer composition. A series of different copolymers and homopolymers were prepared from **Und-6CC** and TMC as summarized in Table 2. The copolymerizations were performed with $Sn(Oct)_2$ as catalyst (1 mol.% with respect to **Und-6CC** + TMC) and BnOH as initiator (also 1 mol.% with respect to **Und-6CC** + TMC) at 120°C in toluene for 5 hours ($[\mathbf{Und\text{-}6CC}]_0+[TMC]_0 = 4$ mol.L^{-1}). Due to the poor reactivity of **Und-6CC**, its homopolymerization producing P(**Und-6CC**) was performed during 48h.

In order to purify the (co)polymers, free monomers were removed by precipitating the polymer in cold methanol. Copolymers were obtained as viscous oils. The yield of the polymerization was calculated by gravimetry.

Table 2: Ring-Opening (Co)polymerization of Und-6CC with TMC with different co-monomer ratios[a]



Entry	Und-6CC/ TMC molar feed ratio	Und-6CC incorporation (%)[b]	Yield (%)	M_n (g.mol^{-1})[c]	[Đ][c]	T_g (°C)[d]	T_d (°C)[e]
P(Und-6CC)	100/0	100	13	2 500	1.25	-60.8	218
P2	50/50	34	35	1 800	1.37	-65.8	180
P3	10/90	9.1	72	5 400	1.49	-34.1	206

P4	5/95	3.9	88	7 400	1.53	-26.1	203
PTMC	0/100	0	90	53 000	1.48	-19.3	196

[a]: reaction conditions: 1 mol % of BnOH, 1 mol % of $Sn(Oct)_2$, 120°C, 5h ; [b] :Calculated from ^1H NMR spectra; [c] :Estimated by SEC with polystyrene standards; [d]: Measured from the second heating run of DSC; [e]: Determined by TGA at 10°C.min^{-1} under nitrogen after 5 wt.% loss

Und-6CC unit content was calculated from the integration of characteristic signals of both monomer units (Equation 1). The results showed that P(**Und-6CC**-*co*-TMC) copolymers were obtained with **Und-6CC** contents ranging from 3.9 to 34 mol.%, **Und-6CC** feed ratio varying from 5 to 50 mol.% with respect to TMC. Since **Und-6CC** is less reactive in ROP, its incorporation in the copolymer is close to the one predicted only for low **Und-6CC** feed ratio. Indeed, for 10 mol.% and 5 mol.% (entries P3 and P4, Table 2) of **Und-6CC**, the composition of the copolymer is in relative good agreement with the feed ratio. For higher lipidic monomer feed ratio, the amount of **Und-6CC** incorporated in the copolymer is lower than the expected value. For example, only 34 mol.% of **Und-6CC** was incorporated in the copolymer whereas 50 mol.% was present in monomer feed (entry P2, Table 2). The lack of reactivity of the fatty acid-based monomer in comparison with TMC is presumably the reason of this difference.

In addition, an increase of **Und-6CC** content in the copolymer is associated with a decrease in molar mass. Indeed, under the same polymerization conditions, the polymer molar mass dropped significantly (from 53 000 g.mol^{-1} to 7 400 g.mol^{-1}) when 5 mol.% of functional bio-based units was incorporated into PTMC backbone. Similarly, the yield of polymerization decreases as a function of the bio-based monomer content. Due to the difficulty of **Und-6CC** to undergo ROP, the yield of its homopolymerization is only 15%.

The thermal properties of the copolymers were evaluated by DSC (see Figure 10). As expected, all the random copolymers are amorphous and exhibit only one T_g. Indeed, the presence of **Und-6CC** units bringing long pendant alkyl chains lowers the T_g values. The latter range from -19.2 °C for PTMC to -60.8 °C for P(**Und-6CC**). The lowest T_g of -65.8°C exhibited by the copolymer with 34 mol.% of **Und-6CC** units was reflecting the copolymer composition.

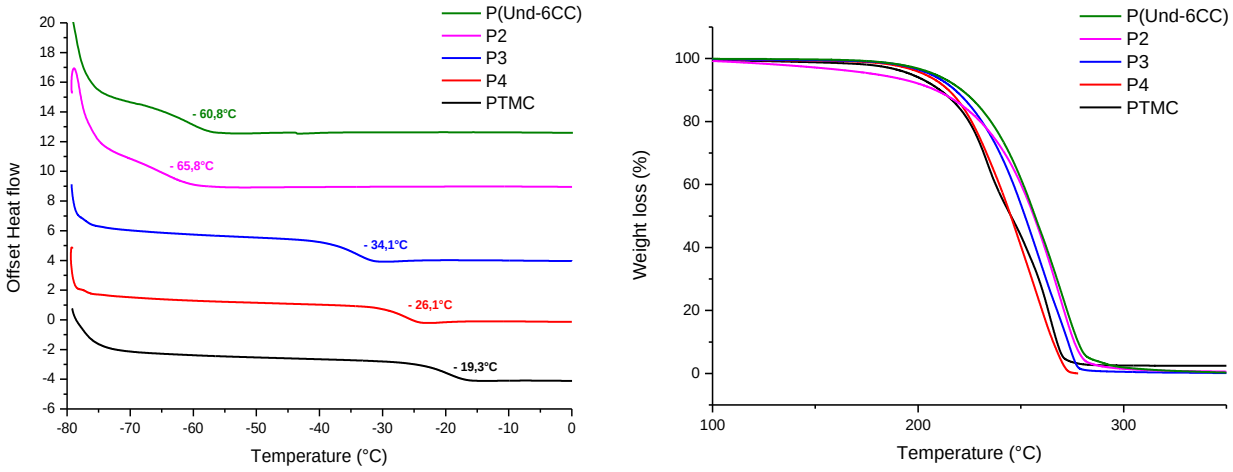


Figure 10: DSC and TGA traces of PTMC and P(Und-6CC) and of random copolymers

The copolymers exhibit thermal stabilities ranging from 196 to 218 °C with respect to the content of bio-based carbonate functions present in the copolymer (Figure 10). As can be seen, the incorporation of pendant alkyl chains on the polycarbonate backbone does not affect the thermal stability of the copolymers.

Another series of polymerization was performed from **Ole-6CC, Ric-6CC and Lin-6CC** in toluene ([**bio-based monomer**]$_0$ = 4 mol.L^{-1}), at 120°C for 48 hours using Sn(Oct)$_2$ as catalyst and benzyl alcohol as initiator with [**Und-6CC**]$_0$/[Catalyst]$_0$/[BnOH]$_0$ ratio of 100:1:1. The objective of this study is to see the influence of the starting fatty acid on the polymer properties.

Table 3: ROP of bio-based cyclic monomers from different fatty acid derivatives[a]

Polymer	Yield (%)	M_n (g.mol^{-1})[b]	DP	[Đ][b]	T_g (°C)[c]	T_d (°C)[d]
P(Und-6CC)	13	2 500	11	1.25	-60.8	218
P(Ole-6CC)	25	5 950	18	1.34	-80.7	222
P(Lin-6CC)	18	3 100	10	1.17	-30.0	230
P(Ric-6CC)	15	2 600	8	1.35	-54.8	218

[a]: reaction conditions: 1 mol % of BnOH, 1 mol % of Sn(Oct)$_2$, 120°C, 48h; [c]:Estimated by SEC with polystyrene standards; [c]: Measured from the second heating run of DSC; [d]: Determined by TGA at 10°C.min^{-1} under nitrogen after 5 wt.% loss;

At a first glance, the very low yields indicate that the long pendant alkyl chain on the cyclic carbonate tends to deactivate the monomer. In addition, the resulting bio-based polycarbonates exhibit rather low molar mass although the dispersity remained relatively narrow. The degree of polymerization remains between 10 and 20 which is very low compared to the targeted one (DP=100). Due to the poor reactivity of the monomers, propagation reactions are competing with transfer and termination reactions.

Regarding the polymer thermal properties, increasing the number of carbon atoms in the side chain makes the T_g of the polymer lower. Indeed, P(**Ole-6CC**) bearing 16 carbon atoms in side chain displays a T_g of -80.7°C whereas P(**Ole-6CC**) bearing only 9 carbon atoms as side chain has a T_g of -60.8°C. Therefore, the T_g of such lipidic polycarbonate could be tailored by the length of the side chain. In addition, the T_g is also influenced by the number of unsaturations present on the side chain. For a same chain length, a polycarbonate with two double bonds on the lateral chain (P(**Lin-6CC**)) exhibits a T_g fifty degrees higher than a polycarbonate having a unique unsaturation (P(**Ole-6CC**)), -80.7°C and -30.0°C respectively. This feature could be the consequence of some arrangements of the polymer chains due to the conjugated double bonds. As expected, the polymerization of **Ric-6CC** yields to a low molar mass polymer which is most probably hyper-branched due to hydroxyl functions on the monomer side chain.

Concerning the thermal stability, the length and the number of unsaturations does not affect significantly the properties of the resulting polycarbonates.

To summarize this part, the ability of lipidic 6CCs from the first platform (**Und-6CC**, **Ole-6CC**, **Lin-6CC**, **Ric-6CC**) to undergo ring-opening polymerization has been evaluated. First, different catalysts were screened in the copolymerization of **Und-6CC** with TMC (feed ratio: 10/90). The best catalyst in terms of activity, polymer molar mass and **Und-6CC** incorporation was the tin-based compound $Sn(Oct)_2$. Then, keeping the latter as catalyst, different monomer feed ratios were applied to synthesize various copolymers with different content of **Und-6CC** incorporated in the PTMC backbone. The resulting aliphatic polycarbonates exhibited tunable properties depending on **Und-6CC** content in the copolymer. As an example, a copolymer with 4.1 mol.% of **Und-6CC** displays a T_g of -26.1°C whereas the T_g decreases to -65.8°C for 34 mol.% of **Und-6CC** incorporated in the copolymer. Finally, the bio-based 6CCs have been homopolymerized using $Sn(Oct)_2$ as catalyst for 48h reaction. Such bio-based polycarbonates exhibit low T_gs and

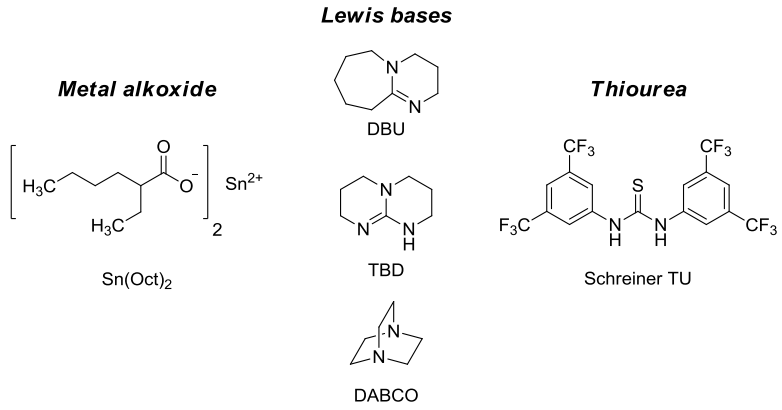
low molar masses due to a poor reactivity of the monomers with long pendant side chains. In addition, all these polymerizations were performed in a small scale because of the low overall yield of the monomer synthesis. The second platform of lipidic 6CCs (**NH-Und-6CC**, **NH-Ole-6CC**, **NH-Eru-6CC**), of which syntheses are more straightforward, should be able to give polycarbonates in larger quantities. In this context, the next part is dedicated to investigate the ring-opening polymerization of the second bio-based cyclic carbonate platform.

2.2. Aliphatic polycarbonates from the second platform of 6CCs

As mentioned above, the first advantage of this second series of cyclic carbonates illustrated in Figure 5 is their ease of synthesis. Various catalysts were first employed to polymerize this second generation of bio-based cyclic carbonates. The structure-properties relationship of the polycarbonates so-formed was then investigated.

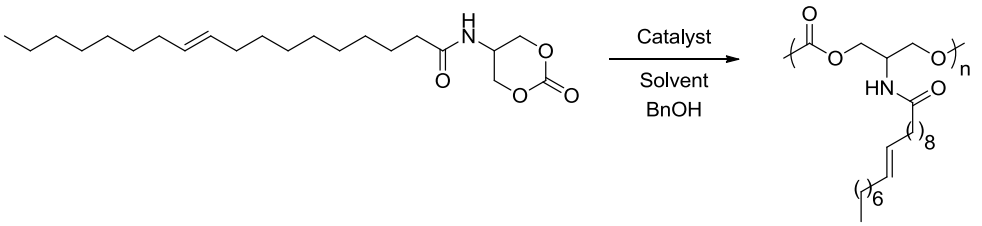
2.2.1. Catalyst screening

The screening of catalysts was conducted for the polymerization of **NH-Ole-6CC** in toluene, THF or DCM ($[\mathbf{NH\text{-}Ole\text{-}6CC}]_0$ = 2 mol.L^{-1}) with benzyl alcohol acting as an initiator during 5h (see Table 4). The initiator to monomer ratio was kept constant to 1:25 meaning that a degree of polymerization (DP) of 25 was targeted. After 4 hours, the reaction was quenched by adding 2 equiv. of benzoic acid with respect to benzyl alcohol and the polymer was precipitated in cold methanol. The catalysts used for the polymerization are represented in Scheme 5. All the results are presented in Table 4. The resulting molar mass of the polymers so-formed were analyzed and correlated to the catalyst employed.



Scheme 5: Catalysts used during the polymerization of NH-Ole-6CC

Table 4: Catalyst screening on the polymerization of NH-Ole-6CC



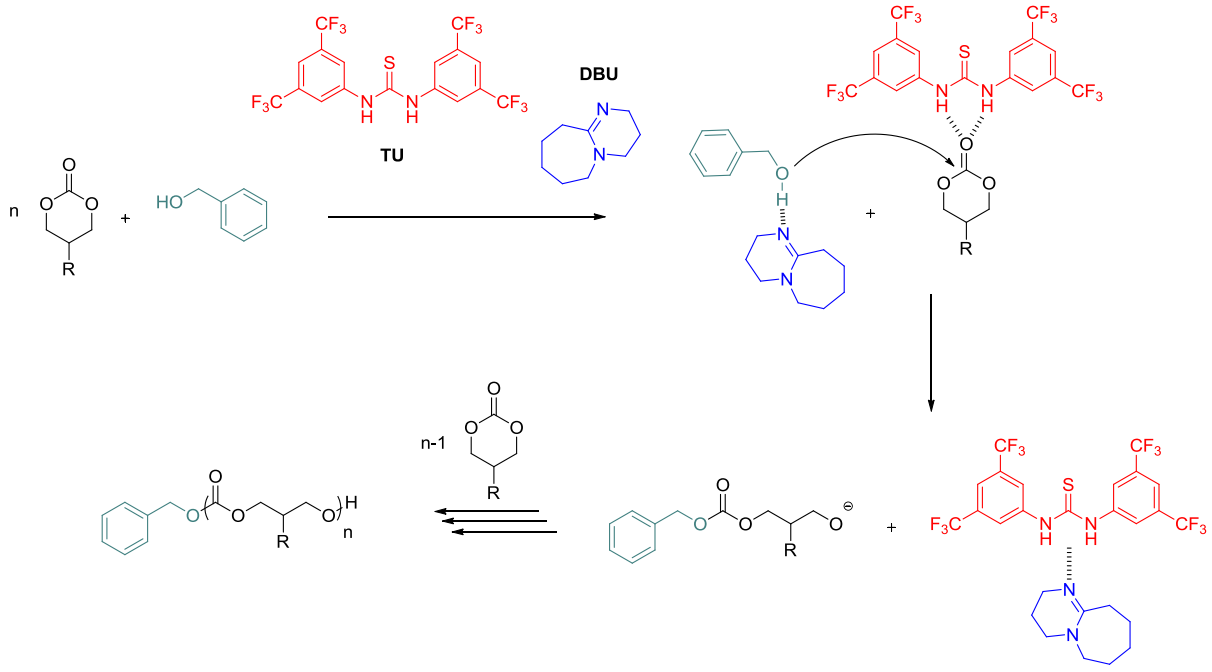
Entry	Catalyst	$[NH\text{-}Ole\text{-}6CC]_0/[Catalyst]_0/[BnOH]_0$	Solvent/Temp	M_n (g.mol^{-1}) [Đ][a]	DP[a]
1	$Sn(Oct)_2$	100:1:4	Toluene/120°C	Oligomers	4
2	DABCO	50:1:2	THF/60°C	Oligomers	4
3	TBD	50:1:2	THF/60°C	Few oligomers	5
4	DBU	50:1:2	THF/60°C	Few oligomers	5
6	DBU	50:1:2	DCM/RT	6 000 [1.23]	23[b]
7	DBU/Schreiner TU (4 mol.%)	50:1:2	DCM/RT	6 200 [1.10]	28[b]

[a]: Estimated by SEC with polystyrene standards; [b]: calculated by ^1H NMR spectroscopy

As described in chapter 1, all the tested catalysts are known to be suitable for the polymerization of cyclic carbonates. For example, cooperative hydrogen-bond pairing is a method to obtain well-controlled, highly active "living" organo-catalytic ring-opening polymerizations of cyclic esters and carbonates.[41,61,71] The challenge was then to find out an active catalyst affording the polymer synthesis within few hours with a relatively good control of the polymerization.

First, the catalytic system involving $Sn(Oct)_2$ which afford the synthesis of the polycarbonates in the previous part was tested for the polymerization of **NH-Ole-6CC** (Table 4, entry 1). Unfortunately, only oligomers were formed after 5 hours of reaction. Then, Lewis bases were used in THF (Table 4, entries 2-4) for the same unsatisfactory results. The poor solubility of **NH-Ole-6CC** in THF might be the cause of these results. However, when the polymerization was performed in DCM with a Lewis base as a catalyst (Table 4, entry 6), much higher molar masses were obtained. Indeed, the resulting polymer displayed a molar mass of 6 000 g.mol^{-1} with a low dispersity (1.23) and a high yield (Y=85 %).

Finally, DBU was associated to the Schreiner thiourea in order to narrow the molar mass distribution (Table 4, entry 7). Kiesewetter *et al.*[55] explained that the system behaves kinetically as a unimolecular catalyst species. According to the author, the strong binding between the two co-catalysts is the main reason to explain the high selectivity and activity exhibited by these organo-catalysts. Such binding mechanism is illustrated in Scheme 6.



Scheme 6: Binding mechanism for the ROP of cyclic carbonates

As expected, the above-illustrated catalytic system led to a controlled ring-opening polymerization of the cyclic carbonate yielding a 6 700 g.mol^{-1} polycarbonate (Y= 88%) with a narrow dispersity of 1.10 (Table 4, entry 7) as observed with the SEC trace (Figure 11).

The ^{1}H NMR spectrum (Figure 12) also confirms the good control over the degree of polymerization. Indeed, after full conversion of the monomer, the signal at 5.17 ppm assigned to the methylene protons of the initiator integrates for 0.07 when the signal of the double bond on the polymer integrated for 2. The ratio is roughly equal to 28, value close to the targeted degree of polymerization. Besides, as illustrated in Figure 12, well-defined peaks of the cyclic carbonate protons have been replaced by broad signals between 3.90 ppm and 5.70 ppm confirming the polymer formation.

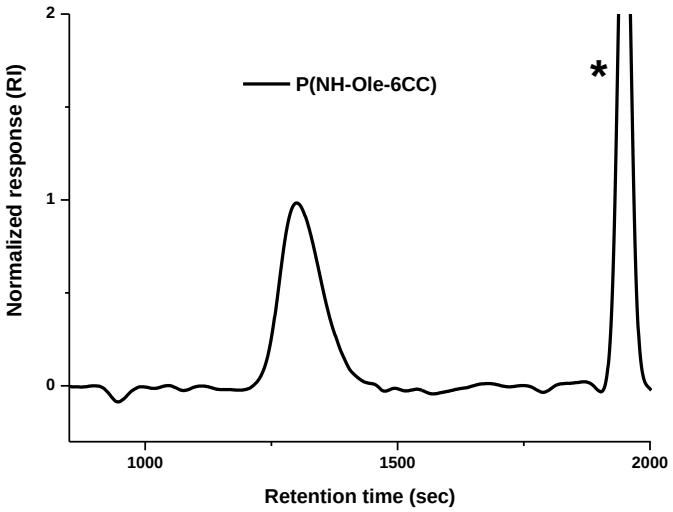


Figure 11: SEC trace of P(NH-Ole-6CC) (*:flow marker) (Table 4, entry 7) in THF

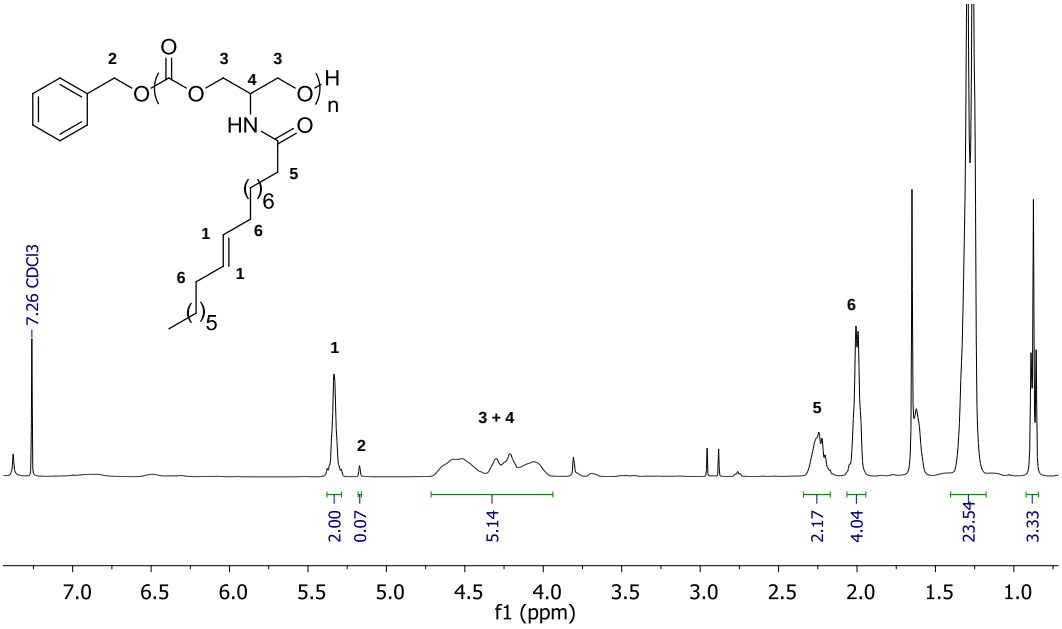


Figure 12: ^{1}H NMR spectra of P(NH-Ole-6CC), in $CDCl_3$ (Table 4, entry 7)

Keeping the cooperative catalytic system composed by DBU and the Schreiner TU, the polymerizations of **NH-Und-6CC** and **NH-Eru-6CC** were performed in DCM. The aim was to investigate the influence of both the chain length and the nature of the unsaturation (internal or terminal) on the polymerization behaviour of the monomer.

A degree of polymerization of 50 was targeted for the synthesis of P(**NH-Und-6CC**) in order to have comparable polymer molar masses since **NH-Ole-6CC** exhibits a higher molar mass than **NH-Und-6CC**. P(**NH-Und-6CC**) was successfully obtained with more than 90% yield in a controlled manner (DP=50, Đ=1,07) as observed by SEC (Figure 13) and ^{1}H NMR (Figure 14), demonstrating that terminal pendant double bonds do not deactivate the catalytic system.

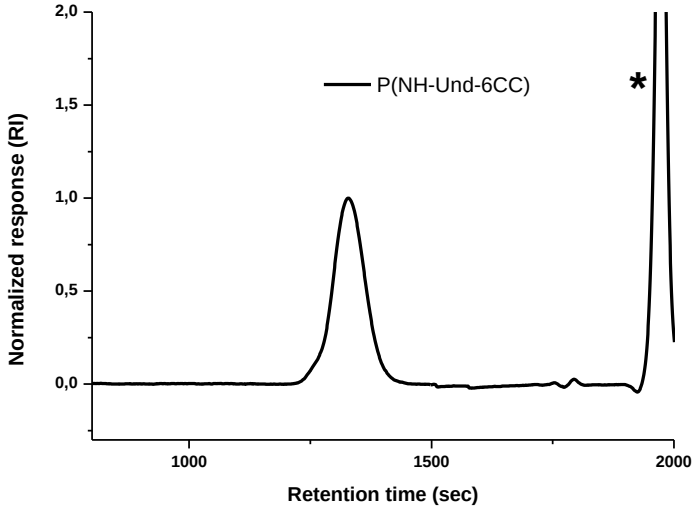


Figure 13: SEC trace of P(NH-Und-6CC) (*:flow marker) in THF

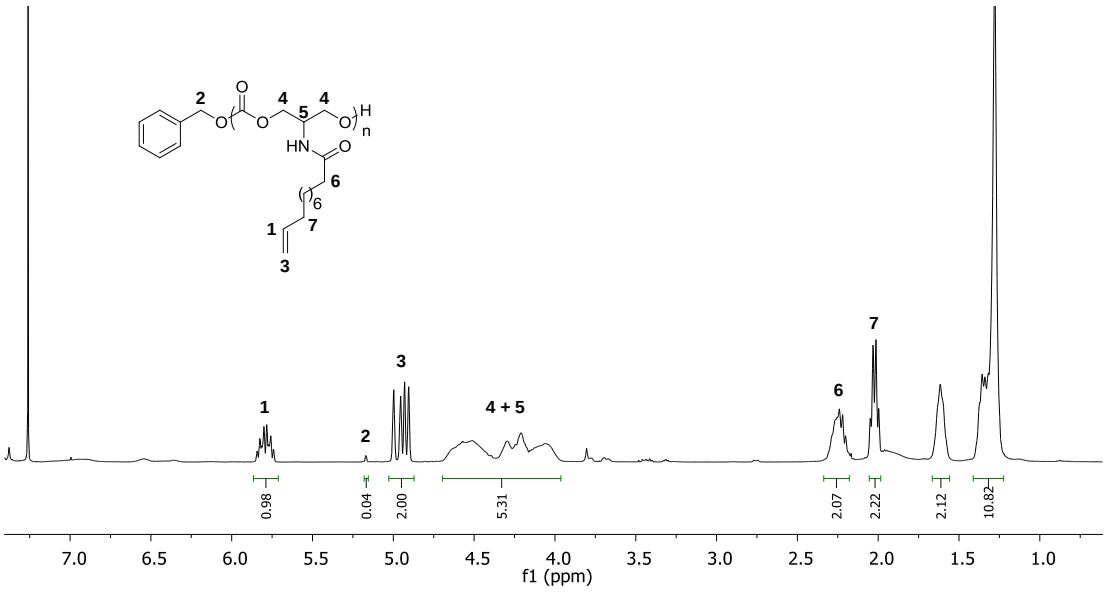


Figure 14: ^{1}H NMR spectrum of P(NH-Und-6CC) in $CDCl_3$

As shown in Figure 15, polymerization kinetic of **NH-Und-6CC** was performed over 5h. The polymerization was followed by the disappearance of the protons at 4.30 and 4.60 ppm on the cyclic carbonate and the appearance of the characteristic signals of the polymer backbone between 3.90 and 4.70 ppm.

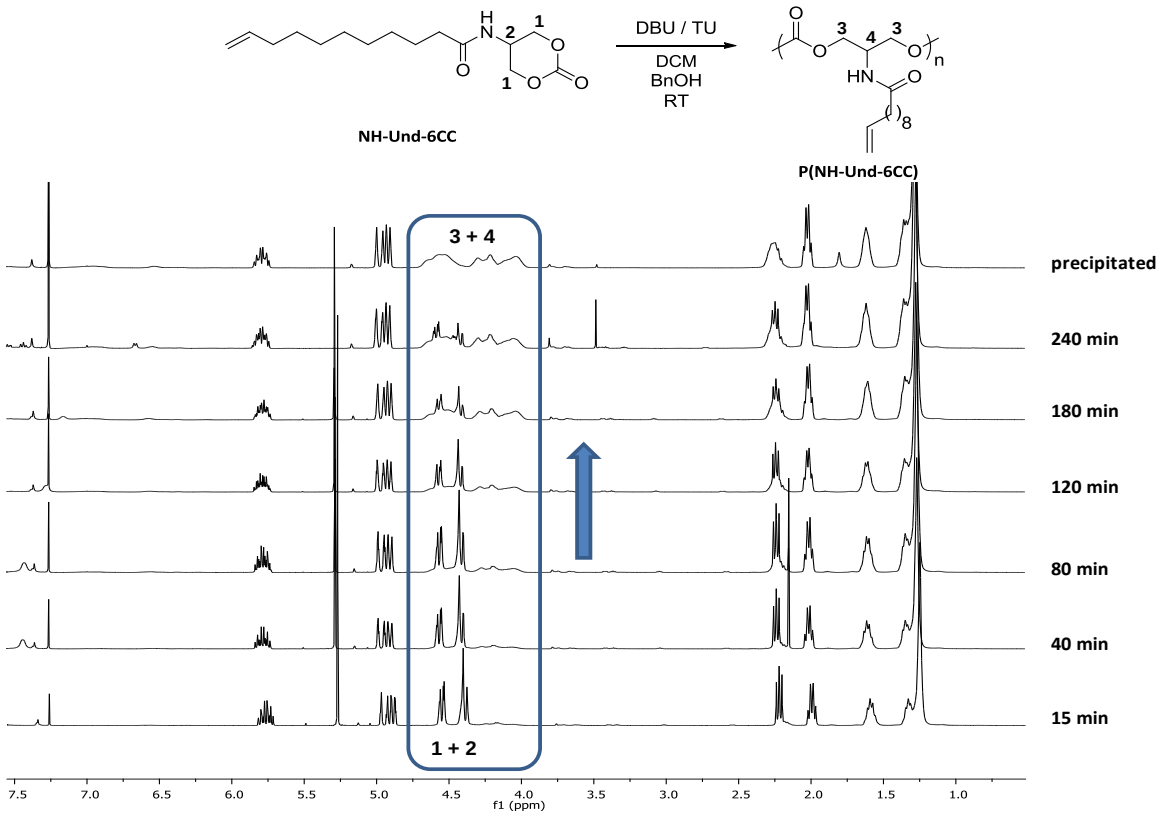


Figure 15: Kinetic study of the NH-Und-6CC polymerization over 5h

Unfortunately, in the same experimental conditions, P(**NH-Eru-6CC**) was not successfully obtained. This is probably due to the very poor solubility of the monomer in DCM. The polymerization was also tried in THF with the same negative results.

2.2.2. Polycarbonate characterization

In order to investigate the influence of the pendant fatty acid chain on the polycarbonate features prepared from this second cyclic carbonate platform, DSC and TGA analyses were performed.

Results are presented in Table 5. As a reminder, data from P(**Und-6CC**) and P(**Ole-6CC**) are also indicated in Table 5.

Table 5: Properties of P(NH-Und-6CC) and P(NH-Ole-6CC) compared to analogous P(Und-6CC), P(Ole-6CC) and PTMC

Polymer	Yield (%)	M_n [b] ($g.mol^{-1}$)	[Đ] [b]	T_g (°C) [c]	T_f (°C) [ΔH] [c]	T_d (°C) [d]
PTMC	95	53 000	1.48	-19.3	-	196
P(NH-Und-6CC)	91	5 700	1.07	23.1	-	144
P(NH-Ole-6CC)	85	6 200	1.10	34.8	63.9 [1.6 $J.g^{-1}$]	142
P(Und-6CC)	13	2 500	1.25	-60.8	-	218
P(Ole-6CC)	25	5 950	1.34	-80.7	-	222

[b]: Determined by SEC in THF (PS Std); [c]: Determined by DSC at 10°C.min^{-1} from the second cycle. ; [d]: Determined by TGA at 10°C.min^{-1} under nitrogen after 5wt.% loss

Surprisingly, as can be seen from Table 5 and in Figure 17-(1), P(**NH-Und-6CC**) and P(**NH-Ole-6CC**) displayed a relative high glass transition temperature given the long pendant chain on the polymer backbone, i.e. 23.1°C and 34.8°C, respectively. This feature was attributed to the presence of amide groups, which could induce a ladder-like organization of the polymer chains through hydrogen bonding (Figure 16).[72] Indeed, in comparison with the former polycarbonates obtained from the first 6CC platform, polycarbonates from this second 6CCs generation exhibit an enhanced T_g of about 80°C. Moreover, in the case of P(**NH-Ole-6CC**), a semi-crystalline state was observed, with a melting temperature of 63.9°C and a crystallization temperature of 58.3°C.

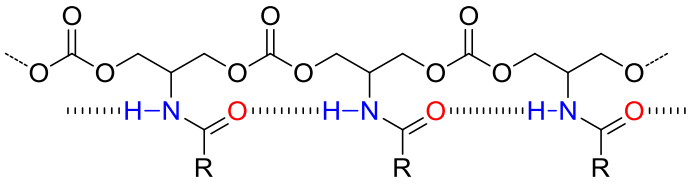


Figure 16: Hydrogen bonding in polycarbonates from the second generation of six membered ring cyclic carbonate

The thermal stability of these polycarbonates (T_d around 140°C) was found lower than the ones of the first generation (Figure 17-(2)). These lower values were attributed to the presence of thermally degradable amide function nearby the polymer backbone.

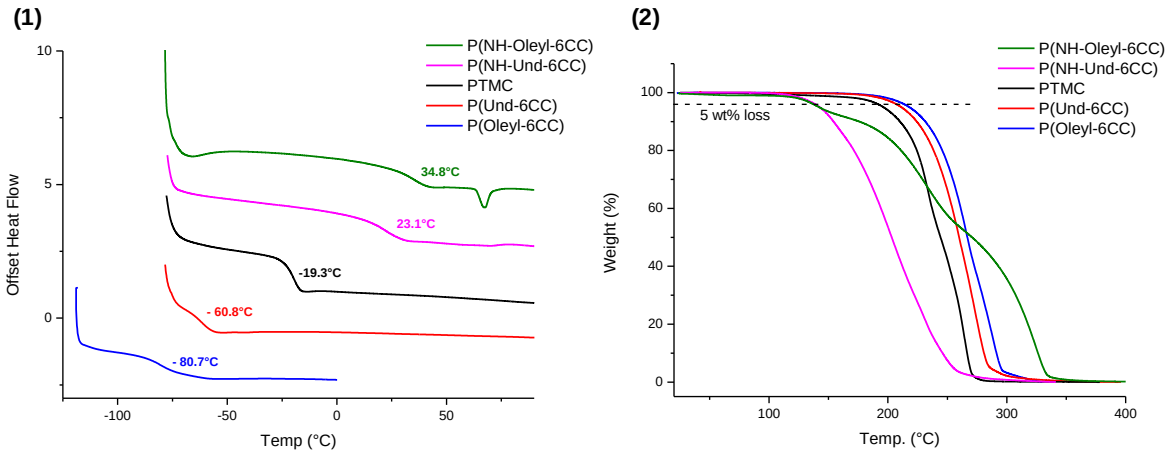


Figure 17: DSC (1) and TGA (2) curves of different functional polycarbonates

To sum up, this part highlighted the investigations on the ROP of the second platform of lipidic 6CCs (**NH-Ole-6CC**, **NH-Und-6CC** and **NH-Eru-6CC**). The first two bio-based monomers were successfully polymerized in a controlled manner using an organo-catalytic system composed of DBU and Schreiner thiourea associated with BnOH as initiator. The so-formed polycarbonates showed enhanced T_g presumably due to hydrogen bonding. In addition, the catalyst screening demonstrated the influence of the solvent in the ROP process. Indeed, only oligomers were obtained in THF while polycarbonates with reasonable molar masses were obtained when THF was switched to DCM. We could anticipate that the ROP of the first 6CCs platform would have been much more efficient with DBU and Schreiner TU in DCM but this catalytic system was not tested with the first platform of 6CCs. Nevertheless, bio-based aliphatic polycarbonates with pendant double bonds were obtained on a large scale and will be derivatized through post-polymerization reactions to yield cross-linked polycarbonate materials with original properties.

Conclusion

In this chapter, two platforms of fatty acid-based six-membered ring cyclic carbonates were designed and polymerized yielding original bio-based aliphatic polycarbonates bearing pendant alkyl chains.

First, a method developed by Maisonneuve *et al.*[3] implying a malonate intermediate was used to produce a first platform of lipidic-based cyclic carbonates. ROP of these carbonates in the presence of $Sn(Oct)_2$ catalyst, yielded low T_g aliphatic polycarbonates as a result of long pendant side chains (Figure 18, in blue). Interestingly, the T_g of these polycarbonates could be tuned by copolymerizing these carbonates with TMC. Nevertheless, the overall low yield of this monomer platform synthesis was a limitation concerning this strategy.

Then, adapted from the work of Venkataraman and coll.,[5] a second platform of 6-membered cyclic carbonates was prepared. The synthetic methodology is more straightforward and affords the monomer synthesis in a multi-gram scale. A screening study performed with different catalytic systems demonstrated that DBU/Schreiner thiourea in DCM was the most suitable system for the ring-opening polymerization of carbonate monomers in a controlled fashion. The resulting polycarbonates displayed unexpected thermal properties (Figure 18, in orange). Indeed, although long alkyl side chains were linked to the polymer backbone, the corresponding polymer T_gs were relatively high (above 20°C). This feature was explained by the presence of hydrogen bonding due to amide functions nearby the polymer backbone.

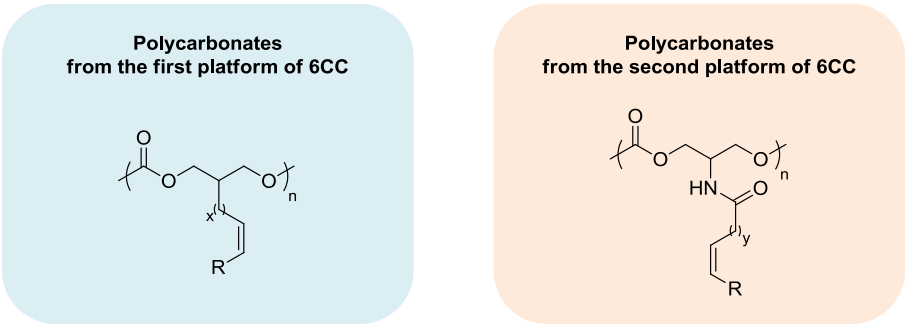


Figure 18: General structures of lipidic polycarbonates prepared from the first and second platform of 6CC

These functional polycarbonates will be used as precursors for cross-linked polycarbonate materials as it is discussed in the next chapter.

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Experimental Methods and Appendices

Experimental Methods

1. Synthesis of first platform of cyclic carbonates

1.1 General procedure for fatty-acid-Malonate synthesis:

The fatty-acid derivative (1 equiv.) was stirred with DMC (40 equiv.), NaH via a 60 wt% dispersion in mineral oil (2.5 equiv.) and DMF (1 equiv.) at 60 °C. After 24 hours of reaction, 20 equiv. 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 **fatty-acid-Malonate** was purified by flash chromatography using a mixture of cyclohexane and ethyl acetate (90:10 to 50:50).

Und-malonate: The malonate was obtained as a transparent liquid after flash column chromatography. Yield: 51 %. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.79 (m, 1H), 4.95 (m, 2H), 3.73 (s, 6H), 3.35 (t, 1H), 2.04 (m, 2H), 1.88 (m, 2H), 1.29 (m, 10H). ^{13}C NMR ($CDCl_3$, 25 °C, 100 MHz) δ (ppm): 170.1 ($\underline{C}OOCH_3$), 139.3 ($\underline{C}H=CH_2$), 114.3 ($CH=\underline{C}H_2$), 52.6 ($COO\underline{C}H_3$), 51.9 ($\underline{C}H–(COOCH_3)_2$), 33.9 ($\underline{C}H2–CH=CH_2$), 29.3–27.5 ($CH_2$). IR ($cm^{-1}$): 2924, 2854, 1734.

Ole-malonate: The malonate was obtained as a transparent liquid after flash column chromatography. Yield: 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.34 (m, 2H), 3.73 (s, 6H), 3.35 (t, 1H), 1.99 (m,4H), 1.88 (m, 2H), 1.30 (m, 22H), 0.86 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.97 ($\underline{C}OOCH_3$), 130.06 and 129.66 ($\underline{C}H=CH$), 52.43 ($COO\underline{C}H_3$), 51.72 ($\underline{C}H–(COOCH_3)_2$), 31.90 ($\underline{C}H-CH_2-OCOO$), 29.9-22.7 ($CH_2$), 27.3 ($\underline{C}H_2-CH=CH$), 14.1 ($CH_3$).

Lin-malonate: The malonate was obtained as a transparent liquid after flash column chromatography. Yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.27, 5.93, 5.62 and 5.35 (m, 4H), 3.73 (s, 6H), 3.35 (t, 1H), 2.76 (t, 2H), 2.03 (m, 4H), 1.90 (m, 2H), 1.31 (m, 12H), 0.89 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.10 ($\underline{C}OOCH_3$), 130.38, 130.11, 128.25 and 128.03 ($\underline{C}H=CH$), 52.58 ($COO\underline{C}H_3$), 51.86 ($\underline{C}H–(COOCH_3)_2$), 31.63-22.72 ($CH_2$), 28.98 ($\underline{C}H-CH_2-OCOO$), 27.34 and 25.71 ($\underline{C}H_2-CH=CH$), 14.21 ($CH_3$).

1.2 General procedure for fatty-acid-1,3-diol synthesis:

A solution of **fatty-acid-Malonate** (1 equiv.) in THF was added to a solution of $LiAlH_4$ (4.1 equiv.) in THF 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 fatty-acid-1,3-diol was purified by flash chromatography using a mixture of cyclohexane and ethyl acetate.

Und-1,3-diol: The diol was obtained as a transparent liquid. Yield = 51%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.81 (m, 1H), 4.93 (m, 2H), 3.78 and 3.63 (m, 4H), 2.68 (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): 139.4 ($\underline{C}H=CH_2$), 114.4 ($CH=\underline{C}H_2$), 67.0 ($CH–\underline{C}H_2–OH$), 42.2 ($\underline{C}H–CH_2–OH$), 34.0 ($\underline{C}H_2–CH=CH_2$), 30.1–27.4 (CH_2). IR (cm^{-1}): 3277, 2919, 2850

Ole-1,3-diol: The diol was obtained as a transparent liquid. Yield = 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.34 (m, 2H), 3.80 and 3.63 (m, 4H), 2.58 (S, 2 OH), 2.01 (m, 4H), 1.76 (m, 1H), 1.38-1.25 (m, 22H), 0.87 (t, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 130.02 and 129.73 ($\underline{C}H=CH$), 66.59 ($CH–\underline{C}H_2–OH$), 41.92 ($\underline{C}H–CH_2–OH$), 31.9-22.7 (CH_2), 27.2 ($\underline{C}H_2$-CH=CH), 14.11 (CH_3).

Lin-1,3-diol: The diol was obtained as a transparent liquid. Yield = 32%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.28, 5.94, 5.63 and 5.35 (m, 4H), 3.79 and 3.65 (m, 4H), 2.76 (t, 2H), 2.29 (s, 2 OH), 2.03 (m, 4H), 1.74 (m, 1H), 1.40-1.20 (m, 12H), 0.89 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 131.45, 129.89, 128.08 and 127.89 ($\underline{C}H=CH$), 67.2 ($CH–\underline{C}H_2–OH$), 42.10 ($CH–\underline{C}H_2–OH$), 31.54-21.90 (CH_2), 27.29 and 25.80 ($\underline{C}H_2$-CH=CH), 14.20 (CH_3).

1.3 General procedure for fatty-acid-6CC synthesis:

To a solution of triethylamine (2 equiv.) in THF, fatty-acid-1,3-diol (1 equiv.) was added. Then ethyl chloroformate (2 equiv.) 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 fatty-acid-6CC was isolated from the reaction mixture by flash chromatography using a mixture of cyclohexane and ethyl acetate.

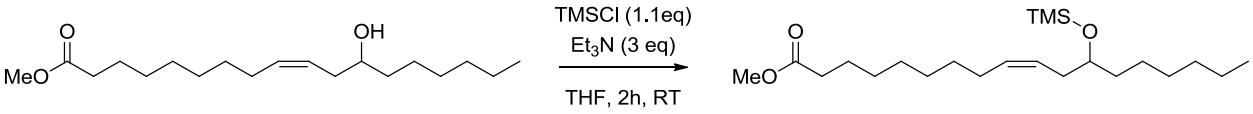
Und-6CC: Viscous transparent oil was obtained after purification. Yield: 55%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 5.73 (m, 1H), 4.94 (m, 2H), 4.41 (m, 2H), 4.06 (m, 2H), 2.17 (m, 1H), 2.02 (m, 2H), 1.35-1.30 (m, 12H). ^{13}C NMR ($CDCl_3$, 25°C, 100 MHz), δ (ppm): 148.3 (OCOO), 139.1 ($\underline{C}H=CH_2$), 114.7 ($CH=\underline{C}H_2$), 72.5 ($\underline{C}H_2$-OCOO), 34.0 ($\underline{C}H_2$-$CH=CH_2$), 31.4 ($\underline{C}H$-CH_2-OCOO), 29.5-26.7 (CH_2). IR (cm^{-1}): 3075, 2979, 2928, 2850, 1760

Ole-6CC: Viscous transparent oil was obtained after purification. Yield: 43%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 5.33 (m, 2H), 4.41 (m, 2H), 4.13 (m, 2H), 2.22 (m, 1H), 2.02 (m, 4H), 1.28 (m, 22H), 0.91 (t, 3H). ^{13}C NMR ($CDCl_3$, 25°C, 100 MHz), δ (ppm): 148.6 (O$\underline{C}$OO), 130.6 and 129.2 ($\underline{C}H=CH$), 72.4 ($\underline{C}H_2$-OCOO), 32.0 (CH_2), 31.4 ($\underline{C}H$-CH_2-OCOO), 29.9-22.7 (CH_2). 27.3 ($\underline{C}H_2$-CH=CH), 14.1 (CH_3). IR (cm^{-1}): 3000, 2979, 2925, 2853, 1754.

Lin-6CC: Viscous transparent oil was obtained after purification. Yield: 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.27, 5.91, 5.62 and 5.34 (m, 4H), 4.41 and 4.06 (m, 4H), 2.76 (t, 2H), 2.18 (m, 1H), 2.03 (m, 4H), 1.40-1.24 (m, 12H), 0.88 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 130.41, 129.91, 128.39 and 127.94 (OCOO), 72.22 ($\underline{C}H_2$-OCOO), 31.69-22.63 (CH_2), 31.33 ($\underline{C}H$-CH_2-OCOO), 27.22 ($\underline{C}H_2$-CH=CH), 14.21 (CH_3).

1.4 Procedure for Ric-6CC synthesis

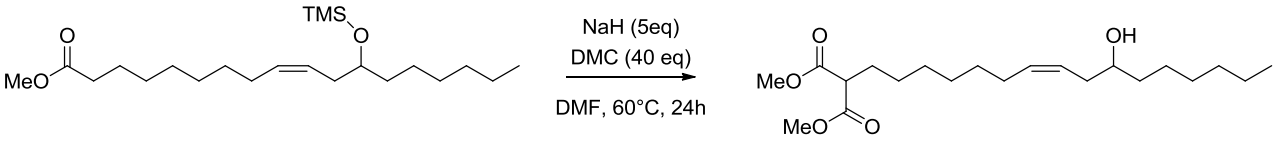
Protection of the hydroxyl group:



General procedure: To a solution of triethylamine (3 equiv.) in THF, methyl oleate (1 equiv.) was added. Then Trimethylsilyl chloride (2 equiv.) was added to the mixture at 0°C. The reaction mixture was stirred at room temperature for 2 hours. Precipitated triethylamine hydrochloride was filtered off, and the filtrate was concentrated under vacuum. Yield: 95%

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.42 (m, 2H), 3.66 (s, 3H), 3.61 (m , 1H), 2.29 (t, 2H), 2.17 (t, 2H), 2.02 (q, 2H), 1.61 (t, 2H), 1.30 (m, 18H) , 0.88 (t, 3H), 0.10 (s, 9H).

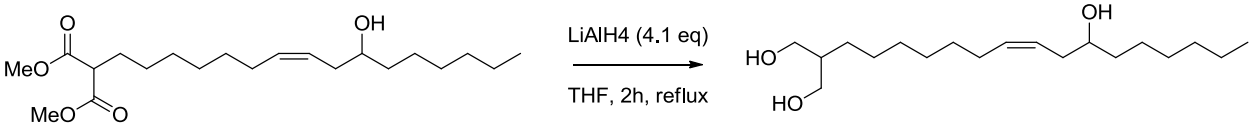
Ric-Malonate synthesis:



The protected methyl ricinoleate (1equiv.) was stirred with DMC (40 equiv.), NaH via a 60 wt.% dispersion in mineral oil (5 equiv.) and DMF (1 equiv.) at 60 °C. After 24 hours of reaction, 20 equiv. 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 **Ric-Malonate** was purified by flash chromatography using a mixture of DCM and methanol (98:2 to 95:5). Yield: 60%

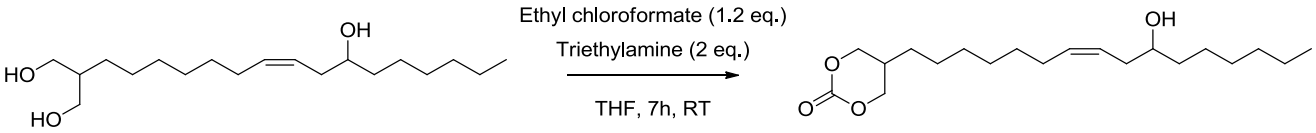
^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.45 (m, 1H), 5.33 (m, 1H), 4.69 (m, 1H), 3.73 (s, 6H), 3.33 (m, 1H), 2.32 (m, 2H), 1.98 (m, 2H), 1.88 (m, 2H), 1.58 (m, 3H), 1.30 (m, 16H), 0.87 (m, 3H).

Ric-1,3-diol synthesis:



Same procedure used for the synthesis of other fatty acid-1,3-diol. Yield: 20%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.51 (m, 1H), 5.38 (m, 1H), 3.74 (m, 2H), 3.60 (m, 2H), 2.66 (3 OH), 2.17 (m, 2H), 2.02 (m, 2H), 1.72 (m, 1H), 1.44 (m, 2H), 1.28 (m, 18H), 0.85 (t, 3H).

Ric-6CC synthesis:



Same procedure used for the synthesis of other fatty acid-6CC. Yield 49%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.53(m, 1H), 5.39 (m, 1H), 4.39 (m, 2H), 4.08 (m, 2H), 3.61 (m, 1H), 2.20 (t, 3H), 2.04 (q, 2H), 1.70 (OH), 1.47 (m, 2H), 1.32(m, 16H), 0.88 (3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.72 (O<u>C</u>OO), 133.23 (<u>C</u>H=CH-CH2-CH(OH)-CH_2), 125.59 (CH=<u>C</u>H-CH_2-

CH(OH)-CH_2), 72.21 ($\underline{C}H_2$-OCOO), 71.58 (CH=CH-CH_2-$\underline{C}$H(OH)-CH_2), 36.99 (CH=CH-CH_2-CH(OH)-$\underline{C}H_2$), 35.49 (CH=CH-$\underline{C}$H2-CH(OH)-CH_2), 31.96-22.74 (CH_2), 31.37 ($\underline{C}$H-CH_2-OCOO), 27.42 ($\underline{C}H_2$-CH=CH), 14.21(CH_3)

2. Synthesis of the second platform of cyclic carbonates

2.1 General procedure for NH-fatty-acid-1,3-diol synthesis:

Fatty acid derivative (1 equiv.), was mixed with 2-amino-1,3-propanediol (1.3 equiv.). TBD (0.05 equiv.) was added to the reaction mixture and heated up at 80°C under a nitrogen flow to remove methanol formed. The reaction mixture was heated for 3h. Depending on the matrix, the reaction mixture might become solid indicating the end of the reaction. The product is then extracted with $CHCl_3$ and washed 3 times with water. Brine is added in case of emulsion. The organic phase was dried over Na_2SO_4 and the solvent was removed under vacuum to yield NH-fatty-acid-1,3-diol.

NH-Und-1,3-diol: The diol was obtained as white crystals. Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.22 (s, NH), 5.81 (m, 1H), 4.93 (m, 2H), 3.96 (m, 1H), 3.84 (m, 2H), 3.78 (m, 2H), 2.72 (2 OH), 2.24 (t, 2H), 2.04 (q, 2H), 1.65 (m, 2H), 1.38-1.25 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.39 (CH_2-$\underline{C}$O-NH), 139.33 (CH_2=$\underline{C}$H-CH_2), 114.31 ($\underline{C}H_2$=CH-CH_2), 63.76 (CH-($\underline{C}H_2$-OH)$_2$), 52.49 ($\underline{C}$H-(CH_2-OH)$_2$), 36.94 ($\underline{C}H_2$-CO-NH), 33.92 (CH_2=CH-$\underline{C}H_2$), 29.44-29.02 (CH_2), 25.84 ($\underline{C}H_2$-CH_2-CO-NH).

NH-Ole-1,3-diol: The diol was obtained as white solid. Yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.52 (s, NH), 5.33 (m, 2H), 4.03 (2 OH), 3.91 (m, 1H), 3.76 (m, 2H), 3.69 (m, 2H), 2.19 (t, 2H), 1.99 (m, 4H), 1.60 (m, 2H), 1.38-1.15 (m, 20H), 0.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.67 (CH_2-$\underline{C}$O-NH), 130.14 and 129.80 ($\underline{C}$H=CH), 62.34 (CH-($\underline{C}H_2$-OH)$_2$), 52.63 ($\underline{C}$H-(CH_2-OH)$_2$), 36.85 ($\underline{C}H_2$-CO-NH), 29.88-22.80 (CH_2), 27.34 ($\underline{C}H_2$-CH=CH-$\underline{C}H_2$), 25.88 ($\underline{C}H_2$-CH_2-CO-NH), 14.23 (CH_3).

NH-Eru-1,3-diol: The diol was obtained as a white solid. Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.44 (s, NH), 5.33 (m, 2H), 3.90 (m, 1H), 3.80 (m, 2H), 3.71 (m, 2H), 2.82 (2

OH), 2.21 (t, 2H), 2.01 (m, 4H), 1.59 (m, 2H), 1.26 (m, 28H), 0.87 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.68 (CH_2-CO-NH), 130.05 and 130.01 (CH=CH), 62.75(CH-(CH_2-OH)$_2$), 52.59 (CH-(CH_2-OH)$_2$), 36.90 (CH_2-CO-NH), 32.04-22.82 (CH2), 27.36 (CH_2-CH=CH-CH_2), 25.90 (CH_2-CH_2-CO-NH), 14.25 (CH_3).

2.2 General procedure for NH-fatty-acid-6CC synthesis:

In a 500 mL round bottom flask at 0°C equipped with magnetic stirrer, NH-fatty-acid-1,3diol (1.0 equiv.) and ethyl chloroformate (4.0 equiv.) were dissolved in 300 mL THF. To the cold reaction mixture, triethylamine (4.0 equiv.) was added dropwise over 10 min. The reaction was allowed to proceed in ice-cold conditions for about 1 hour and then allowed to proceed at room temperature overnight. The precipitated solids were filtered off and the volatiles were removed to result in crude product, which was subjected to flash column chromatography, using a gradient of DCM (100 %) to DCM (95 %) and methanol (5 %) solvent mixture, followed by the removal of volatiles to result in white solid NH-fatty-acid-6CC as the functional monomer.

NH-Und-6CC: White solid. Yield: 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.63 (s, NH), 5.76 (m, 1H), 4.93 (m, 2H), 4.54-4.40 (m, 5H), 2.22 (t, 2H), 1.99 (q, 2H), 1.60 (t, 2H), 1.25 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.33 (CH_2-CO-NH), 148.66 (OCOO), 139.19 (CH_2=CH-CH_2), 114.21 (CH_2=CH-CH_2), 71.45 (CH-(CH_2-OCOO)$_2$), 40.94 (CH-(CH_2-OCOO)$_2$), 36.14 (CH_2-CO-NH), 33.81 (CH_2=CH-CH_2), 29.34-28.93 (CH_2), 25.57 (CH_2-CH_2-CO-NH).

NH-Ole-6CC: White solid. Yield: 48%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.06 (s, NH), 5.33 (m, 2H), 4.56-4.44(m, 5H), 2.27 (t, 2H), 2.01 (m, 4H), 1.61 (m, 2H), 1.26 (m, 20H), 0.87 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.11 (CH_2-CO-NH), 148.36 (OCOO), 130.16 and 129.86 (CH=CH), 71.49 (CH-(CH_2-OCOO)$_2$), 41.15 (CH-(CH_2-OCOO)$_2$), 36.34 (CH_2-CO-NH), 32.04-22.82 (CH_2), 27.32 (CH_2-CH=CH-CH_2), 25.60 (CH_2-CH2-CO-NH), 14.25 (CH3).

NH-Eru-6CC: White solid. Yield: 20%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.16 (s, NH), 5.35 (m, 2H), 3.97 (m, 1H), 3.85-3.79 (m, 4H), 2.23 (t, 2H), 2.02 (m, 4H), 1.63 (m, 2H), 1.27 (m, 28H), 0.88 (CH_3).

3. Polymerizations of cyclic carbonate monomers

3.1 General procedure for the polymerization of first platform of 6CC

All polymerizations were performed under inert atmosphere (nitrogen) in 20-mL ampules using standard Schlenk, vacuum line, and glovebox techniques. In a typical procedure fatty acid-6CC (10 equiv.) and TMC (90 equiv.) were added to a solution of $Sn(Oct)_2$ (1 equiv.) and benzyl alcohol (1 equiv.) in toluene ($[\text{fatty acid-6CC}]_0 + [TMC]_0 = 4$ mol.L^{-1}). The mixture was then stirred at 120°C over the appropriate period of time (conversion of monomers monitored by ^{1}H NMR). After full conversion of TMC, the reaction mixture was concentrated to dryness under vacuum. The conversion of fatty acid-6CC was determined from the crude reaction mixture. The crude polymer was next dissolved in CH_2Cl_2 and precipitated in cold methanol, filtered and dried under vacuum. The final P(fatty acid-6CC-co-TMC) copolymers were obtained as viscous liquid and were then analyzed by NMR, SEC, DSC and TGA.

P(Und-6CC): Yield: 13%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.79 (m, 1H), 4.94 (m, 2H), 4.13 (m, 4H), 2.04 (m, 4H), 1.28 (m, 12H). SEC (THF, RI): M_n= 2 500 g.mol^{-1}, Đ=1.25

P(Ole-6CC): Yield: 25%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.34 (m, 2H), 4.13 (m, 4H), 2.01 (m, 5H), 1.27 (m, 22H), 0.88 (t, 3H). SEC (THF, RI): M_n= 5 950 g.mol^{-1}, Đ=1.34

P(Lin-6CC): Yield: 18%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.28-5.35 (m, 4H), 4.13 (m, 4H), 2.76 (t, 2H), 2.04 (m, 5H), 1.30 (m, 12H), 0.89 (t, 3H). SEC (THF, RI): M_n= 3 100 g.mol^{-1}, Đ=1.17

P(Ric-6CC): Yield: 15%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.54-5.39 (m, 2H), 4.14 (m, 4H), 3.61 (m, 1H), 2.20 (m, 2H), 2.05 (m, 3H), 1.46-1.31 (m, 16H), 0.88 (t, 3H). SEC (THF, RI): M_n= 2 600 g.mol^{-1}, Đ=1.35

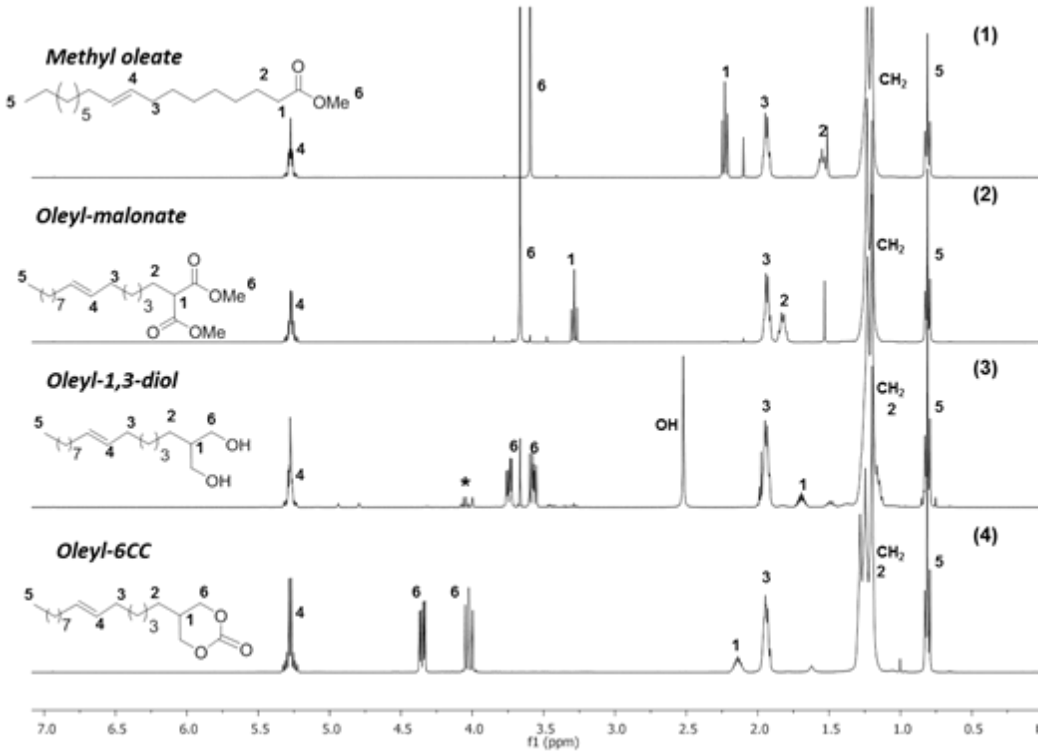
3.2 General procedure for the polymerization of the second platform of 6CC

In a 15 mL schlenk flask containing a magnetic stirrer, in glove box, fatty-acid-6CC (50 equiv.), BnOH (2.0 equiv.) and Schreiner TU (1.0 equiv.) were dissolved in dry DCM ([fatty-acid-6CC] = 2 $mol.L^{-1}$). To this solution, DBU (1.0 equiv.) was added to initiate polymerization. The reaction mixture was allowed to stir at room temperature. After 5h, the reaction was quenched by the addition of benzoic acid (2 equiv.) and purified by precipitation in cold methanol to yield P(fatty-acid-6CC).

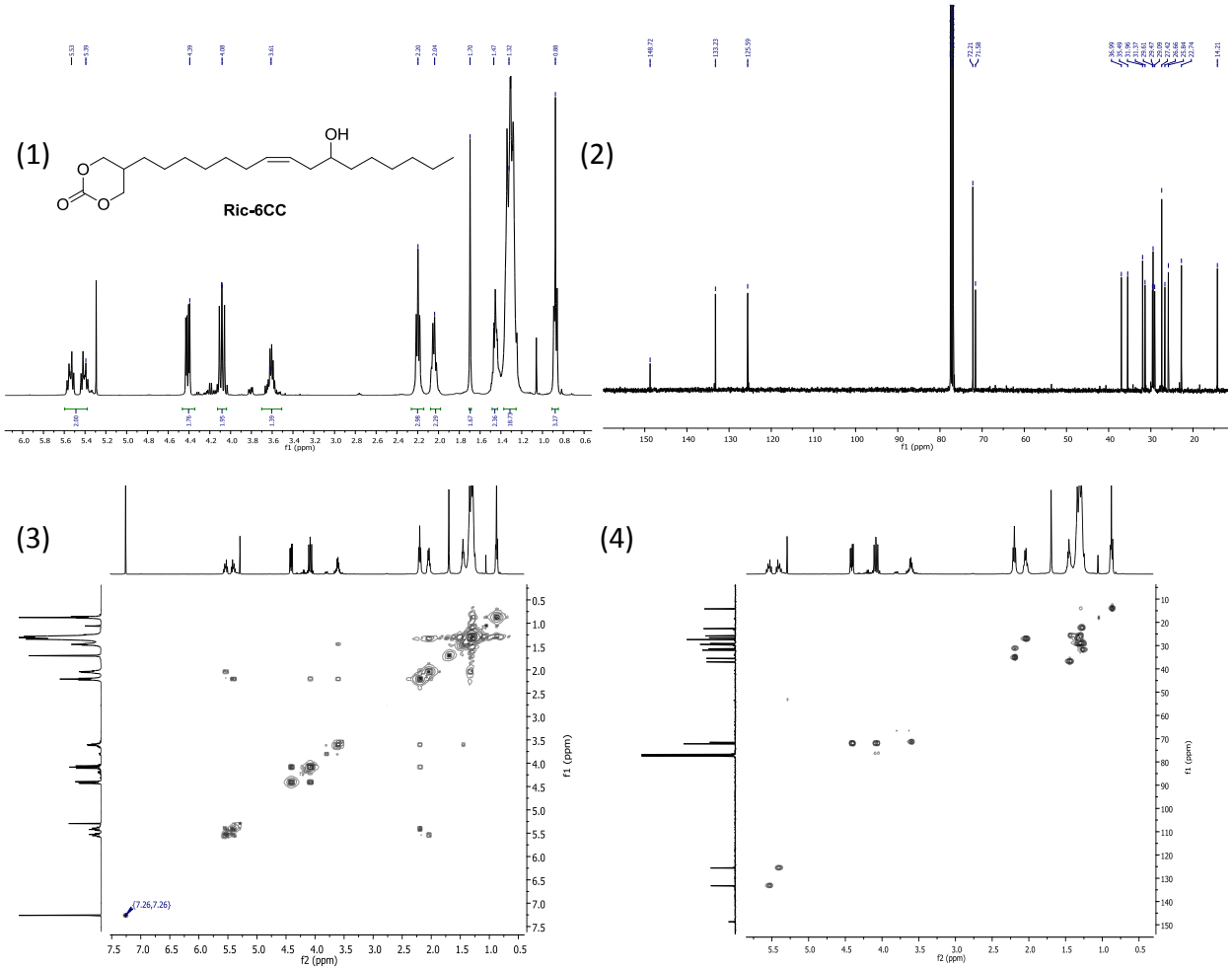
P(NH-Und-6CC): The polymer was obtained as white solid. Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.80 (m, 1H), 4.93 (d, 2H), 4.64-3.93 (m, 5H), 2.24 (m, 2H), 2.01 (q, 2H), 1.62 (m, 2H), 1.28 (m, 10H). SEC (THF, RI): M_n= 5 700 $g.mol^{-1}$, Đ=1.07

P(NH-Ole-6CC): The polymer was obtained as white solid. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.33 (m, 2H), 4.61-4.04 (m, 5H), 2.25 (m, 2H), 2.00 (m, 4H), 1.61 (m, 2H), 1.26 (m, 20H), 0.85 (t, 3H). SEC (THF, RI): M_n= 6 200$g.mol^{-1}$, Đ= 1.15

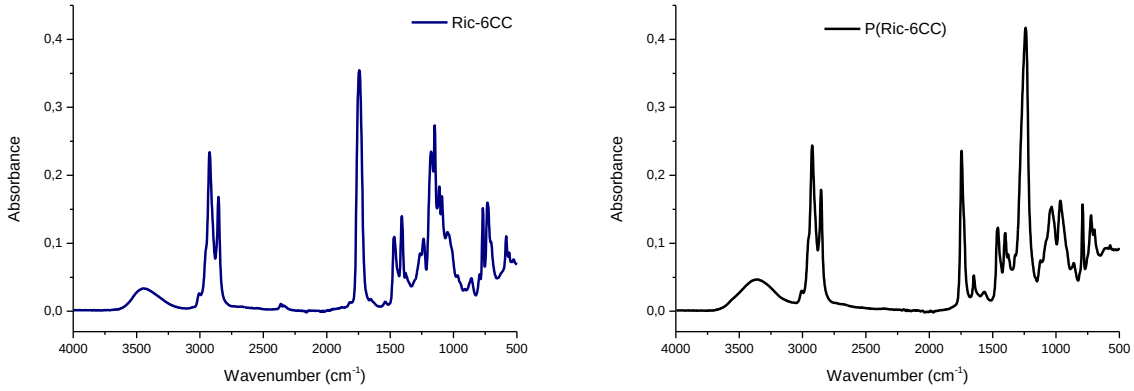
Appendices



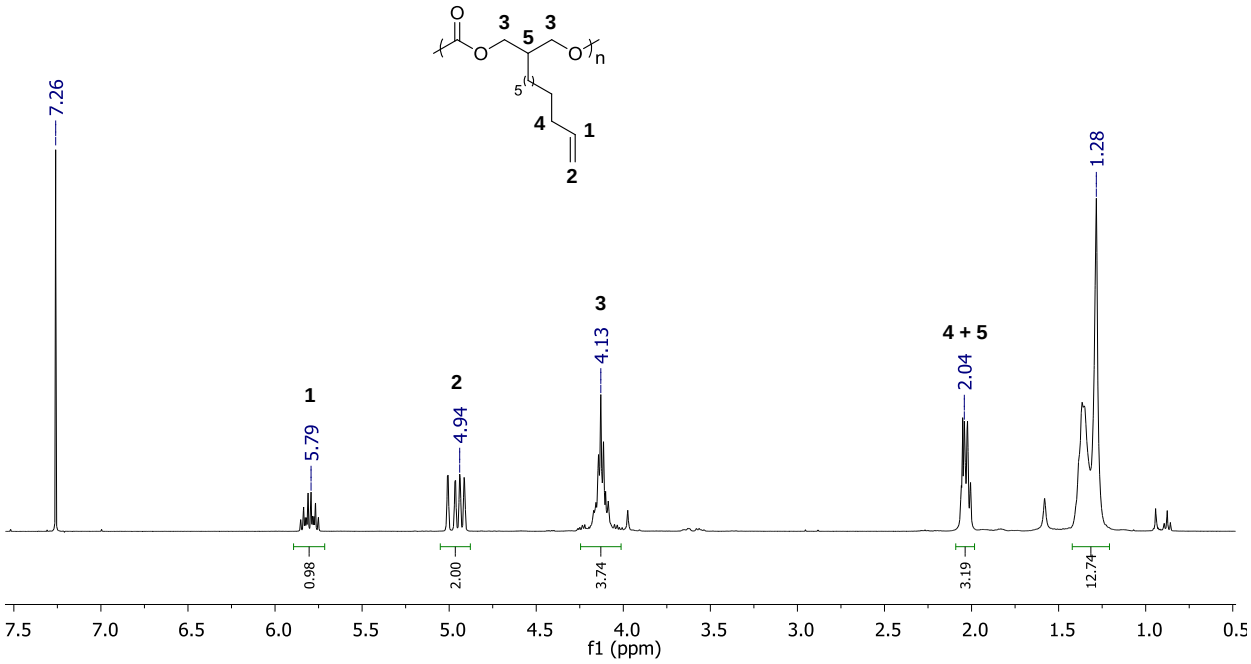
ESI Figure 1: Stacked ^{1}H NMR spectra of (1) methyl oleate, (2) Ole-malonate, (3) Ole-1,3-diol and (4) Ole-6CC. (All analyses were performed in $CDCl_3$.)(* impurities).



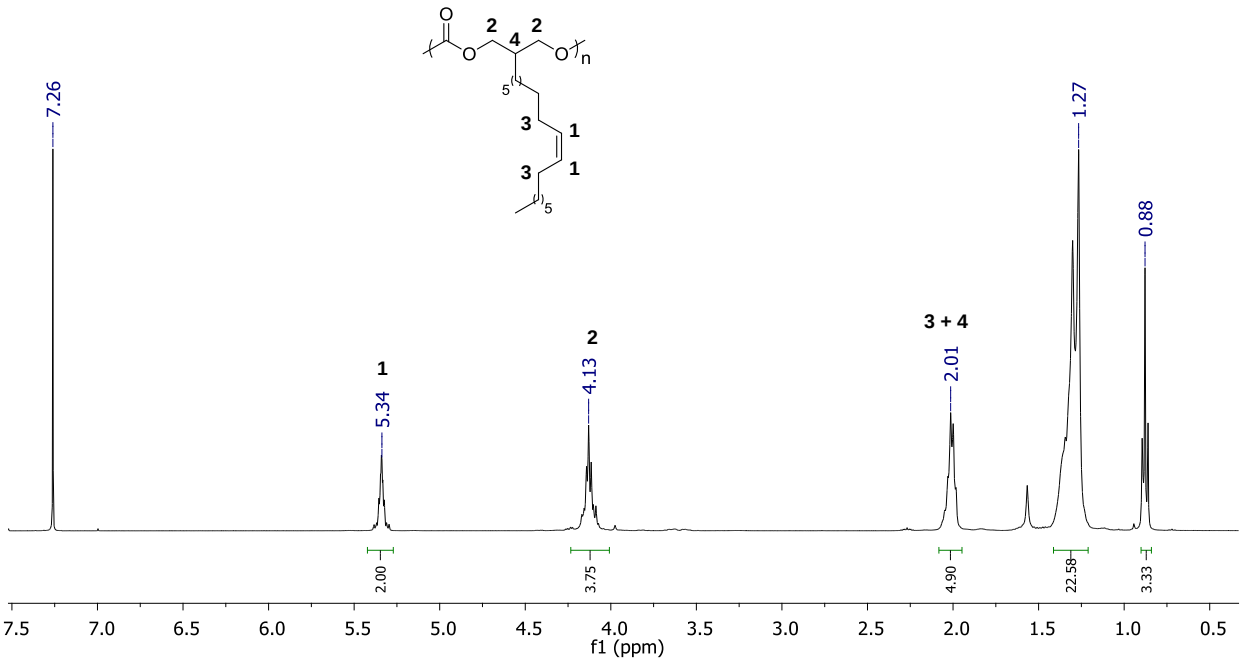
ESI Figure 2: Characterization of Ric-6CC (1) ^{1}H NMR (2) ^{13}C NMR, (3) ^{1}H-^{1}H COSY NMR and (4) ^{1}H-^{13}C HSQC-NMR. (Analysis performed in $CDCl_3$)



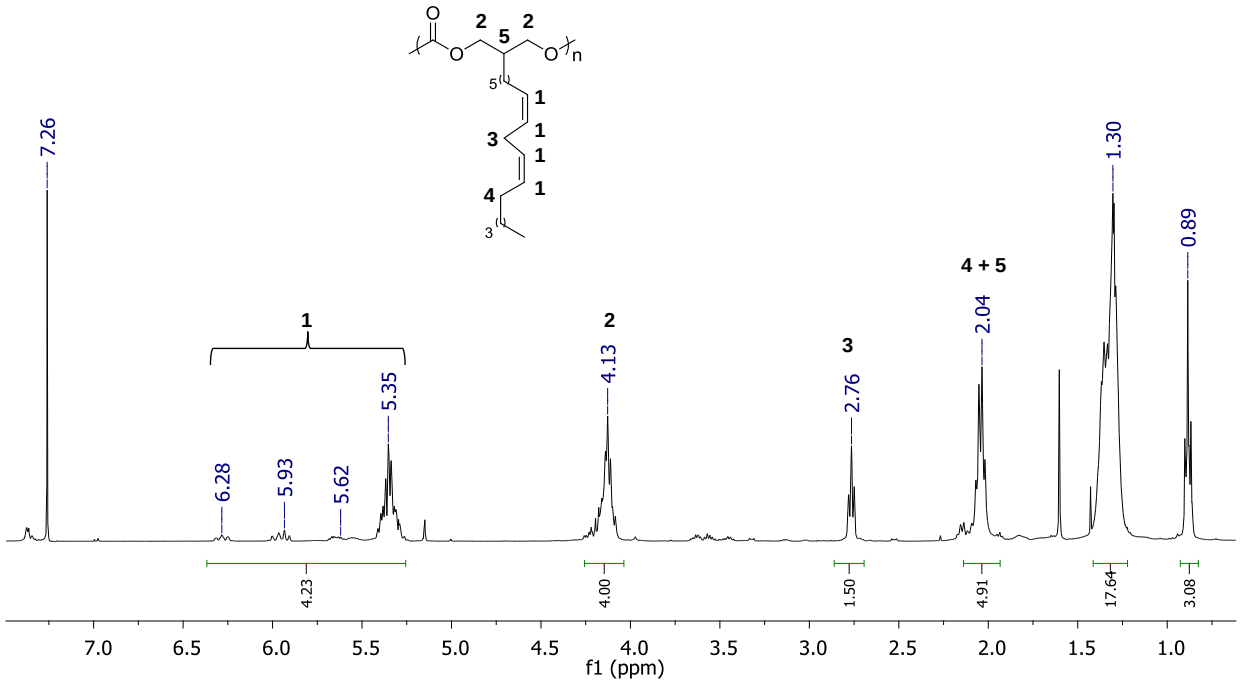
ESI Figure 3: FTIR spectra of Ric-6CC and P(Ric-6CC)



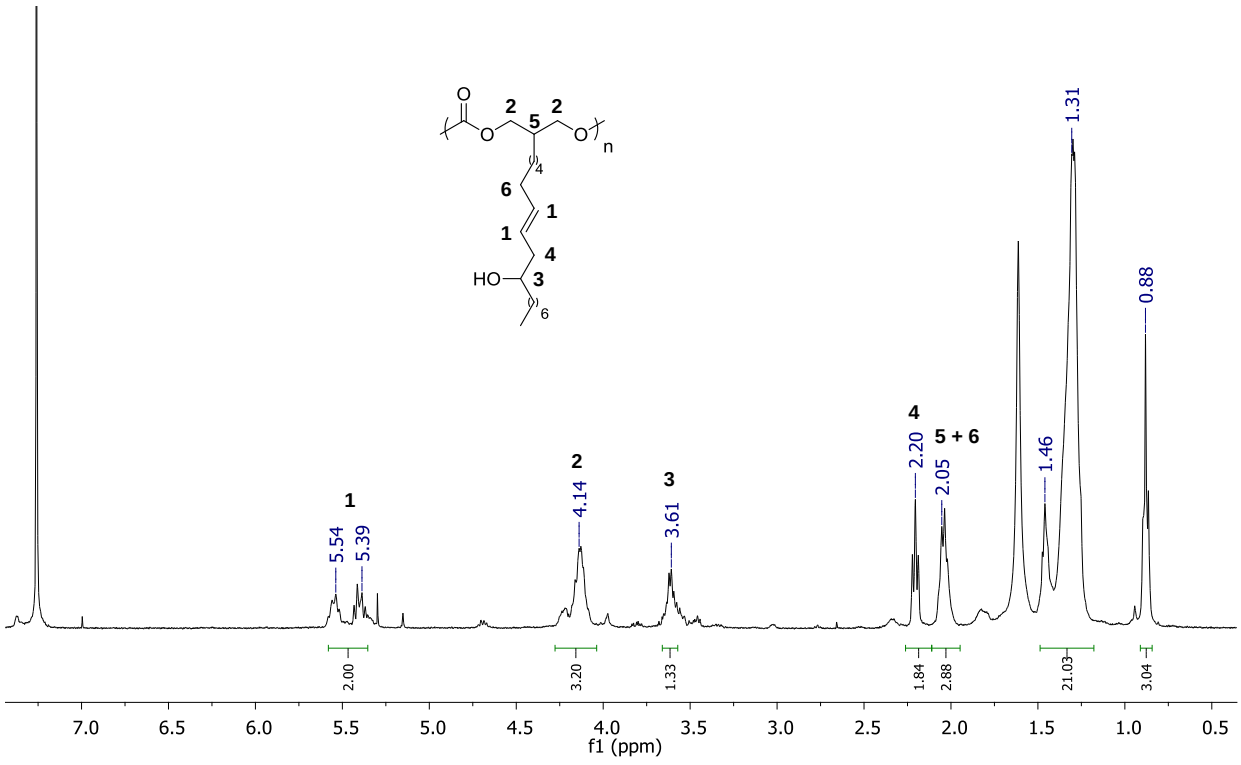
ESI Figure 4: ^{1}H NMR spectra of P(Und-6CC) in $CDCl_3$



ESI Figure 5: ^{1}H NMR spectra of P(Ole-6CC) in $CDCl_3$



ESI Figure 6: ^{1}H NMR spectra of P(Lin-6CC) in $CDCl_3$



ESI Figure 7: ^{1}H NMR spectra of P(Lin-6CC) in $CDCl_3$

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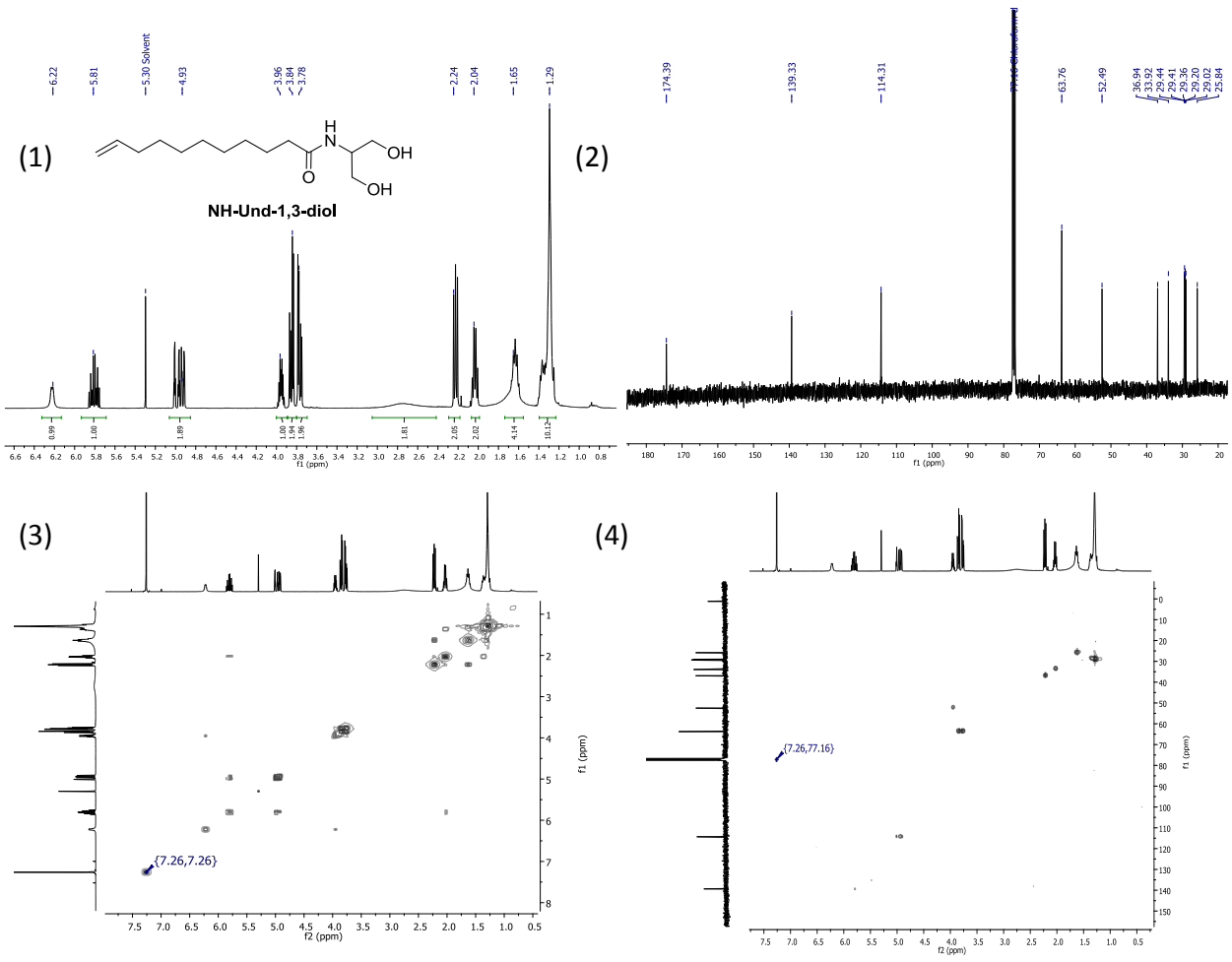
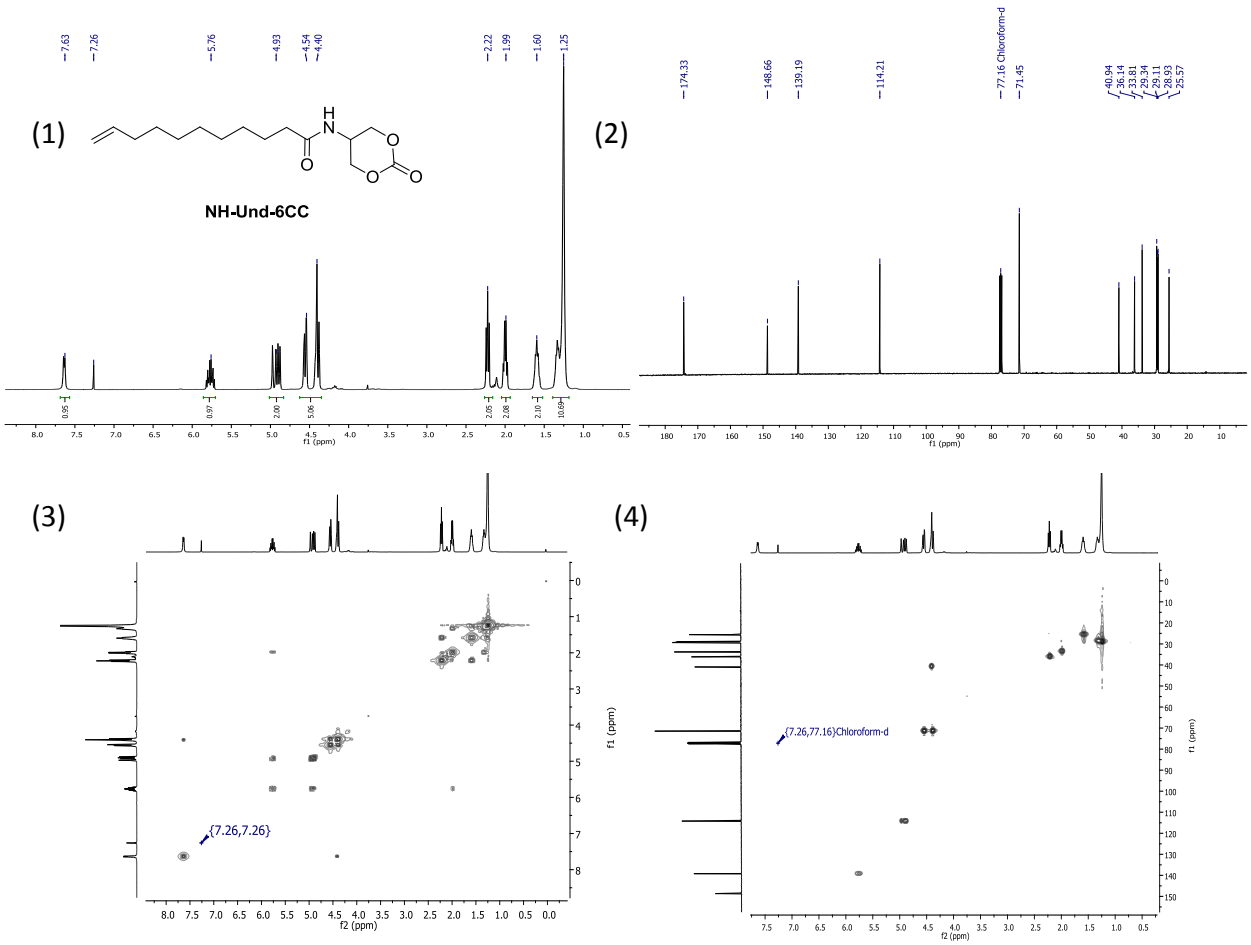
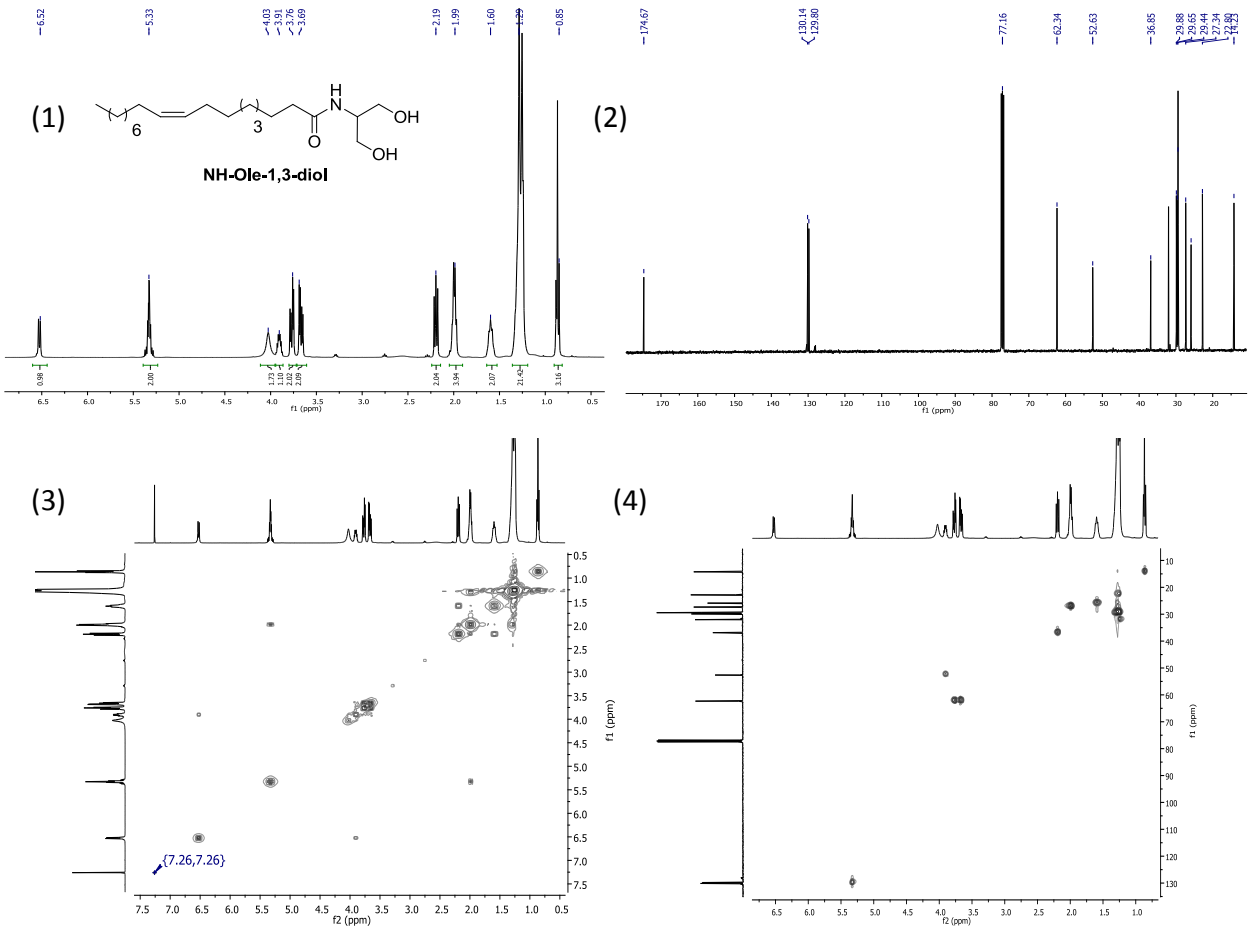


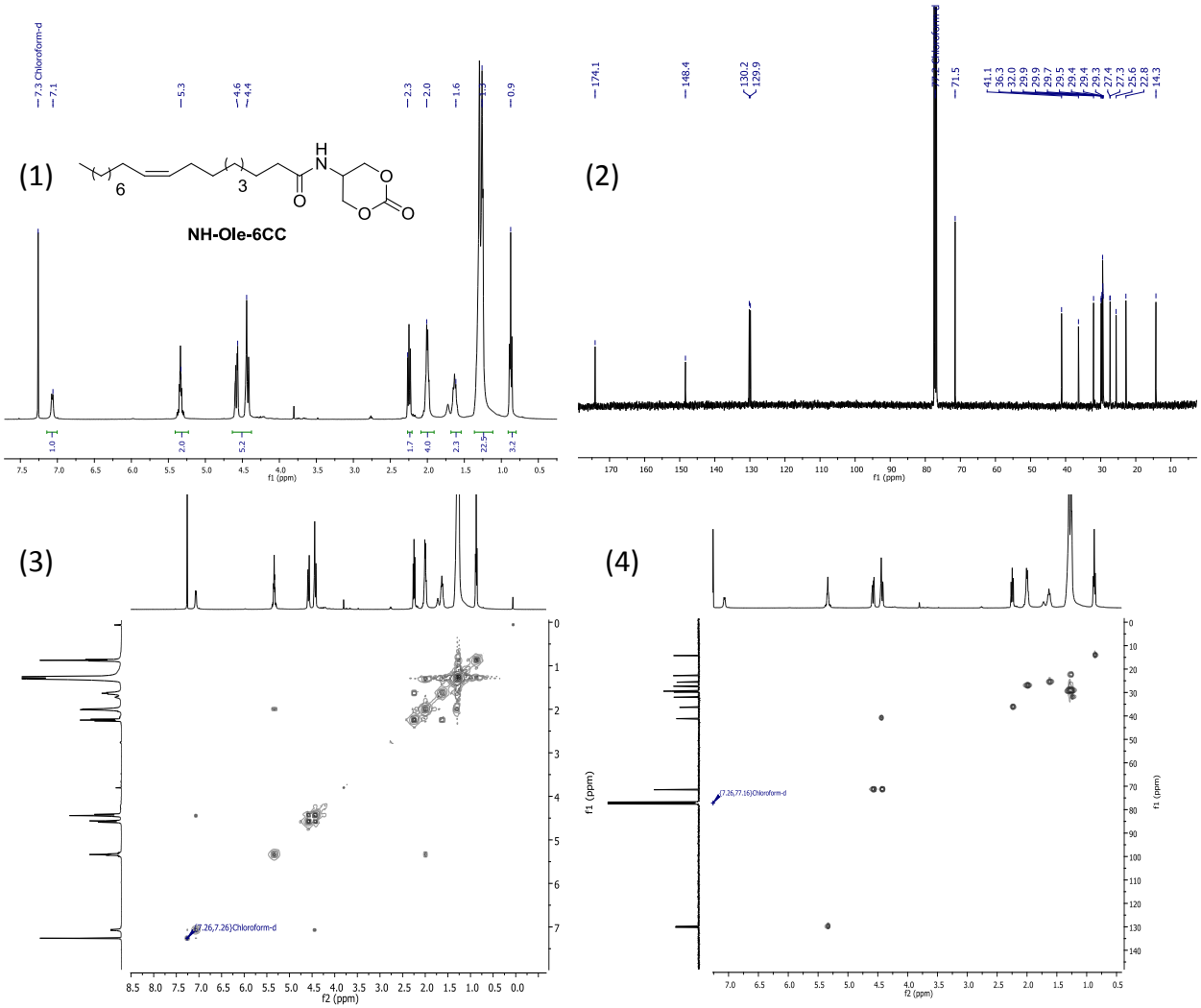
ESI Figure 8: Characterization of NH-Und-1,3-diol (1) ^{1}H NMR (2) ^{13}C NMR, (3) ^{1}H-^{1}H COSY NMR and (4) ^{1}H-^{13}C HSQC-NMR. (Analysis performed in $CDCl_3$)



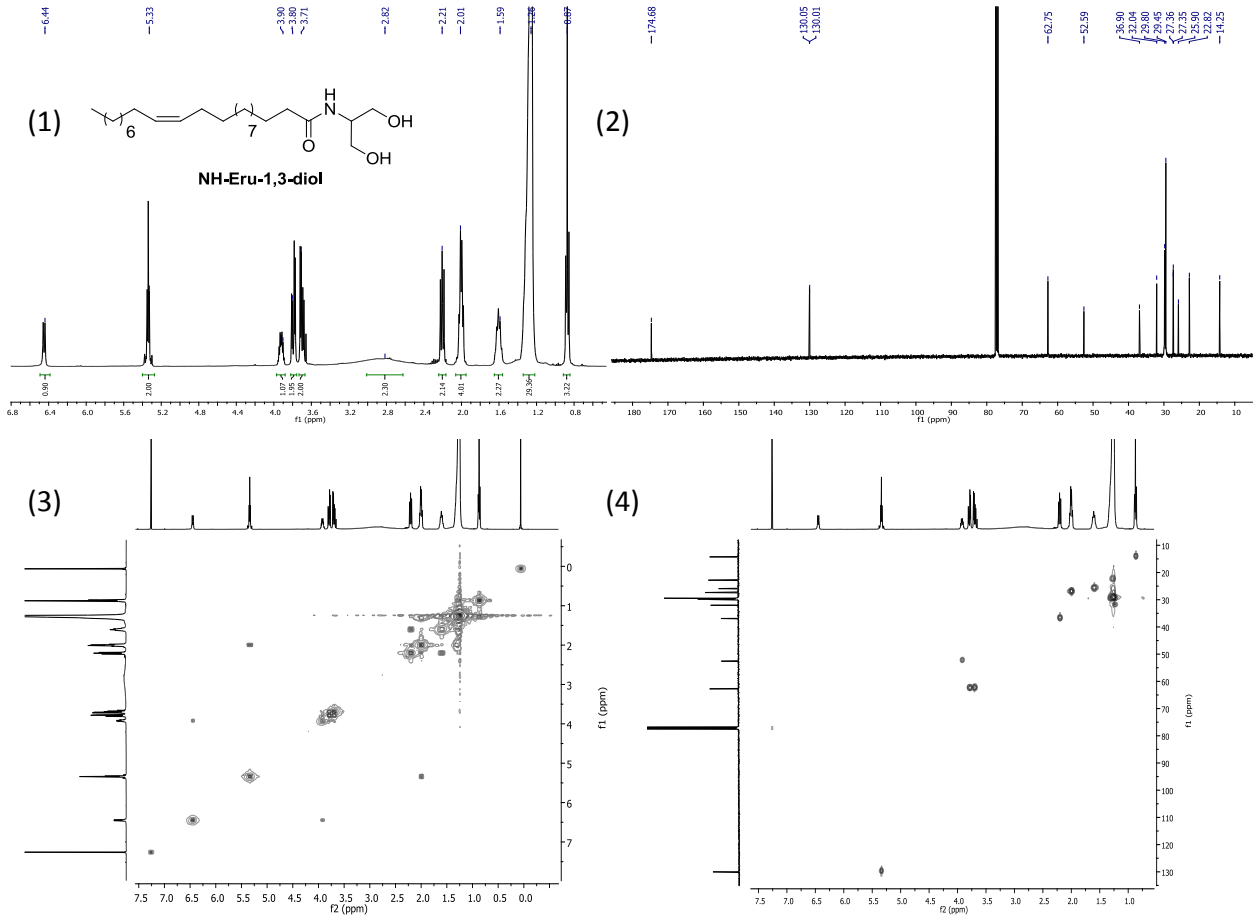
ESI Figure 9: Characterization of NH-Und-6CC (1) ^{1}H NMR (2) ^{13}C NMR, (3) ^{1}H-^{1}H COSY NMR and (4) ^{1}H-^{13}C HSQC-NMR. (Analysis performed in $CDCl_3$)



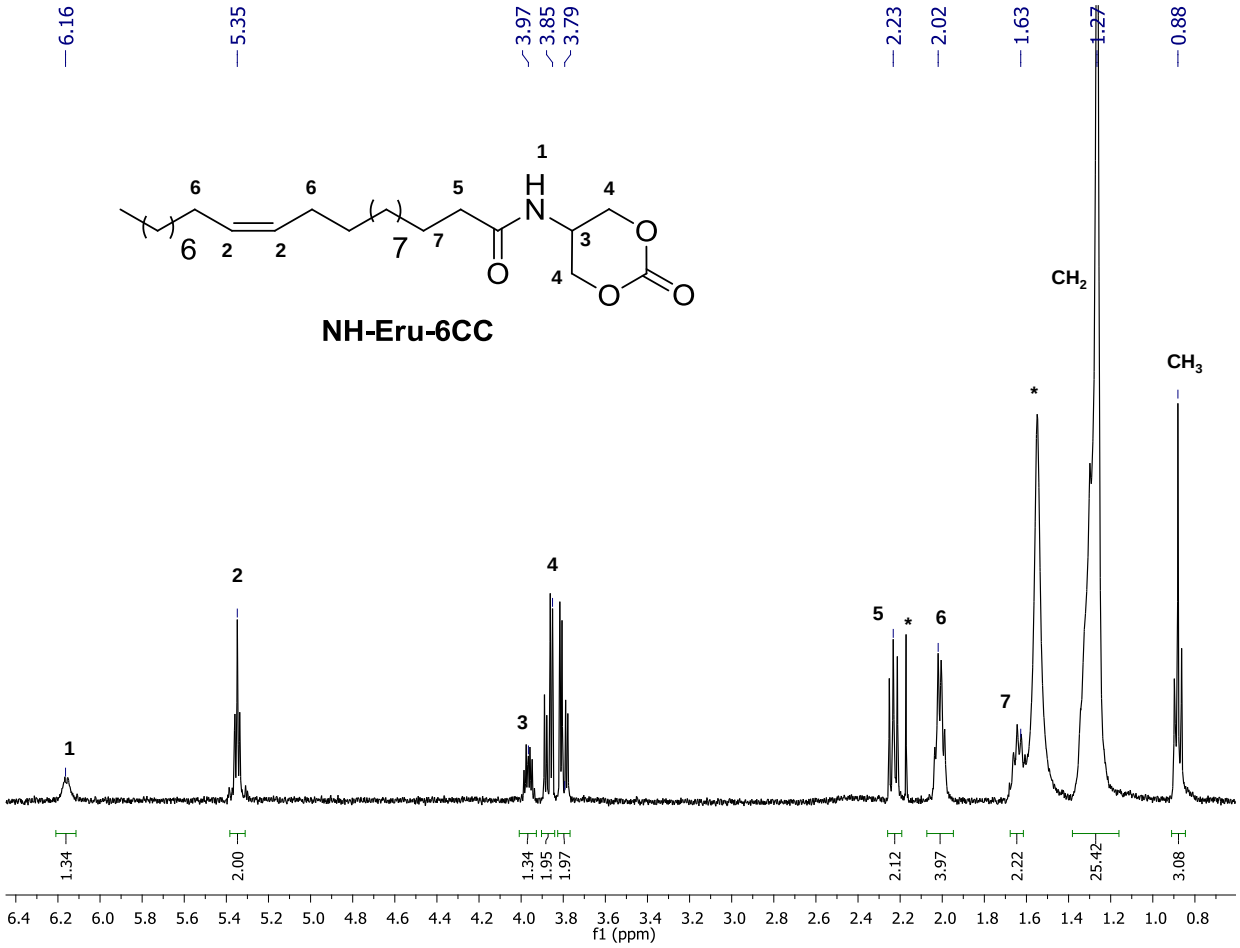
ESI Figure 10: Characterization of NH-Ole-1,3-diol (1) ^{1}H NMR (2) ^{13}C NMR, (3) ^{1}H-^{1}H COSY NMR and (4) ^{1}H-^{13}C HSQC-NMR. (Analysis performed in $CDCl_3$)



ESI Figure 11: Characterization of NH-Ole-6CC (1) ^{1}H NMR (2) ^{13}C NMR, (3) ^{1}H-^{1}H COSY NMR and (4) ^{1}H-^{13}C HSQC-NMR. (Analysis performed in $CDCl_3$)



ESI Figure 12: Characterization of NH-Eru-1,3-diol (1) ^{1}H NMR (2) ^{13}C NMR, (3) ^{1}H-^{1}H COSY NMR and (4) ^{1}H-^{13}C HSQC-NMR. (Analysis performed in $CDCl_3$)



ESI Figure 13: ^{1}H NMR of NH-Eru-6CC

Chapter 4

Design of cross-linked polycarbonate materials

Keywords: Aliphatic polycarbonates, Bio-sourced, Cross-linking, Self-healing materials

Mots-clés: Polycarbonates aliphatiques, Bio-sourcés, Réticulation, Matériaux auto-cicatrisants

Table of contents

Introduction

The previous chapter described the development of a versatile platform of bio-based cyclic carbonate monomers as precursors of aliphatic bio-based polycarbonates. It has been shown that polycarbonate properties could be tuned with respect to the structure of the starting fatty acid monomers and synthesis thereof.

In order to enhance the thermo-mechanical properties of these aliphatic polycarbonates, the present work is dedicated to the design of novel cross-linked polycarbonate materials. Only the chemical cross-linking methods involving the creation of covalent bonds will be discussed.

Such biodegradable polycarbonate networks exhibiting elastomeric properties are desirable thanks to a large number of applications in the biomedical area, especially in the emerging field of soft-tissue engineering or drug delivery.[1–6]

Several methods can be employed to generate chemically cross-linked materials. Some of them are depicted in Figure 1. The mechanical properties of these materials are controllable by the cross-linking density that can be regulated by the concentration of the cross-linker, the nature of the prepolymer structure and the distance between the cross-linking points. However, the main drawback of such cross-linked materials is their inability to be reshaped or recycled. As a consequence, several research groups developed new self-healing materials involving reversible cross-linking reactions.[7–10]

Herein, the first part of this chapter covers the formation of polycarbonate materials irreversibly cross-linked. After, a brief review of the recent examples described in the literature, several cross-linking methods were investigated from the first generation of polycarbonates described in chapter 3. Then, the second generation of polycarbonates were used to prepare cross-linked materials in a larger scale *via* thiol-ene cross-linking. In this study, several parameters were considered in order to tune the mechanical properties of the obtained networks.

In a second part, a focus was made on the reversible cross-linking reactions leading to the formation of self-healing materials. Two routes were investigated namely thermo-reversible and photo-reversible ways. The reversibility of the cross-linking reactions was demonstrated and self-healing materials with a large range of properties were synthesized.

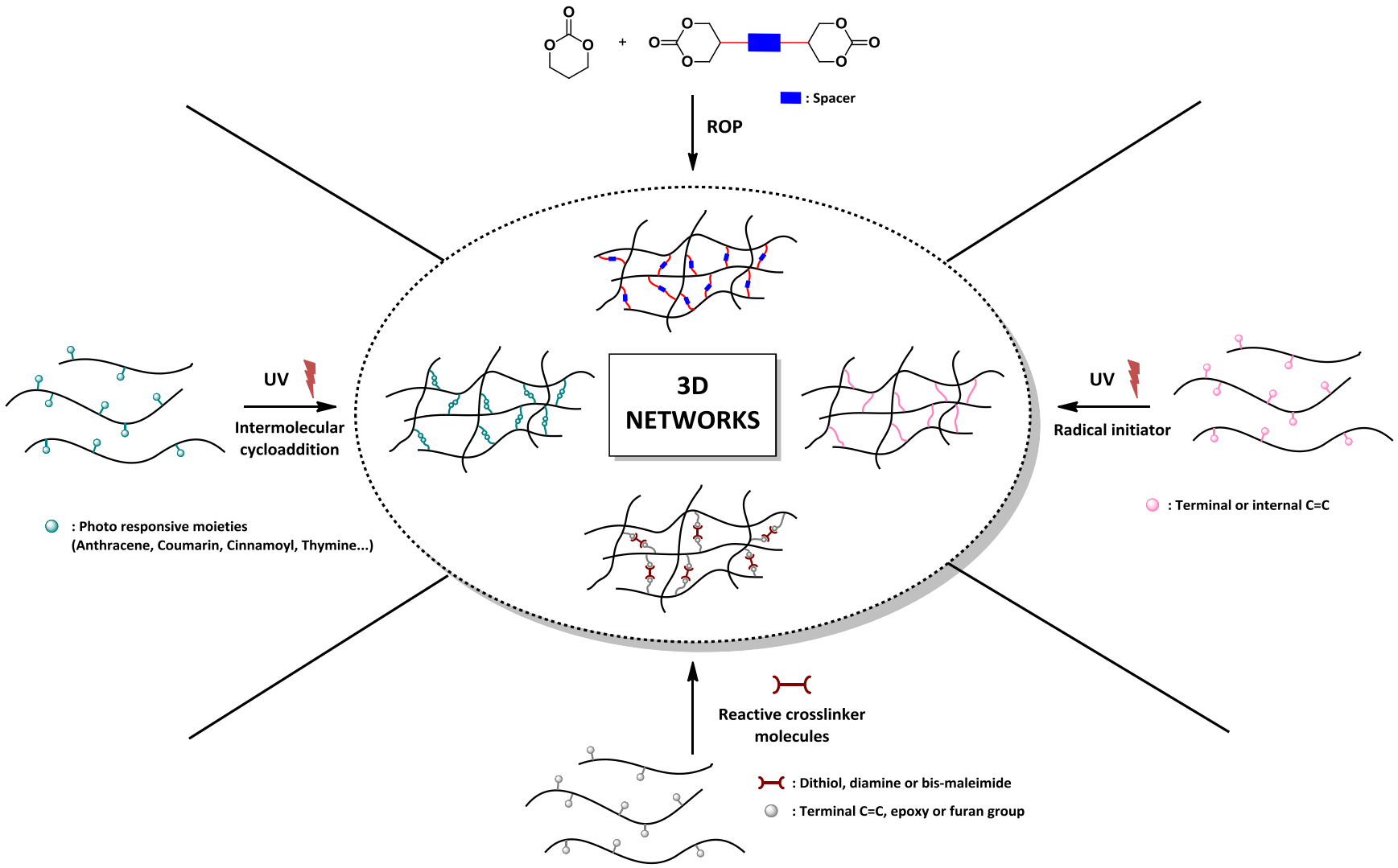


Figure 1: Various methods to obtain 3D networks

1. Non-reversible cross-linking

1.1 State of the art

In order to enhance their thermo-mechanical properties, linear polymer chains can be cross-linked leading to the formation of a network structure.

Two main synthetic methods can be considered to obtain a chemically cross-linked network. The first one is the direct network formation by polymerization of multi-functional monomers (the average monomer functionality being greater than 2). The second route is the post-polymerization cross-linking of functional linear chains with the help of a cross-linking agent.

In the former method, radical or anionic chain-growth polymerizations as well as step-growth polymerization like polycondensation and polyaddition can be performed for the build-up of cross-linked structures (Figure 1, top reaction). Chain-growth polymerization of a monomer with one polymerizable group (e.g., cyclic carbonate) in the presence of a second monomer with two or more polymerizable functional groups (e.g., bis-cyclic carbonate) gives the corresponding cross-linked network. This methodology is often used for the design of hydrogels.[11] In the field of polycarbonates, Pascual *et al.*, prepared cationic hydrogels showing anti-microbial properties *via* ring-opening polymerization (ROP) of N-substituted eight-membered cyclic carbonates, which were then quaternized with methyl iodide.[12] Similarly, Yuen *et al.* reported, very recently, the direct ring-opening polymerization of cationic N-substituted eight-membered cyclic carbonates to produce cationic polycarbonate hydrogels with antimicrobial properties (Figure 2).[13] Such hydrogels demonstrated antibacterial activity against *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive).

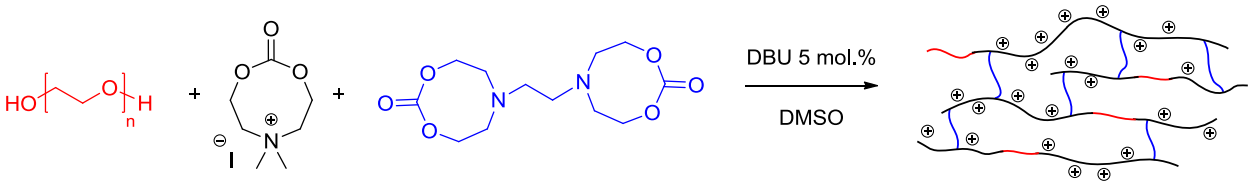


Figure 2: Polycarbonate ion gels using a cyclic carbonate and bis-cyclic carbonate[13]

In the second method, the post-polymerization cross-linking between linear polymer chains is usually carried out by reaction between reactive groups of the polymer chains in the presence (or

not) of a cross-linker agent (Figure 1, bottom reaction). Cross-linking reactions are usually promoted by heating or photo-irradiation. Several reactive groups such as unsaturations or oxirane groups have been widely used for cross-linking purpose. In particular, the thiol-ene reaction between the pendent terminal unsaturation and a dithiol is a common method to create cross-linked materials.[14–20] For example, Martín et al.[17] reported the formation of a bio-based polycarbonate from the naturally occurring terpene limonene oxide (LO) with a controlled number of functional repeating units. The authors demonstrated that the pendent olefin units enable the post-modification of these terpolymers through thiol-ene chemistry providing materials with improved thermal properties (Figure 3). The advantage of this cross-linking methodology is the control of the cross-linking density.

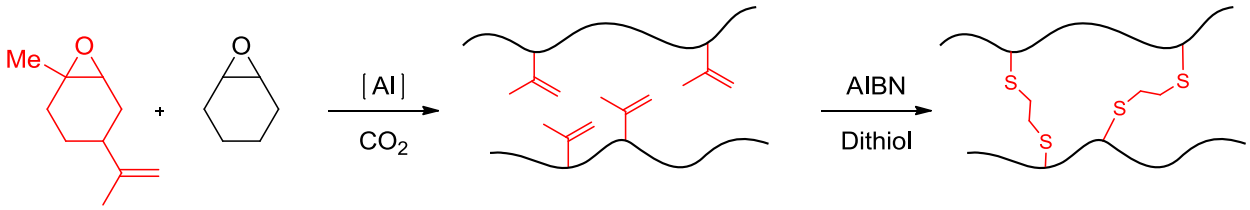


Figure 3: Cross-linked polycarbonate derived from the naturally occurring limonene[17]

In the same context, Stevens *et al.*[20] used epoxide-amine cross-linking chemistry to synthesize nanosponge from an epoxy-functionalized polycarbonate and a diamine as cross-linker.

Finally alkene-functional polycarbonates are able to undergo photo-initiated radical cross-linking to form cross-linked material (Figure 1, right reaction). Due to the absence of additional cross-linker, such materials are often used for biomedical applications.[21]

In the following, several non-reversible cross-linking methods such as thiol-ene coupling, epoxide-amine chemistry or cross-metathesis are described to prepare polycarbonate networks.

1.2 Preliminary studies on cross-linking methods

As exposed in the previous part, various methods are available for the building up of polymer networks. The objective of this preliminary study is to evaluate several methods such as thiol-ene chemistry, epoxide-amine coupling or cross-metathesis to obtain cross-linked polycarbonates (Figure 4). The linear precursor used in this study is P(TMC-*co*-Und-6CC) containing 9.1 mol.% of pendent double bond units (P3, in chapter 3). Since the aim of this part is only to test the

capability of such functional polycarbonate to undergo cross-linking, the reactions were performed in a very small scale (0.1 g) and only thermal characterizations were made. The success of the cross-linking was, on a first basis, checked by the insolubility of the cross-linked polycarbonate in DCM.

It is important to mention that, at the time of this study, the second generation of polycarbonate (i.e, P(**NH-Und-6CC**)) was not elaborated yet.

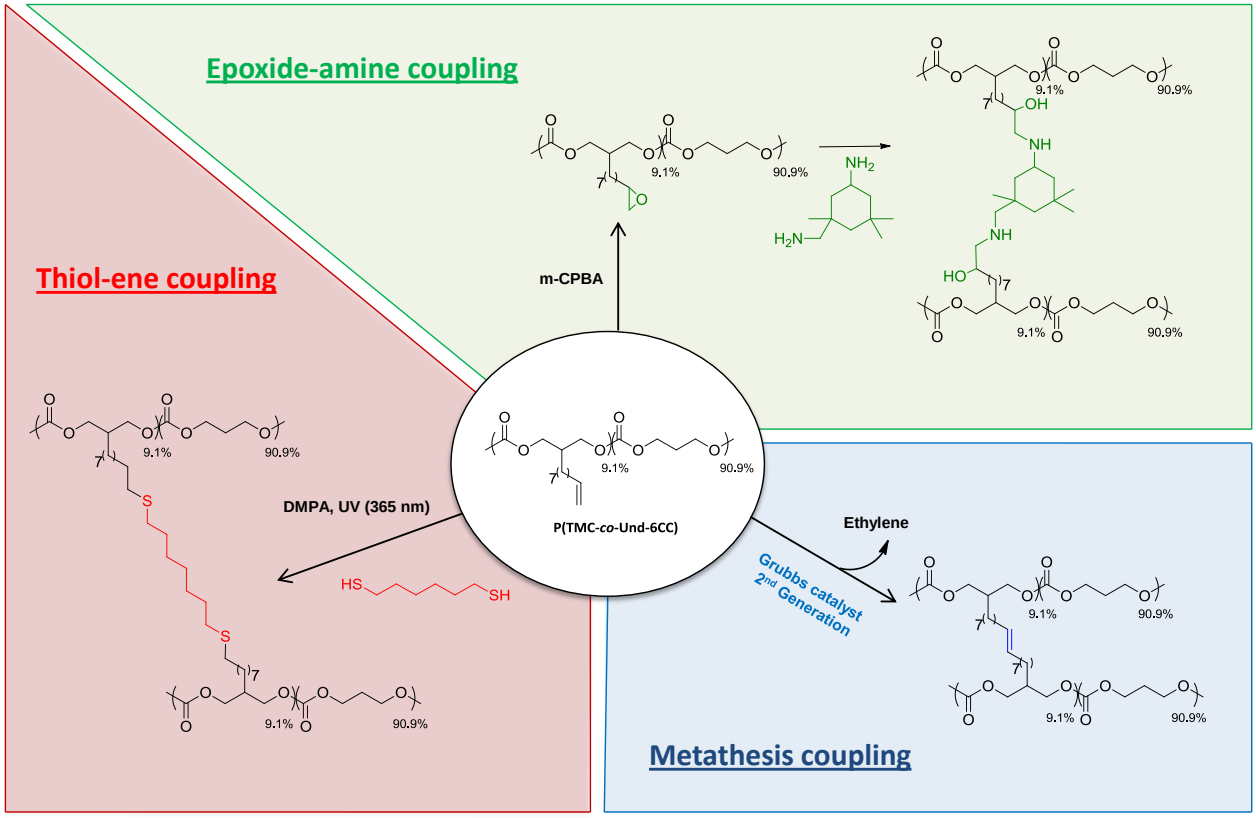


Figure 4: Cross-linking of P(TMC-*co*-Und-6CC) by three methodologies

In the thiol-ene coupling, 1,6-hexanedithiol (HDT) was used as cross-linker with a stoichiometric amount of HDT with respect to unsaturations (i.e., 0.50 equiv. *vs* olefin units in the polymer) in order to reach the highest cross-linking density. The polymer, HDT and the radical initiator DMPA (1 mol.% compared to olefin units) were dissolved in DCM (2 mol.L^{-1}) and transferred to a Teflon mold. The solvent was then gently evaporated overnight and residual DCM was removed under reduced pressure during 4h. The mixture was then irradiated at 365 nm during 4 hours. An insoluble cross-linked polycarbonate was successfully obtained and characterized. As

indicated in Table 1, the glass-transition temperature (T_g) measured using differential scanning calorimetry (DSC) and the thermal stability ($T_{d(5\%)}$) measured by thermogravimetic analysis (TGA) increase after the cross-linking reaction (7.3 °C and 38.3 °C respectively) even though only 9.1 mol.% of functional units are present in the polymer.

Table 1: Thermal properties of cross-linked polycarbonate from P(TMC-*co*-Und-6CC)

Sample	T_g [a] (°C)	$T_{d(5\%)}$ [b] (°C)
P(TMC-co-Und-6CC) with 9.1 mol.% of olefin units	-33.9	206.1
Network cross-linked by thiol-ene coupling	-26.6	244.4
Network cross-linked by epoxide-amine coupling	-20.9	240.3
Network cross-linked by cross-metathesis coupling	-18.9	211.1

a: Determined by DSC at 10°C.min^{-1} from the second cycle; b: Determined by TGA after 5 wt.% loss

The second cross-linking method often used to produce epoxy thermosets involves the coupling reaction between an oxirane group and an amine.[22] The oxirane units were obtained by epoxidizing the terminal double bond. Four equivalents of meta-chloroperoxybenzoic acid (m-CPBA) with respect to olefin units were used as oxidizing agent and the reaction was performed in refluxing chloroform during 12 hours. The structure of the epoxy-functionalized polycarbonate was followed by ^{1}H NMR (Figure 5) by the total disappearance of characteristic signals of olefin groups (5.0 and 5.8 ppm) and the appearance of the specific peaks attributed to epoxy ring (2.46, 2.75 and 2.90 ppm).

The so-formed epoxy-functionalized polycarbonate was cross-linked in a second stage by addition of 0.50 equiv. *vs* oxirane groups of isophorone diamine (IPDA) in bulk. The mixture was cured at 80°C during 2 hours. The thermal properties of the cross-linked material are detailed in Table 1. As observed with thiol-ene cross-linking, both T_g and thermal stability are increased upon cross-linking by epoxy-amine coupling. Indeed, T_g increases from -33.9°C to -20.9 °C and $T_{d(5\%)}$ increases from 206.1°C to 240.3°C.

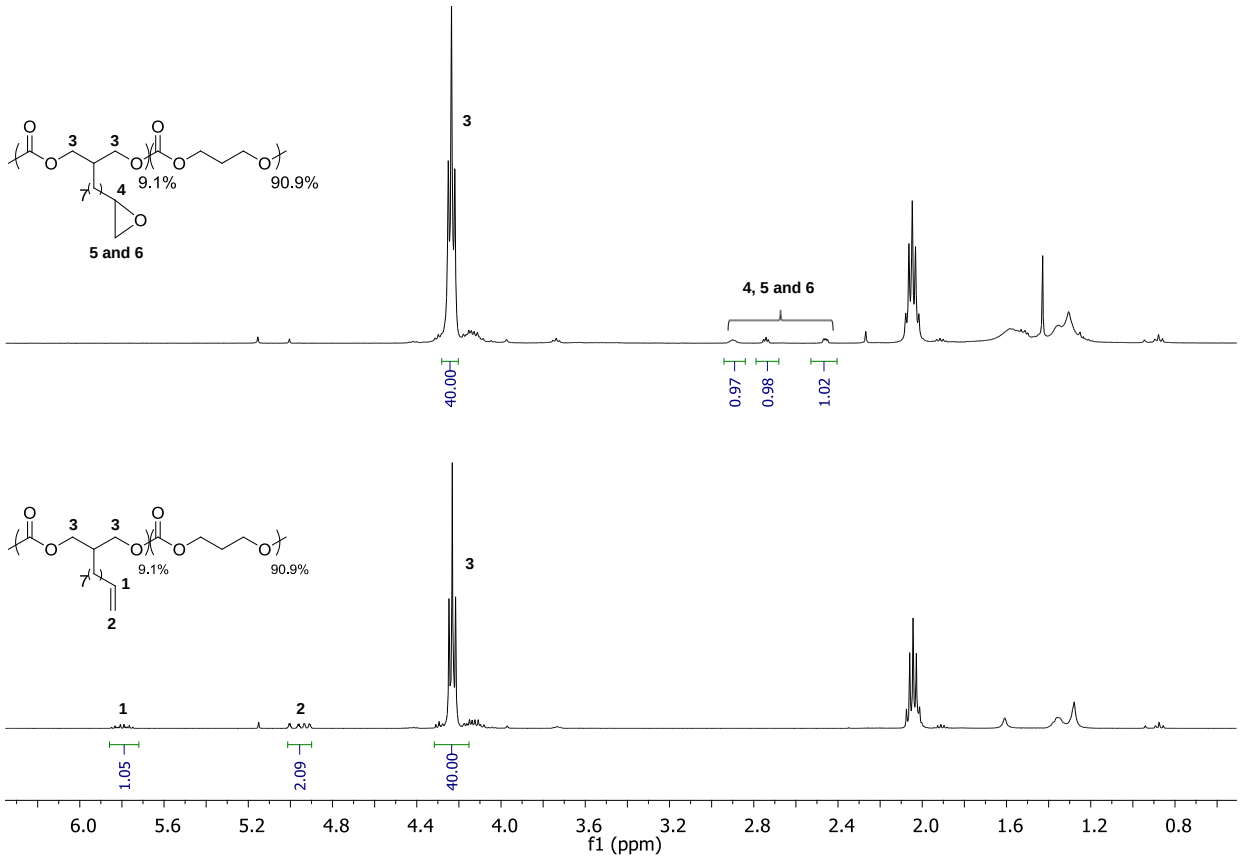


Figure 5: Stacked ^{1}H NMR of P(TMC-*co*-Und-6CC) and epoxidized P(TMC-*co*-Und-6CC) in $CDCl_3$

The last curing method is based on the metathesis reaction. Olefin cross-metathesis and ring-closing metathesis are widely used in polymer chemistry.[23,24] For example, olefin cross-metathesis has been used to cross-link and stabilize supramolecular assemblies, including cylindrical peptide assemblies,[25] the shells of polymeric micelles[26] and the peripheries of dendrimers.[27]

Metathesis reactions of linear polymer chains with pendent vinyl groups give a range of results, depending on reaction conditions. When the vinyl groups are located at suitable distances for cyclization, formation of rings along the chain occurs.[28] When the vinyl groups are spaced too far apart for convenient ring-closing metathesis, functional groups can be attached through olefin cross-metathesis.[29] In the absence of a cross-metathesis partner, the polymer undergoes cross-linking, which can be limited to intramolecular cross-linking under dilute conditions.[30]

In this study, the preparation of a cross-linked polycarbonate was attempted by olefin cross-metathesis thanks to pendent olefin groups. Grubbs catalyst 2nd generation has been used with a

loading of 2 mol.% with respect to olefin units. As above-mentioned, only intramolecular cross-linking occur under dilute conditions. Therefore, the cross-linking was performed in DCM at high concentration (4 mol.L^{-1}) to favor intermolecular process. After 12h of reaction at room temperature, a cross-linked polycarbonate was successfully synthesized. The thermal properties of the obtained network are shown in Table 1. Even though the thermal stability of the network remains similar compared to the polymer, the network T_g increases from -33.9°C to -18.9°C.

In conclusion of this preliminary study, several methods were utilized affording successfully polycarbonate network structures. In terms of thermal properties, all the obtained networks exhibit similar T_g and thermal stability. However, the direct cross-linking (no need of post-polymerization reaction) in thiol-ene and metathesis couplings is an advantage in comparison to the epoxide-amine reaction. In addition, the easiness of the process and the capacity to control the cross-linking density through the thiol-ene reaction make this coupling methodology more versatile with respect to the cross-metathesis coupling.

Consequently, thiol-ene click chemistry has been chosen as the cross-linking method for further investigations. Since the second generation of polycarbonates (P(**NH-Und-6CC**) for example) was prepared in a larger scale, the latter has been chosen as starting material for the design of cross-linked polycarbonates by thiol-ene coupling.

1.3 Cross-linking of the 2nd generation of PCs by thiol-ene reaction

The thiol-ene click chemistry can not only be used to prepare new functionalized polymers but also offer opportunities toward the formation of cross-linked polymers by interconnecting different polymer chains.

The aim of this part is to investigate the influence of several parameters on the polycarbonate network properties. Moreover, since the thiol-ene reaction is much more efficient with terminal olefins rather than internal ones,[31] P(**NH-Und-6CC)** was selected as starting polycarbonate.

The influence of the cross-linker/olefin units ratio on the network properties was first investigated. Then different cross-linkers were compared for a constant ratio.

1.3.1 Influence of cross-linker content on network properties

The thiol-ene reaction proceeds by addition of a functional thiol onto a double bond, most often *via* a free radical mechanism that can be thermally or photo-initiated (see Figure 6). The mechanism involves the formation of a thiol radical from the abstraction of a hydrogen atom initiated by applying UV-light (with or without photoinitiator) or by heating the reaction medium. The so-formed thiol radical attacks the alkene, forming a C-S bond and a carbon centered radical. The latter abstracts a proton from another thiol resulting in an anti-Markovnikov thioether product. The other species can, in turn, propagate the radical.

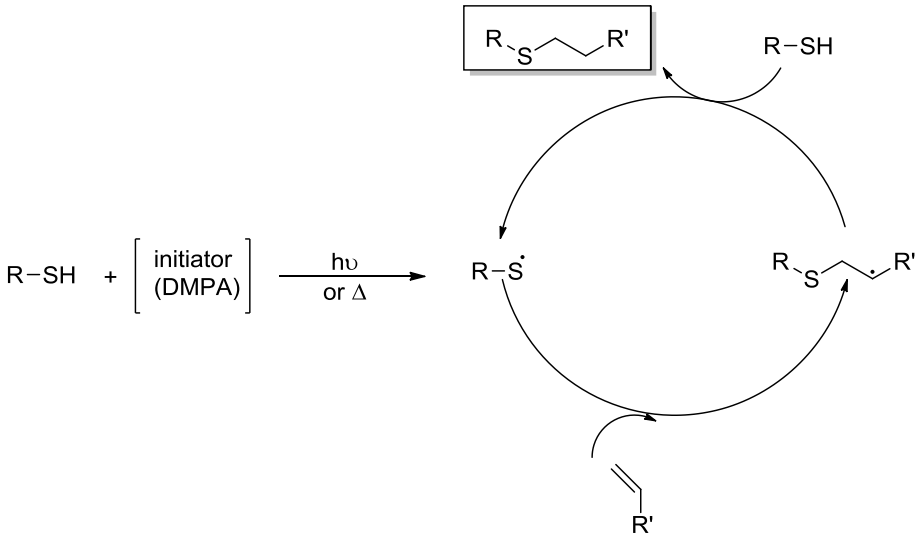


Figure 6: Mechanism of thiol-ene addition on terminal alkene

In this part, 1,6-hexanedithiol (HDT) has been selected as cross-linker to study the effect of the quantity of cross-linker added in the mixture. As above-mentioned, P(**NH-Und-6CC)** was selected as starting polycarbonate and **Irgacure 2959** as photoinitiator (Figure 7).

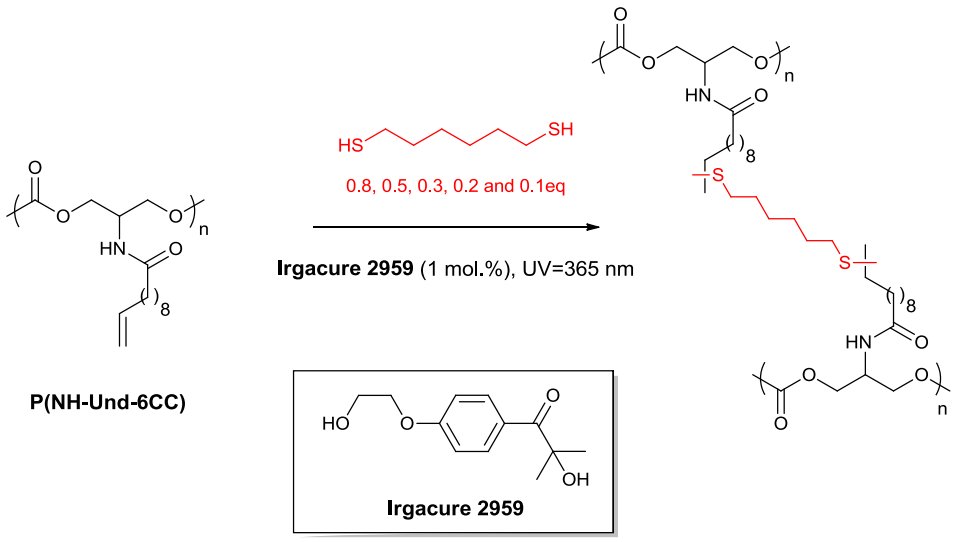


Figure 7: Cross-linking of P(NH-Und-6CC) with 1,6-hexanedithiol

The polycarbonate network was typically synthesized as follows: **P(NH-Und-6CC)** (1.0 g, 3.53 mmol), hexanedithiol (264.5 mg, 1.76 mmol, 0.5 equiv.) and **Irgacure 2959** (7.9 mg, 0.0035 mmol, 0.01 equiv.) were dissolved in 1mL of DCM and transferred to a Teflon mold. The solvent was gently evaporated overnight and residual DCM was removed under reduced pressure during 4h. The mixture was then irradiated at 365 nm during 4 hours. The obtained cross-linked film was flexible and transparent (Figure 8).

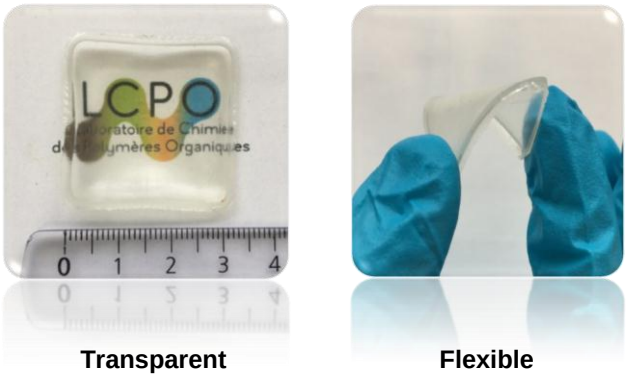


Figure 8: Transparent and flexible P(NH-Und-6CC) cross-linked with thiol-ene process

In theory, 0.5 equivalent of dithiol with respect to olefin groups should be added to fully cross-link the polymer. However, in order to tune thermo-mechanical properties of

polycarbonate networks, different cross-linker/olefin ratios have been studied. The results are summarized in Table 2.

Table 2: Thermo-mechanical properties of cross-linked P(NH-Und-6CC) with different dithiol/olefin ratios

Dithiol/olefin ratio	T_g (°C)[a]	E' (MPa)[b]	Young modulus (Mpa)[c]	Elongation at break (%)[c]	Max stress (MPa)[c]	Gel content (%)	Swelling ratio (%)
0.8	7.4	1.0	1.4 ± 0.5	121 ± 10	1.2 ± 0.5	83	214
0.5	15.1	4.5	50 ± 4	76 ± 5	6.1 ± 0.8	89	97
0.3	14.7	4.2	31 ± 5	64 ± 1	5.8 ± 0.5	86	102
0.2	8.6	2.0	2.4 ± 0.2	134 ± 12	2.2 ± 0.2	71	180
0.1	5.3	0.1	0.8 ± 0.2	175 ± 20	0.8 ± 0.1	34	283

[a]: Determined by DSC at 10°C.min^{-1} from the second cycle.; [b]: Evaluated with DMA analysis; [c]: Calculated from tensile tests

To determine the equilibrium swelling ratios and gel contents, strip-shaped specimens (0.6 mm thick, 0.5 mm width, 3 mm length) were placed in 10 mL of DCM for 48 hours. DCM was replaced once after 24h. We assume that this procedure ensured complete removal of the sol fraction. Then the swollen gels were dried to constant weight at room temperature in vacuum and weighed.

The gel fraction[32] was calculated according to Equation 1 where m_d is the mass of dried (extracted) samples and m_0 is the mass of the specimens before swelling.

$$\boldsymbol{Gel\ fraction}(\%) = \frac{\boldsymbol{m_d}}{\boldsymbol{m_0}} \times \mathbf{100}$$

Equation 1: Formula used to calculate de gel fraction

The swelling ratio[12] was calculated according to Equation 2 where m_t is the mass of the swollen samples in DCM.

$$\boldsymbol{Swelling\ ratio}\ (\%) = \frac{\boldsymbol{m_t - m_d}}{\boldsymbol{m_d}} \times \mathbf{100}$$

Equation 2: Formula used to calculate the swelling ratio

The gel contents and the equilibrium swelling ratio values of the networks formed are summarized in Table 2. The effect of the cross-linker content can be clearly seen. As expected, the resulting polycarbonate networks have greatly increased gel contents and decreased swelling ratios with an increasing of cross-linker content. Indeed, the gel content of the network increases from 34% to 89% with 0.1 equiv. and 0.5 equiv. of dithiol respectively. Simultaneously, the swelling ratio of the network decreased from 283% to 97% with 0.1 equiv. and 0.5 equiv. of dithiol respectively. It is important to note that an excess of cross-linker (0.8 equiv.) greatly increases the swelling ratio without decreasing the gel content meaning that the cross-linking density is lower.

Regarding the thermal properties of the polycarbonate networks, $T_{d(5\%)}$ remained nearly constant around 150 °C regardless of the cross-linking density. In addition, all polymers and networks were amorphous with T_g below room temperature in the range 5.3 to 15.1 °C for different dithiol/olefin ratios (Table 2). As expected, the T_g increases when the dithiol/olefin ratio goes from 0.1 to 0.5. However, an increase to 0.8 equivalent of dithiol leads to lower T_g confirming that an excess of dithiol tends to decrease the cross-linking density of the network. It is speculated that pendent thiol groups which could not react due to the excess of dithiol are probably present in the network (Figure 9).

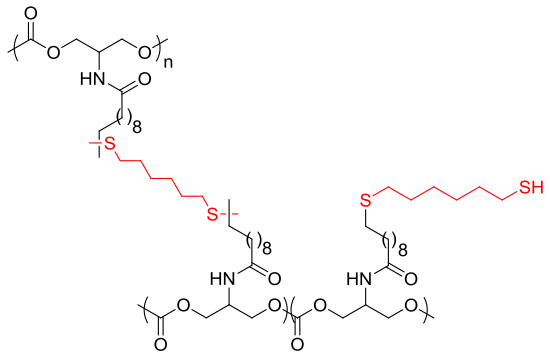


Figure 9: Structure of the polycarbonate network when 0.8 equiv. of dithiol is added with 1 equiv. of olefin

The thermo-mechanical behaviour of the networks was determined by dynamic mechanical analysis (DMA), run in tension. The storage modulus as a function of temperature of each network is shown in Figure 10. These traces are indicative of amorphous cross-linked networks. Three regions with different mechanical response were observed with temperature change. At low temperatures, a glassy modulus plateau at 1 GPa is obtained. The glass

transition region is recognized by the drastic decrease in modulus with increasing temperature. Beyond the glass transition region, the rubbery modulus plateau is nearly constant and, in accordance with the rubber elasticity theory, it is proportional to the cross-link density of the network. We can clearly see, Figure 10, that the storage modulus at 50°C decreases significantly from 4.5 MPa to 0.1 MPa by decreasing the number of equivalents of the cross-linker (from 0.5 to 0.1).

In addition, an excess of dithiol (0.8 equiv.) results in lowering the storage modulus in the rubbery plateau. This result confirms that an excess of cross-linker decreases the cross-linking density. Nevertheless, the elasticity properties of the material can be modulated by tuning the cross-linker content.

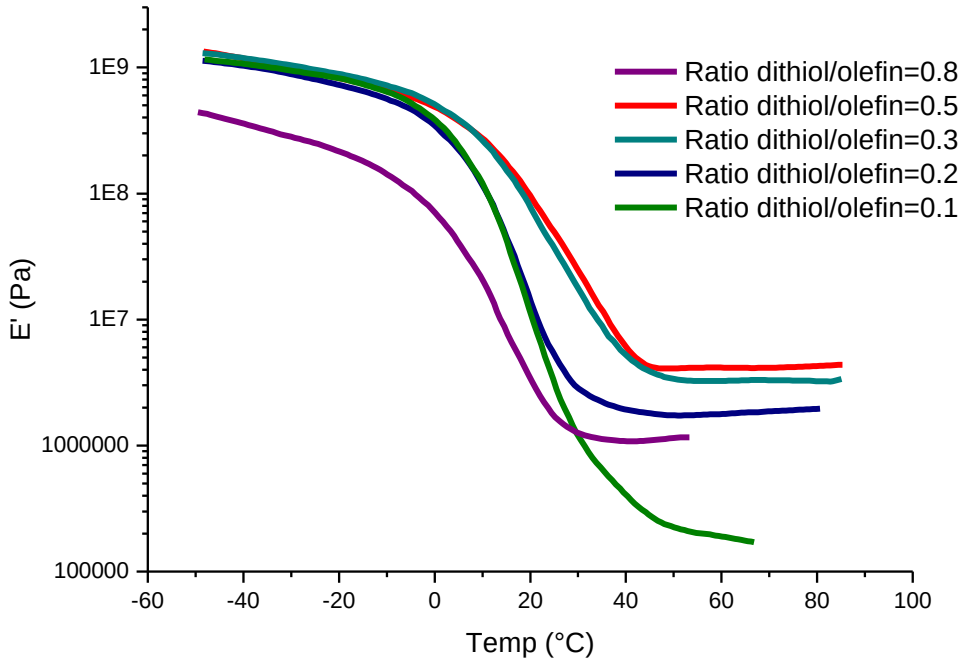


Figure 10: Storage modulus as a function of dithiol/olefin ratio

The tensile properties of the polycarbonate network films are also given in Table 2, while representative stress–strain curves are shown in Figure 11. It can be seen from these data that cross-linked polycarbonates exhibit different stress and strain at break values depending on the cross-linking density. Polycarbonate films containing 0.5 equivalent of cross-linker have

stress at break values 7 times higher than the ones containing 0.1 equivalent of cross-linker (5.7 MPa and 0.8 MPa respectively).

Strain at break values can be also modulated depending of the cross-linker content. The range of values goes from around 70% (with 0.5 equiv. of dithiol) to almost 200% (with 0.1 equiv. of dithiol). Once again, the excess of cross-linker decreases the mechanical properties of the network.

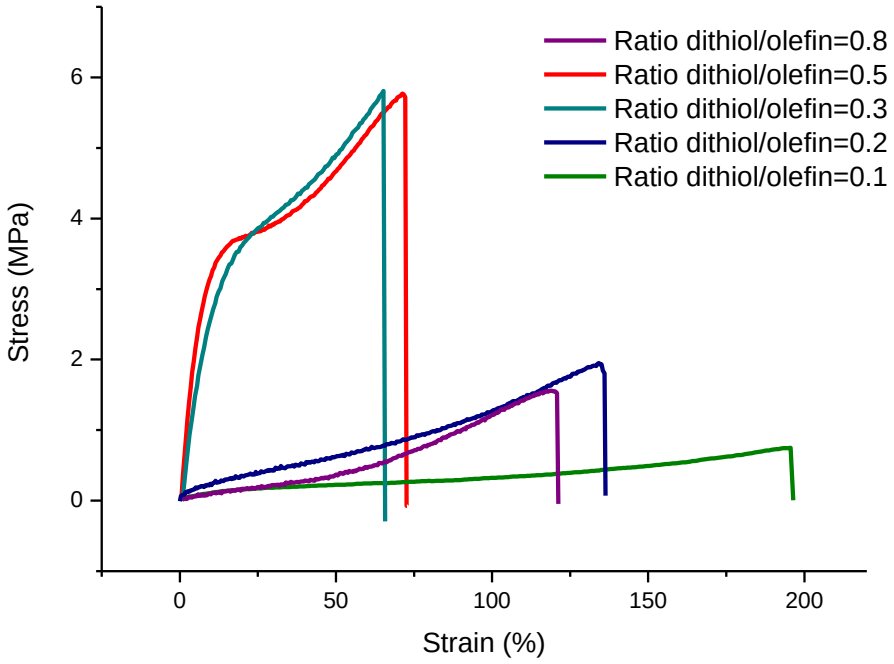


Figure 11: Representative stress-strain curves of polycarbonate networks with different dithiol/olefin ratios

Consequently, the thiol-ene cross-linking method affords the preparation of bio-based aliphatic polycarbonate networks presenting a wide range of mechanical properties depending on the cross-linker content. In addition, an excess of dithiol compared to olefin decreases the cross-linking density of the network. Nevertheless, the so-formed network possesses pendent thiol groups which can be useful in some applications.

1.3.2 Influence of cross-linker structure on network properties

The next part aims at investigating the influence of the cross-linker structure on the network properties keeping the dithiol to olefin ratio constant to 0.5.

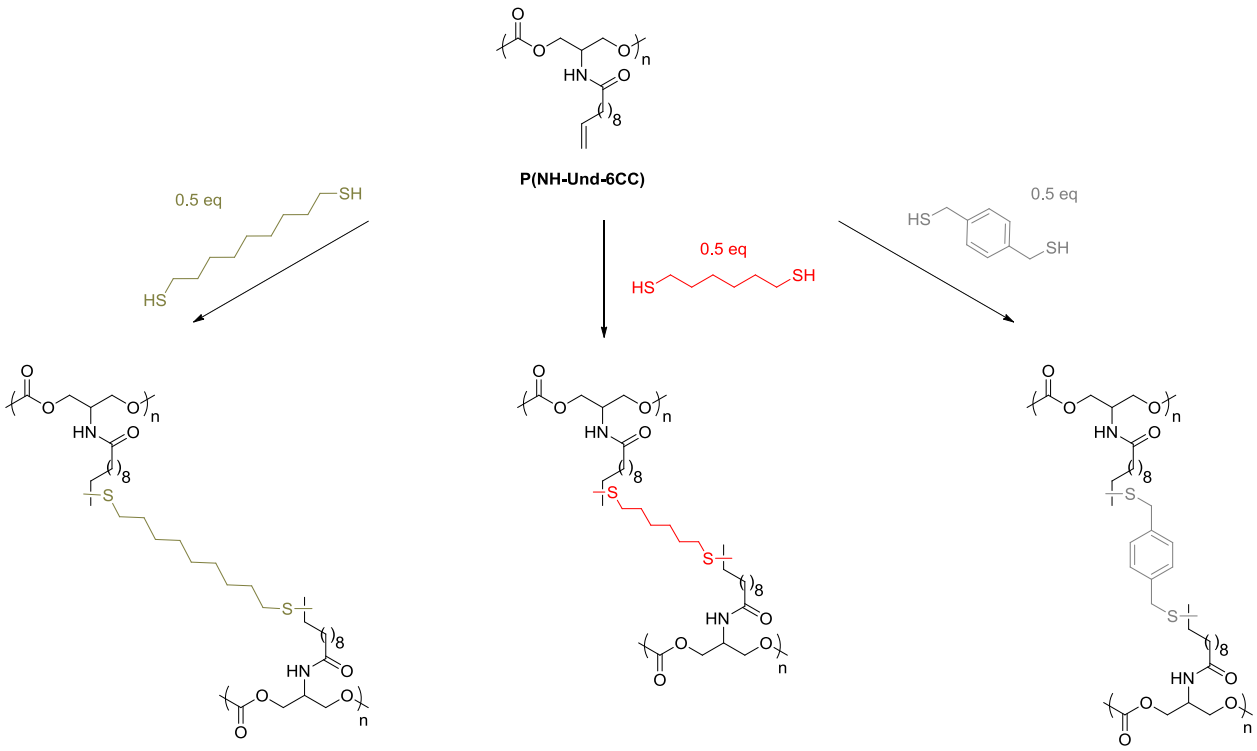


Figure 12: Cross-linking of P(NH-Und-6CC) *via* thiol-ene reaction with different cross-linkers

Using the same above-detailed cross-linking method, HDT was replaced by 1,9-nonanedithiol and 1,4-benzenedimethanethiol (Figure 12). The use of 1,9-nonanedithiol induces more space between reactive groups and 1,4-benzenedimethanethiol brings some rigidity between polymer chains. Mechanical properties have been evaluated by DMA and tensile tests. Results are summarized in Table 3.

Table 3: Mechanical properties of polycarbonate networks cross-linked with different dithiols

Cross-linker	T_g (°C)[a]	E' (MPa)[b]	Young modulus (Mpa)[c]	Elongation at break (%)[c]	Max stress (MPa)[c]
1,6-hexanedithiol	15.1	4.5	50 ± 4	76 ± 5	6.1 ± 0.8
1,9-nonanedithiol	37.7	8.9	240 ± 20	25 ± 6	29 ± 3
1,4-benzenedimethanethiol	8.8	0.9	1.3 ± 0.1	190 ± 5	1.3 ± 0.1

[a]: Determined by DSC at 10°C.min^{-1} from the second cycle.; [b]: Evaluated with DMA analysis; [c]: Calculated from tensile tests

Surprisingly, the network cross-linked with 1,9-nonanedithiol exhibits a higher T_g and better mechanical properties than the one cross-linked with HDT. On the contrary, when the rigid 1,4-benzenedimethanethiol was used instead of HDT, a decrease of the network T_g and mechanical properties was observed. DMA curves and stress-strain traces are shown in Figure 13. The rigidity of the aromatic ring and the relative proximity of the reactive groups in 1,4-benzenedimethanethiol may hinder the access of the thiols to pendent olefins. Therefore, intramolecular coupling could occur instead of intermolecular one resulting in poorly cross-linked network. In contrast, the nine-carbon distance between the two thiol groups in 1,9-nonanedithiol makes C=C double bond more accessible. The so-formed network is highly cross-linked and displays higher mechanical properties.

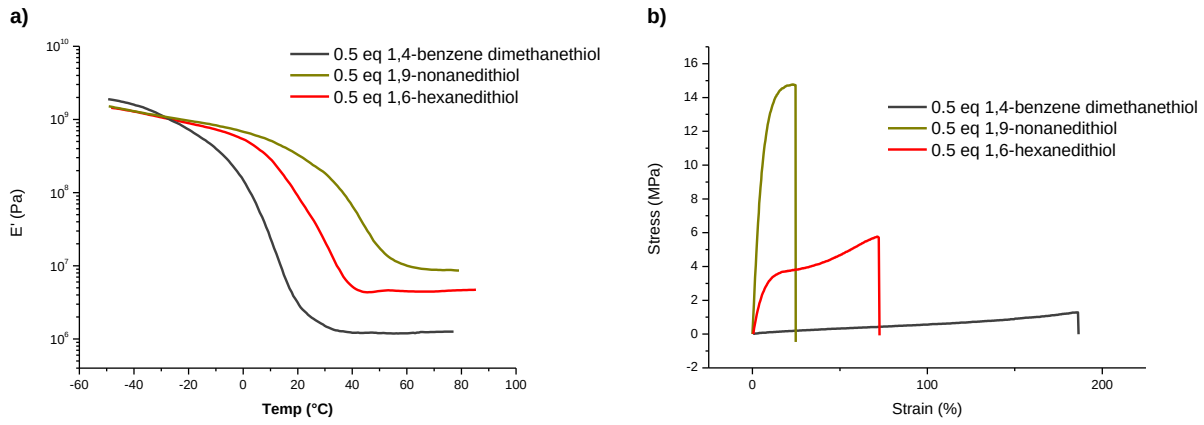


Figure 13: a) DMA curves and b) stress-strain traces of polycarbonate networks with different cross-linkers

In conclusion, novel cross-linked networks were synthesized using bio-based cyclic carbonate monomers. A preliminary study showed that thiol-ene coupling was a convenient method to afford cross-linked polycarbonates from the first generation of polycarbonate. Subsequently, the thiol-ene click chemistry was used to prepare polycarbonate materials in a larger scale with P(**NH-Und-6CC**) as starting linear precursor. It has been shown that the properties of the cross-linked polymers can be greatly tuned ranging from rather tough materials to elastomeric networks (Figure 14)

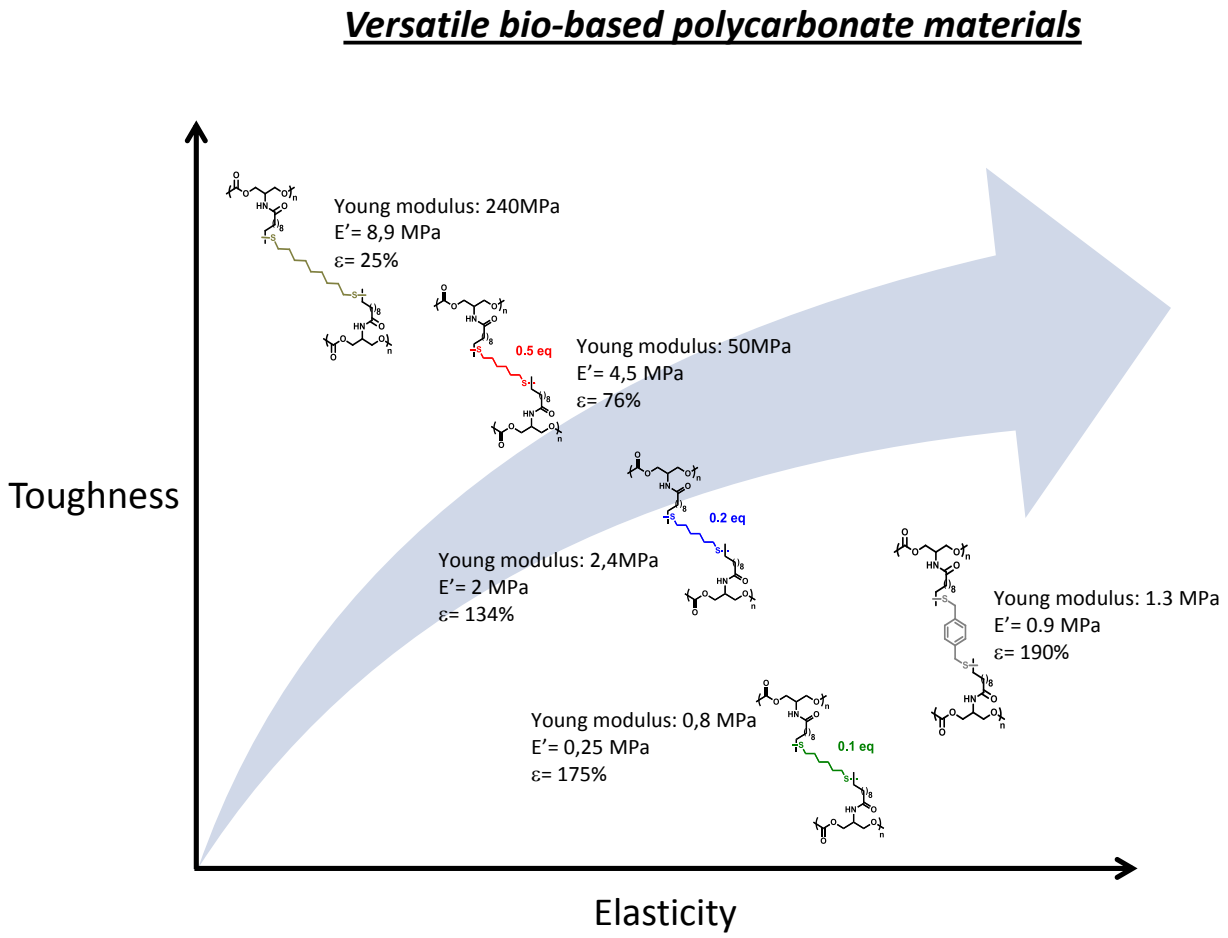


Figure 14: Overall mechanical properties of the bio-based polycarbonate networks

2. Reversible cross-linking

2.1 State of the art

As detailed in the previous part, covalently cross-linked materials are used for various applications, as coatings, composite materials or bio-medical devices, for instance. As mentioned previously, thermo-mechanical properties of the uncross-linked material are significantly enhanced thanks to covalent bonds between polymer chains. Indeed, the presence of the covalent crosslinks in the material makes these materials largely elastic in their response to strain deformations. However, the permanent feature of such cross-linked structure often raises serious limitations especially when the material needs to be reshaped or recycled.

In order to tackle this issue, the introduction of reversible cross-links into a network enables the easy processing of the material without losing its improved thermo-mechanical properties.

The change from the polymeric to the network state is governed by the nature of the reversible covalent bond. A reversible bond can either be dynamic, involving an exchange reaction, or non-dynamic, requiring stimuli to either break or form the covalent linkage (Figure 15).[33]

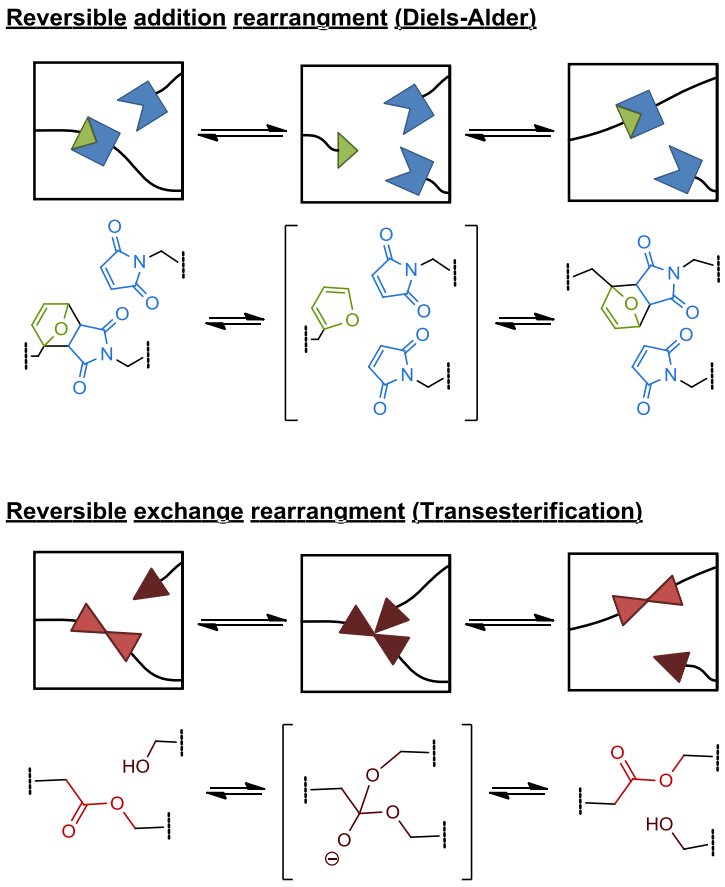


Figure 15: Non-dynamic reversible addition (top) and dynamic reversible exchange (bottom) cross-linking reactions[33]

Reversible addition rearrangement (Figure 15-(top)) follows a bond-breaking, bond-forming reaction sequence. Thus, the rearrangement necessarily involves a decrease in the network connectivity and crosslink density, as for example in the Diels Alder-based networks.

In contrast, reversible exchange reactions (Figure 15-(bottom)) follow a bond-forming, bond-breaking sequence without a decrease in connectivity or crosslink density during the transition, as for example seen with the transesterification-based network. In that case, no change in

macroscopic connectivity occurs, the material behaves like a strong glassy material while remaining processable over a broad temperature range. This class of materials was named "vitrimers" by the group of Leibler[34] due to their similarities to silica-like materials. Research on vitrimers has also been recently published by Nicolaÿ et *al.*[35] and reviewed by Du Prez and coll.[36–38]

In the framework of this PhD work, only non-dynamic reversible bonds have been introduced into the polymer matrix. Upon activation of the reversibility by a stimulus (heat, light, electricity, magnetism), a net breaking of bonds occurs and a solid material can be converted into a viscous liquid. Activation of the reverse reaction (with another stimulus) leads to the reformation of the network and recovery of the solid properties. These classes of materials are also called "self-healing" materials. When they undergo mechanical damage, self-healing materials can heal themselves, meaning that the latter can restore their original shape and recover their original properties. Such materials could be of interest in many fields such as protective coatings, biomedical applications, piping and electronics. In 2013, self-healing materials were even named among the top 10 emerging technologies by the World Economic Forum.[39]

More specifically, the development of self-healing polymers has been a very active area of research over the last decade.[7–10] Various stimuli can be employed to activate the reversibility of the transformation. Nevertheless, temperature and light are the two stimuli, which are most commonly used in the synthesis of "stimuli-responsive" self-healing materials.

A thermal process is convenient and effective for treatment of materials with a wide range of sample architecture and treatment durations. As a result, heat-induced reversible reactions are attractive for building up thermal-responsive self-healing materials. The most studied thermally reversible reactions are based on the Diels–Alder (DA) chemistry. The latter has been widely used in macromolecular chemistry.[40–49]

The Diels–Alder reaction is a [4+2] cyclo-addition involving a diene and a dienophile as precursors (Figure 16). Alkenes and alkynes with electron-withdrawing substituents, which make electron-poor unsaturated groups, are suitable dienophiles to react with a diene to perform the DA reaction.

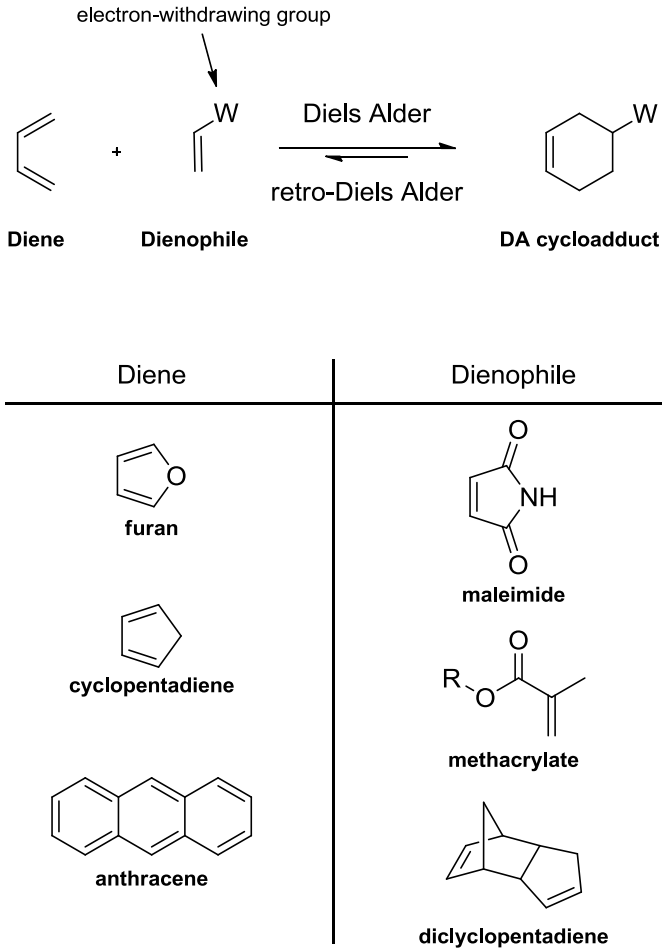


Figure 16: General mechanism of Diels Alder/retro-Diels Alder reactions of dienophile and diene

As illustrated in Figure 16, several pairs composed of dienes and dienophiles can be used in the DA reactions. However, thermally reversible cross-linked polymers based on the DA reaction between furan and maleimide groups are the most studied examples in the topic. A maleimide group contain an unsaturated C=C bond with two electron-withdrawing C=O groups. The C=O groups make the C=C group more electron-insufficient and more reactive toward diene groups in DA reactions. As a result, the maleimide group, as a dienophile, shows a relatively high reactivity in DA reactions. Thermally reversible cross-linked polymers based on the DA reaction between furan and maleimide groups are the most studied examples in the topic.

Three synthetic strategies can be employed for the synthesis of polymer networks (Figure 17) namely (1) direct DA cyclo-addition reactions involving multifunctional monomers, i.e. a di- or tri-furan derivative and a bis-maleimide, (2) DA cyclo-addition of linear polymers bearing

pendent furan and/or maleimide and (3) a cross-linker or an initiator containing a Diels–Alder linkage in the polymerization.

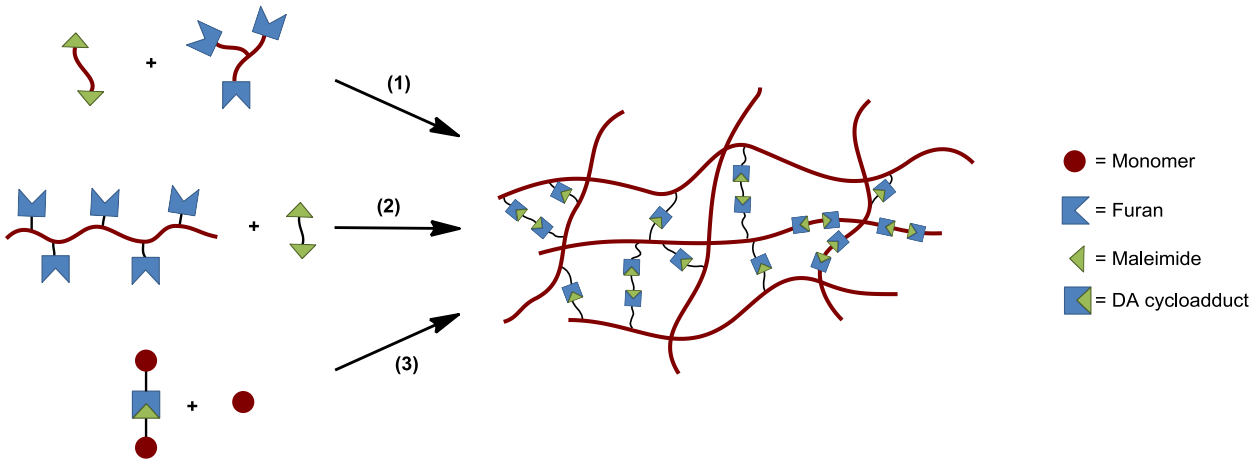


Figure 17: General strategies for the synthesis of polymer network *via* DA cyclo-addition reactions

For the first strategy, Wudl and co-workers[50] reported the synthesis of a highly cross-linked polymer network formed *via* the DA cyclo-addition reaction of a multi-diene (four furan-functionalized monomer) and multi-dienophile (tri maleimide-functionalized monomer). Thermal reversibility of this network has been demonstrated by the retro-DA reaction. Indeed, the DA cyclo-adducts could perform a retro-DA reaction at about 150 °C for 15 min to demonstrate a 30% debonding extent. The disconnected furan and maleimide moieties have enough mobility to heal the cracks of the sample through network reconnection. Since then, a wide variety of mendable materials have been synthesized employing the same diene-dienophile pairing in an effort to improve the rate of the DA and retro-DA reactions, decrease the retro-DA temperature, and increase the applications for this type of self-healing material.

For the second strategy, Wei and co-workers[51–53] have investigated the preparation of thermoresponsive hydrogels based on the aqueous Diels–Alder reaction of various polymer backbone bearing pendent furfuryl groups and bis-maleimide supported on PEO. Using the same method, the preparation of reversibly cross-linked polyurethane were studied by Du Prez and co-workers.[54] In these cases, one of the reacting groups of the DA reaction has been attached to polymer chains.

For the last strategy, a cross-linker or an initiator containing a Diels–Alder linkage can be synthesized by a series of reactions involving DA, retro-DA cyclo-addition and esterification.

The thermally labile cross-linker or initiator was successfully converted to polymer networks *via* different polymerization methods.[55,56]

In addition to the thermally induced [4+2] cyclo-addition DA reaction, some other groups like cinnamoyl groups could undergo photo-induced [2+2] cyclo-addition reaction. The first example of a cross-linked polymer able to heal itself in the presence of light was described by Chung *et al.*[57] The authors exploited the reversible dimerization of cinnamoyl groups under irradiation resulting in the formation of cyclobutane cycles (Figure 18). Thus, like the self-healing polymer based on DA cyclo-adducts, cinnamoyl containing polymers could exhibit self-healing properties through crack-induced bond disconnection and photo-induced bond regeneration.

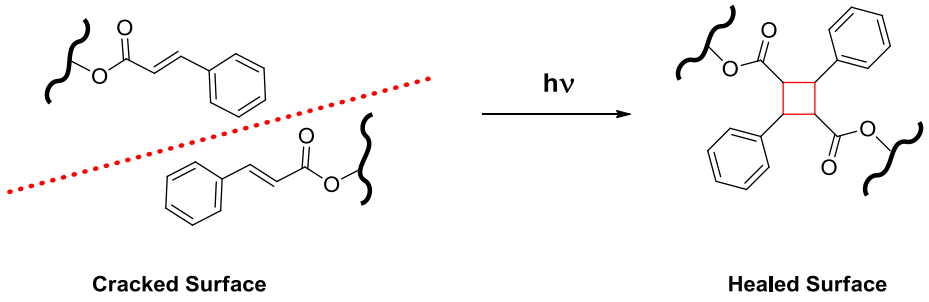


Figure 18: A cinnamoyl functionalized self-healing polymer[57]

In the field of polycarbonates, Hu *et al.*[58] designed and synthesized a cinnamoyl-functionalized cyclic carbonate monomer, the 5-methyl-5-cinnamoyloxy-methyl-1,3-dioxan-2-one. After subsequent polymerization and copolymerization with L-lactide, the UV irradiation-induced photo-crosslinking of the pendent cinnamate moiety was investigated. However, no evidence of the network decross-linking has been shown.

Compared to the thermally induced DA reaction systems, the photo-induced mending process could be completed in a short period of time (about 10 min) combined with high recovery efficiency.

Besides cinnamate, other moieties are capable of undergoing photo-reversible dimerization by UV irradiation (Figure 19). Saito and coll. have reviewed a large range of polymeric systems that employ photo-reversible dimerization reactions and their applications.[59]

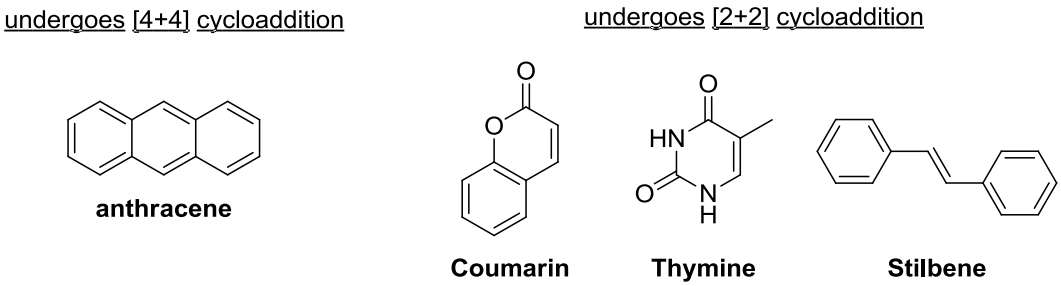


Figure 19: Example of moieties capable of undergoing photo-reversible dimerisation by UV irradiation

Very recently, Van Damme *et al.* synthesized reversible networks combining irreversible thiol-ene chemistry and photo-induced reversible [4+4] cyclo-addition reaction.[16] The authors demonstrated that all anthracene dimer-containing materials decomposed into anthracene functionalized building blocks above 160°C. Thermally dissociated anthracene dimer networks were then readily restored homogeneously to their original state by irradiation with UVA.

Herein, two strategies will be employed to prepare self-healing materials, that are summarized in Figure 20.

The first one is based on the Diels–Alder (DA) chemistry. Indeed thermo-reversible polycarbonate materials were synthesized using the second method described in the Figure 17, i.e. the reaction of furan functionalized polycarbonates with a bis-maleimide as cross-linker.

The second approach involves the reversible photo-induced [2+2] cyclo-addition reaction of cinnamate supported on the polycarbonate backbone.

In each case, thermo-mechanical properties of the polycarbonate networks will be discussed with respect to the cross-linking density.

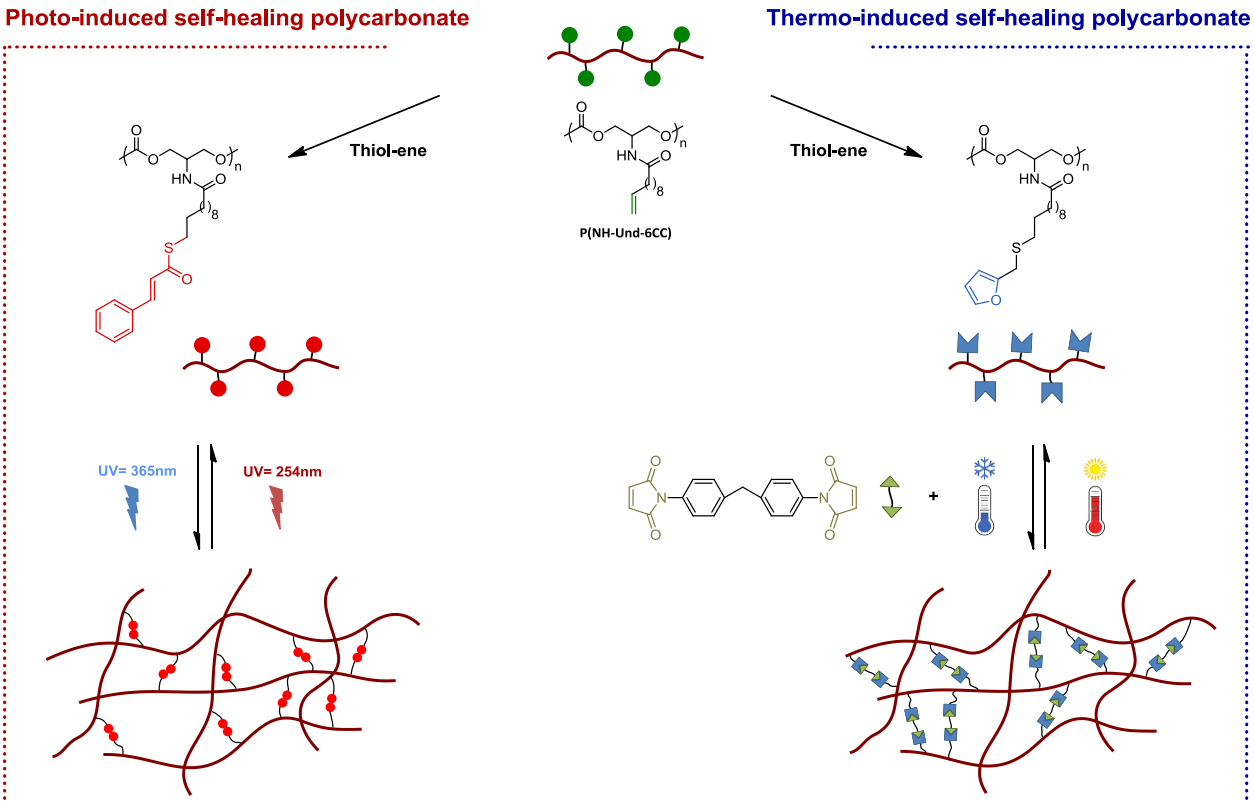


Figure 20: Strategies adopted (in chapter 4) for the synthesis of self-healing polycarbonate materials

2.2 Thermo-reversible cross-linking (Diels-Alder coupling)

Although numerous external stimuli to control the degree of cross-linking can be imagined, one of the most feasible stimuli is temperature also from the viewpoint of future industrial applications.

Therefore, the purpose of this investigation is to synthesize new, thermally reversible, polycarbonate networks *via* Diels-Alder and retro-Diels-Alder reactions. The general method is based on the synthesis of low T_g polymers containing pendent furan groups, followed by their Diels-Alder cross-linking with an appropriate bis-maleimide cross-linking agent.

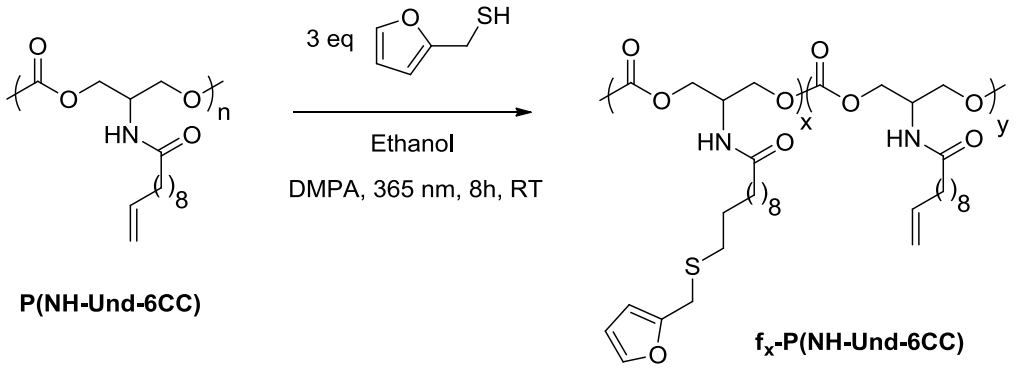
First, the grafting of pendent furan moieties will be detailed. Then the thermal reversibility of the cross-linking will be demonstrated. Finally, the influence of the cross-linking density on the polycarbonate properties will be studied.

2.2.1 Grafting of furan moieties on the polymer

As mentioned in the first part, Diels Alder chemistry allows the synthesis of thermo-responsive materials. Among several options, the functionalization of polymer chains with chemical groups (furan and maleimide) for DA reaction is a convenient approach for the preparation of cross-linked networks. In our case, we decided to post-functionalize P(**NH-Und-6CC**) since the synthesis and ROP of **NH-Und-6CC** were well-controlled in a multi-grams scale as detailed in chapter 3.

Therefore, the first task was the preparation of a furan-functionalized polycarbonate. Thanks to the available terminal unsaturation on each polymer unit, thiol-ene click chemistry appears to be the easiest way to graft a desired functionality to the polymer chain.

Therefore, the thiol-ene reaction between P(**NH-Und-6CC**) and the commercially available furfuryl mercaptan was performed at room temperature in ethanol at 2 mol.L^{-1} during 8 hours under UV irradiation (365 nm) (Scheme 1). DMPA was used as radical initiator. The mixture was irradiated through an optical fiber (365 nm) to improve the conversion and decrease the reaction time. Additionally, 3 equivalents of furfurl mercaptan with respect to C=C double bond were added for the same reasons. The polymer was recovered by precipitation in cold methanol.



Scheme 1: Experimental procedure for the preparation of furan-functionalized P(NH-Und-6CC)

The thiol-ene reaction was followed by ^{1}H NMR spectroscopy for 8h (Figure 21). The disappearance of the typical signals of the external double bond (5.0 and 5.8 ppm) and the appearance of the proton in alpha position of the sulphur atom (towards the polymer chain) enable the monitoring of the reaction. The signal at 2.25 ppm (integrated for 2) of the protons in alpha position of carbonyl from the urethane group was taken as an internal reference.

The furan content in the copolymer was determined from the integration ratio of the peak at 2.25 and 2.50 ppm. The first signal (at 2.25 ppm) arises from CH_2 protons on alpha position to the carbonyl group belonging to both functionalized and non-functionalized units. The signal at 2.50 ppm corresponds to CH_2 protons on alpha position to the sulphur atom only belonging to furan-functionalized units.

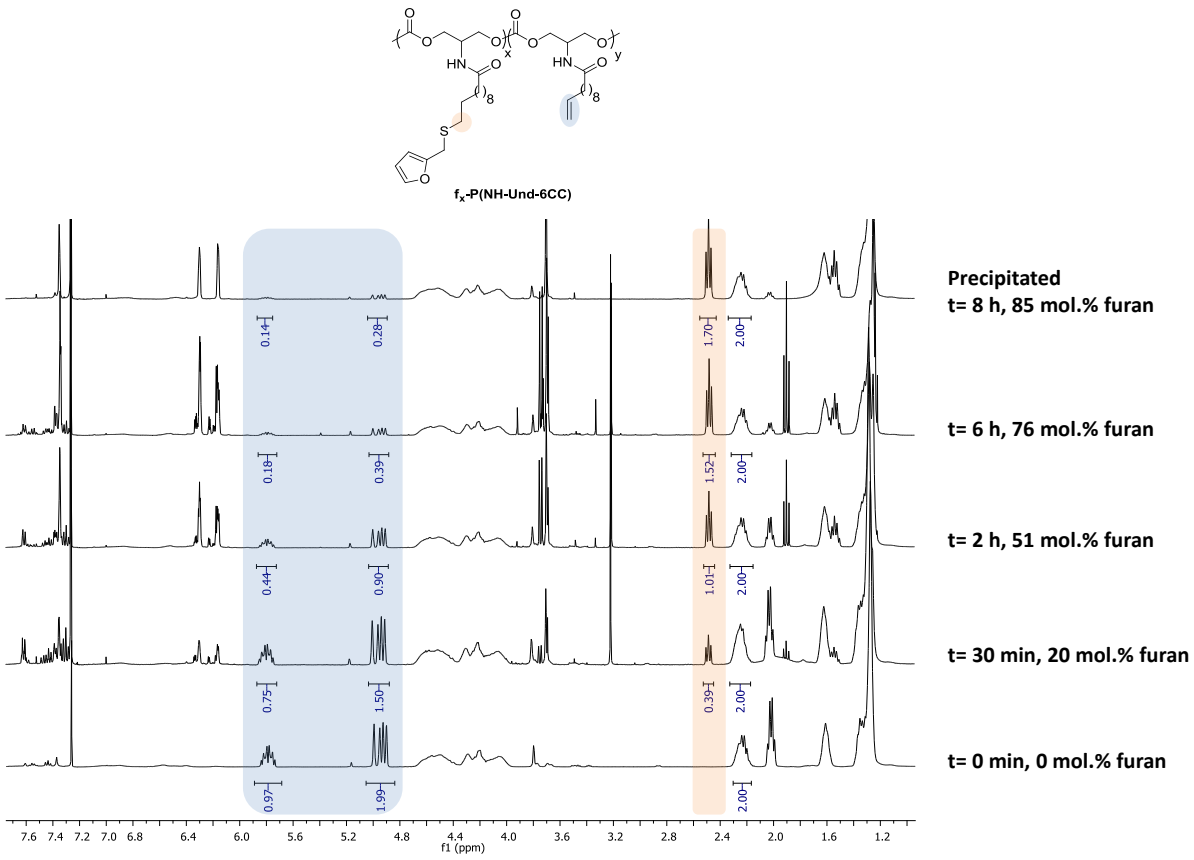


Figure 21: Stacked ^{1}H NMR spectra monitoring the reaction of furfuryl mercaptan with P(NH-Und-6CC)

The evolution of both the furan and the double bond content in the polycarbonate was plotted as a function of time (see Figure 22). The polymer displayed a moderate reactivity towards furfuryl mercaptan since only 85 mol.% of furan was grafted on the polycarbonate backbone after 8 hours. This result indicates that the amount of furan grafted on the polycarbonate can easily be adjusted by varying the reaction time. In addition, we assume that the higher the furan content, the higher the cross-linking density. Thus, this control of the furan content is interesting to investigate the influence of the cross-linking density on the network properties.

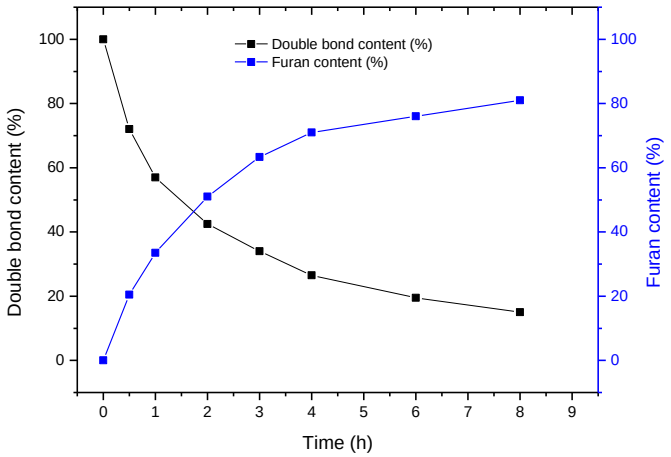


Figure 22: Kinetic profile of the P(NH-Und-6CC) functionalization by furan rings.

The resulting 85 mol.% furan-functionalized polycarbonate (f_{85}-P(**NH-Und-6CC**)) was characterized by ^{1}H NMR (See Figure 23). All peaks were assigned confirming the structure of the furan-functionalized polymer

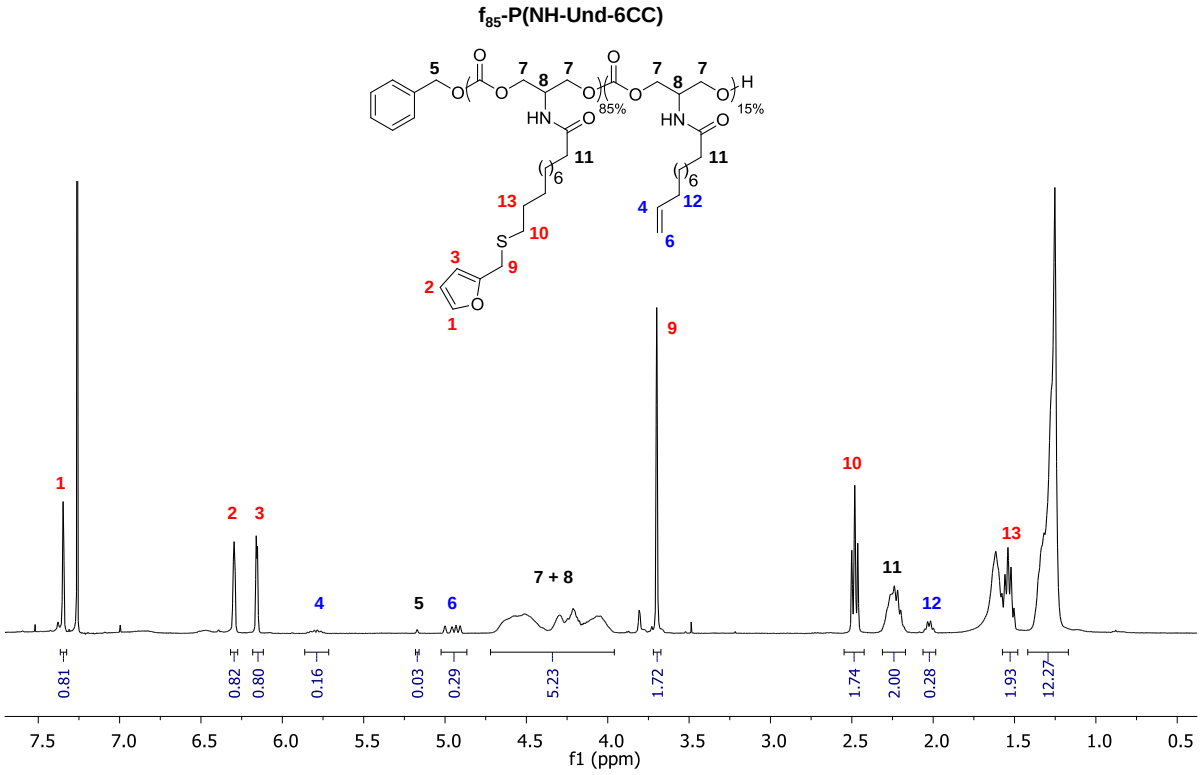


Figure 23: ^{1}H NMR of f_{85}-P(NH-Und-6CC) in $CDCl_3$

Using the kinetic study, various polycarbonates were synthesized with different targeted furan contents. Results are summarized in Table 4.

First, it is noteworthy that the furan content is in a good agreement with respect to the kinetic profile (Figure 22). Then it is observed that T_g of these polycarbonates (Table 4) ranges from 23.1 to -59.6 °C as a function of the furan content increase. Such a T_g decrease is explained by the flexibility introduced by the sulphur atoms to the polymer chains. In addition, the SEC traces (Figure 24) indicated that the polymer molar masses increase as the proportion of the furan content increases.

Table 4: Characteristics of f_x-P(NH-Und-6CC) with pendent furan moieties

Polymer	Reaction time (hours)	Furan content [a] (mol. %)	M_n [b] ($g.mol^{-1}$)	[Đ] [b]	T_g (°C) [c]
P(NH-Und-6CC)	0	0	5 700	1.07	23.1
f_{31}-P(NH-Und-6CC)	1	31	6 200	1.15	-6.6
f_{51}-P(NH-Und-6CC)	2	51	6 650	1.12	-13.5
f_{69}-P(NH-Und-6CC)	4	69	7 300	1.19	-49.0
f_{88}-P(NH-Und-6CC)	12	88	7 850	1.22	-59.6

[a]: Determined by ^{1}H NMR; [b]: Determined by SEC in THF (PS Std); [c]: Determined by DSC at 10°C.min^{-1} from the second cycle.

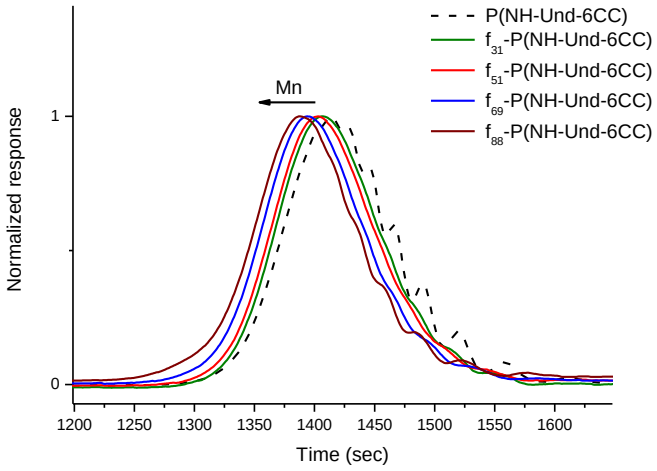
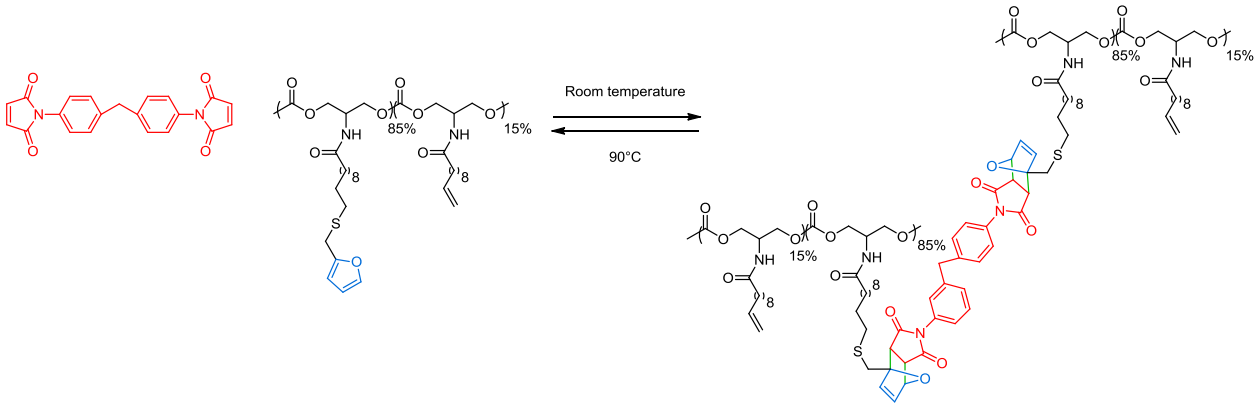


Figure 24: SEC traces of f_x-P(NH-Und-6CC) as a function of furan content

Therefore, several pendent furan-containing polycarbonates have been successfully synthesized. The reversible cross-linking will be now investigated thanks to the introduction of a bis-maleimide as cross-linking agent.

2.2.2 Reversible cross-linking and reprocessability

The present part is dedicated to demonstrate the thermal reversibility of the cross-linking reaction taking f_{85}-P(**NH-Und-6CC**) as starting furan-containing polymer. Scheme 2 summarizes the mechanism involved in the cross-linking reaction.



Scheme 2: Cross-linking reaction between f_{85}-P(NH-Und-6CC) and bis-maleimide

The cross-linked polycarbonate material was obtained as follows. The polymer f_{85}-P(**NH-Und-6CC**) was dissolved in chloroform ($CHCl_3$) at 1 $g.mL^{-1}$ in a vial. The bis-maleimide cross-linking agent was then added to the previous solution (0.5 equiv. with respect to furan groups) and the mixture was homogenized by vortex stirring until a clear yellow solution appears (the colour is due to the bis-maleimide molecule). The vial was then closed tightly and heated up to 60°C for 10 minutes.

The warm solution was poured in a Teflon mold and the chloroform was allowed to gently evaporate overnight at room temperature. A cross-linked film was obtained (Diels-Alder reaction) and was dried under reduced pressure for several hours to remove traces of chloroform.

Placed in chloroform, this cross-linked polycarbonate should be back in solution upon heating at 90°C for 10 min (retro-Diels-Alder reaction). Figure 25 shows the solubility of the polymer after heating at 90°C and the formation of an insoluble network when the solution is cooled down to

room temperature. These transformations can be done several times in a row without any decomposition of the polymer.

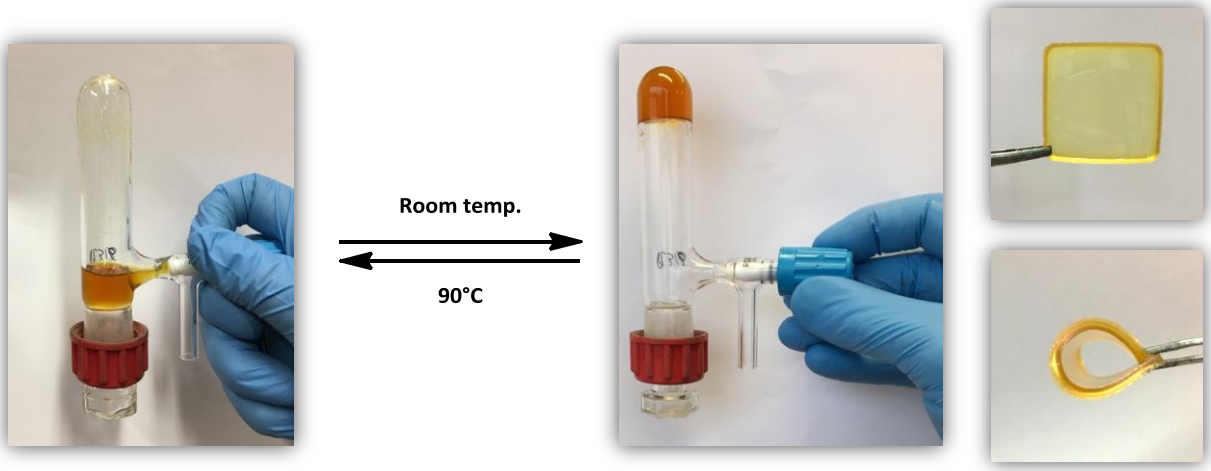


Figure 25: Thermo-reversible bio-based polycarbonate networks: from a soluble polymer (left picture) to an insoluble network (right pictures)

To demonstrate the reversibility of the cross-linking reaction, FT-IR analysis was performed (Figure 26). First, de-cross-linking of the material was followed by increasing the temperature (2°C/min) (Figure 26-(a)). The decreasing of the characteristic DA cyclo-adduct peak at 1190 cm^{-1} confirms the de-cross-linking reaction. However, no increase of characteristic furan peaks was observed.

Once the de-cross-linking of the material was achieved, the temperature was allowed to decrease slowly (2 °C/min). The re-cross-linking reaction was followed by transmission FT-IR (Figure 26-(b)). This time, a significant increase of the DA cyclo-adduct peak was observed at 1190 cm^{-1} highlighting the re-cross-linking reaction.

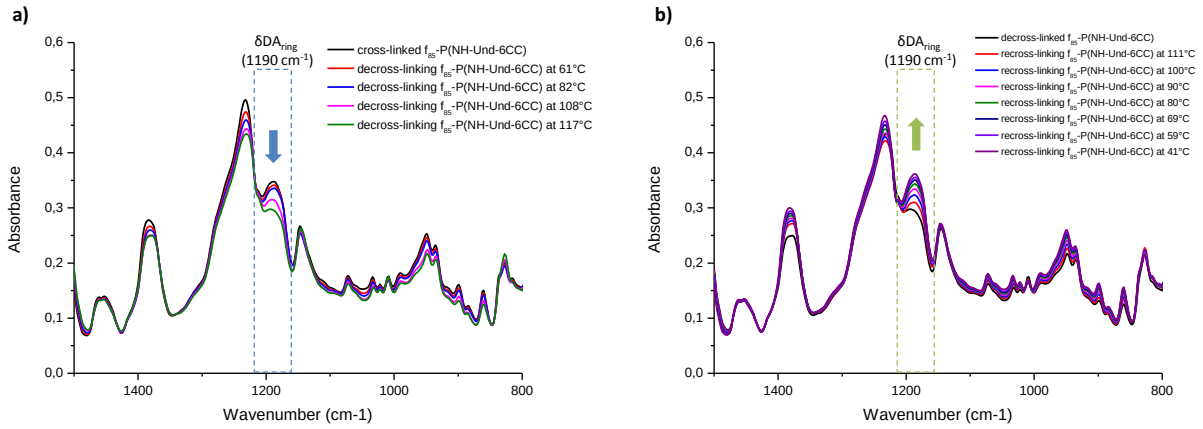


Figure 26: FT-IR traces following a) the de-cross-linking reaction upon heating and b) the cross-linking reaction upon cooling

Figure 27 shows stacked transmission FT-IR spectra of DA (de/re)-cross-linked furan-containing polycarbonate. Some characteristic furan peaks such as ν(COC) at 1013 cm^{-1} and δ(C-H for mono-substituted furan) at 710 cm^{-1}, decrease upon cross-linking and increase after de-cross-linking. The ν(COC) peak, for example, is clearly visible in the spectrum of f_{85}-P(**NH-Und-6CC**). Its magnitude decreases upon the addition of the bis-maleimide cross-linking agent (cross-linked f_{85}-P(**NH-Und-6CC**)). Directly after heating the sample at 120 °C, the magnitude of this peak increases again as the furan groups are decoupled (de-cross-linked f_{85}-P(**NH-Und-6CC**)). After the sample has been cooled down at room temperature, the peak disappears again (re-cross-linked f_{85}-P(**NH-Und-6CC**)). The reverse phenomenon is observed with the cyclo-adduct peak δ(DA cycloadduct) at 1190 cm^{-1}.

Both observations prove cross-linking and decross-linking *via* a reversible DA reaction between the grafted furan groups and the added bis-maleimide cross-linking agents.

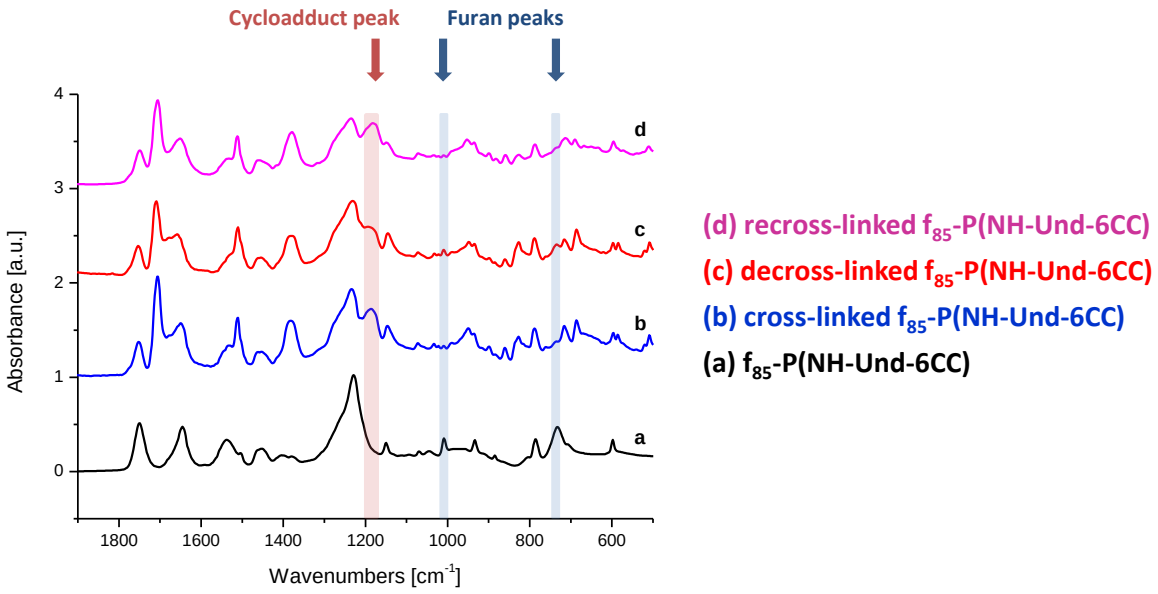


Figure 27: FT-IR absorption spectra of furan-containing polycarbonate and DA (de/re)-cross-linked furan-containing polycarbonate

In order to prove the reprocessability of the cross-linked material, the obtained film was cut in several pieces as illustrated in Figure 28. Theoretically, it should be possible to cut the used thermo-reversible cross-linked material, break the existing cross-links by increasing the temperature and re-mold the material into a new shape with the same properties.

These tests on the reprocessability were performed with f_{51}-P(**NH-Und-6CC**) as starting polymer.

Figure 28: Reprocessability of the cross-linked polycarbonate material

The temperature response of the material's mechanical behaviour was measured by Dynamic Mechanical Analysis (DMA) (Figure 29-(a)). The moduli of the samples were measured, while heating and cooling at a controlled rate (4°C/min) with an oscillation frequency of 1 Hz and a strain of 0.04%. Tensile tests at room temperature were also performed with a strain rate of 50 mm/min on 3 samples (Figure 29-(b)).

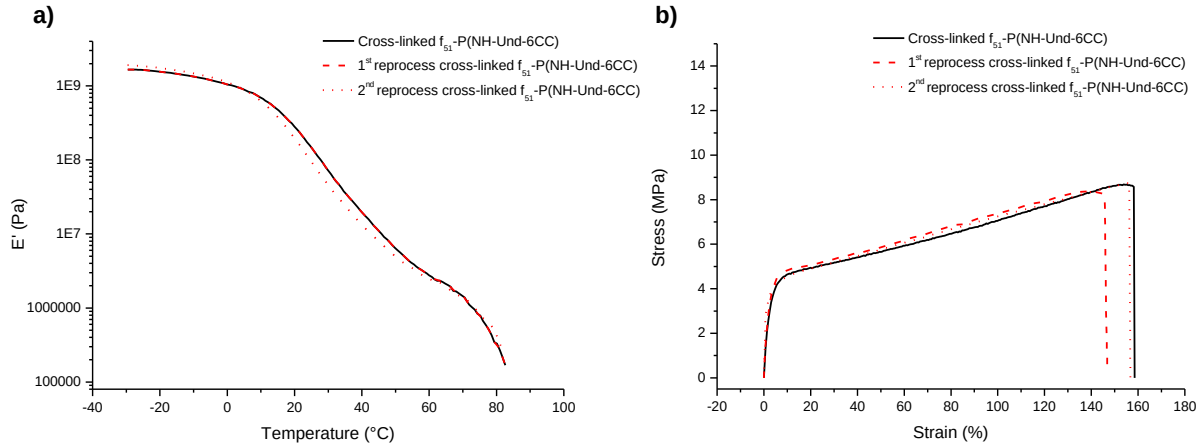


Figure 29: Reprocessability testing: a) DMA traces and b) Strain-Stress traces of f_{51}-P(NH-Und-6CC)

DMA traces show that DA cross-linked polycarbonate, before and after 2 reprocessing, display exactly the same mechanical behaviour upon heating (Figure 29-(a)). Indeed, the storage modulus (E′), which largely determines the elasticity of the rubber, follows the same trend before and after reprocessing. The cross-linked samples show high moduli (>1 000 MPa) before 0°C (glassy state) with only a modest decrease upon heating. A large glass transition is then observed from 0°C to 50°C associated by a significant decrease of E' upon heating. Although a very narrow elastic plateau (E'≈3 MPa) from 50°C to 70°C (rubbery state) is detected where the decrease of E' is less marked, a drastic loose of mechanical resistance appears after 70°C which implies the start of the retro-DA reaction (de-cross-linking of the material).

Following the same trend, tensile tests prove that the reprocessing of the polycarbonate materials does not affect its mechanical properties such as young modulus, elongation at break and strain at break (Figure 29).

Having demonstrated the thermo-reversibility of the DA cross-linking and the reprocessing ability of the so-formed cross-linked polycarbonates, the next part discusses the influence of the cross-linking density on the mechanical properties of these materials.

2.2.3 Tuneable network properties

In this part, we aim at investigating the influence of several parameters on the thermo-mechanical properties of the networks. For this purpose, the cross-linking procedure exposed in Scheme 2 was applied to all the polycarbonates with different furan contents, as shown in Table 5, to obtain in each case a high yield of cross-linked product. The thermo-mechanical properties of the DA cross-linked polycarbonates are summarized in Table 5.

Table 5: Thermo-mechanical properties of DA cross-linked polycarbonate materials

			Performed at RT	Performed at 65°C				
Furan content[a]	**$T_{d(5\%)}$ f_x-network (°C)[b]**	**T_g f_x-network (°C)[b]**	**Young modulus (MPa)[c]**	**Young modulus (MPa)[d]**	**Max stress (MPa)[d]**	**Elongation at break (%)[d]**	**Gel content (%)**	**Swelling ratio (%)**
88%	108	4.6	31	5.3	1.7	70	96.5	238
69%	107	6.8	43	3.9	1.5	79	93.7	296
51%	110	13.4	90	2.7	1.3	98	96	318
31%	112	10.2	230	0.85	0.8	170	71	765

[a] Calculated with ^1H NMR. [b] Measured by TGA analysis. [b] Measured by DSC analysis. [c] Calculated with tensile tests at RT. [d] Calculated with tensile tests at 65°C.

Table 5 shows that DA cross-linked polycarbonates are not very thermally stable. Indeed, the decomposition of the networks starts at around 110°C which is just after the retro-DA reaction temperature. Such feature is a limitation for these materials. Table 5 also indicates that T_g of the different cross-linked polycarbonates range from 4.6°C to 13.4°C. These values are not folloing a trend with respect to the furan content grafted on the P(**NH-Und-6CC**). Indeed, the highest furan content network (i.e. 88 mol.%) which potentially have the highest cross-linking density, exhibits

a T_g of 4.6°C while the network prepared from the linear precursor only containing 31 mol.% of furan moieties displays a higher T_g of 10.2°C. At a first glance, this result seems to be not logical but taking into account that the T_g of the polymer f_{88}-P(**NH-Und-6CC**) is -59.8°C and those of f_{31}-P(**NH-Und-6CC**), -6,6°C, the difference between the T_g of the network and the T_g of the linear precursor is much more significant for high furan content samples.

Nevertheless, due to these different T_g values, the mechanical properties of the networks evaluated at room temperature will be influenced by the state of the material (rubbery or glassy) and not only by the cross-linking density.

Thus, mechanical properties were tested at 65°C where all cross-linked polymers are in a rubbery state. Tensile tests were performed on the various cross-linked samples (Figure 30-(a)). The tensile strength, the Young's modulus and the elongation at break were determined from these tensile tests and averaged over four measurements (Figure 30-(b)). These values are also reported in Table 5. Figure 30 shows that high furan-containing materials exhibit significantly higher tensile modulus and lower elongation at break values compared to those containing lower furan moieties. This is typical as high tensile moduli and low elongation values are indicative of material with high cross-linking densities. Consequently, the cross-linking density increases as a function of the pendent furan content in the former polycarbonate.

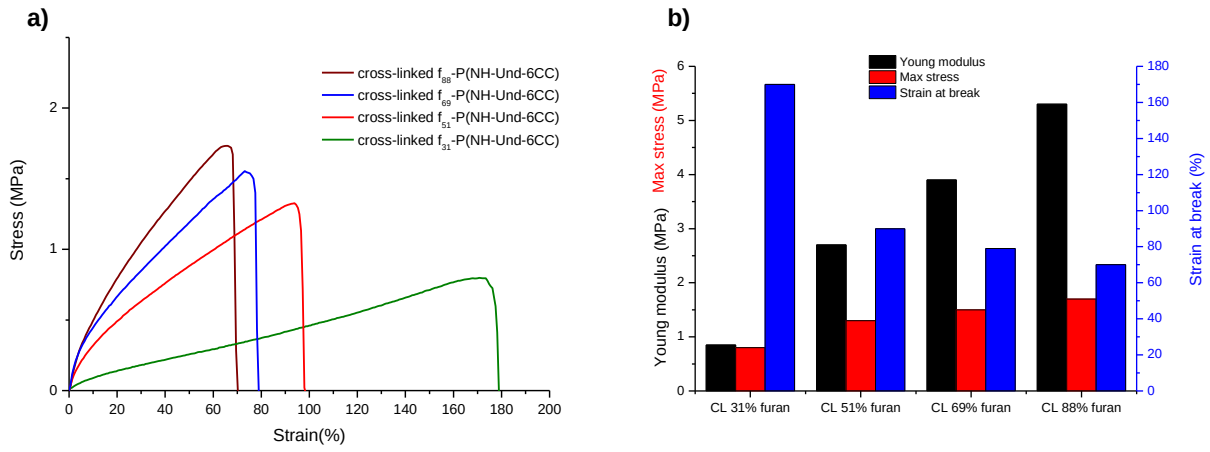


Figure 30: a) Tensile tests performed at 65°C for various polycarbonate materials and b) the corresponding Young's modulus, max stress, and strain at break

In addition, the mechanical behaviour with temperature of the cross-linked polycarbonates was measured by DMA (Figure 31). The test was performed under the same conditions than mentioned previously.

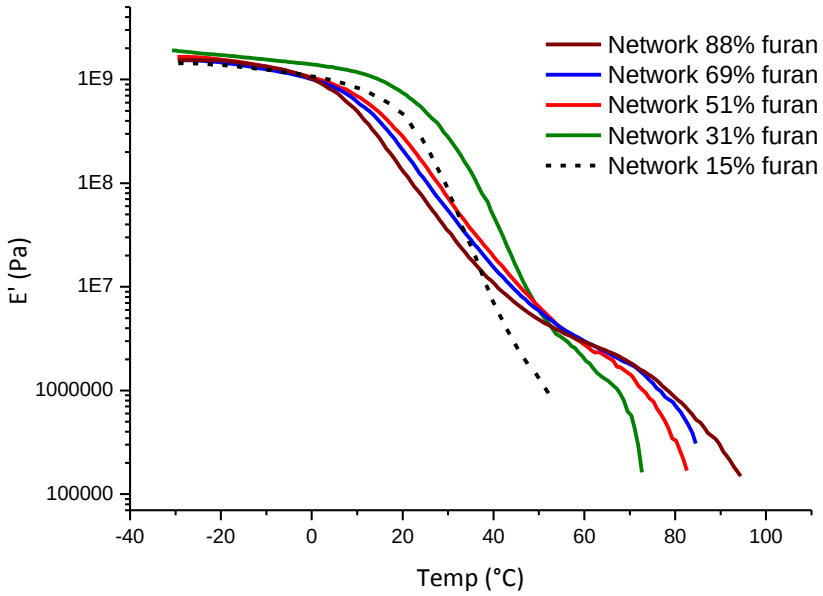


Figure 31: DMA traces for cross-linked polycarbonates samples

Figure 31 confirms the results obtained by DSC i.e. the T_α slightly decreases with the increase of cross-linking density. Additionally, the cross-linking density influences also the retro DA reaction. Indeed, DMA traces show that the higher the cross-linking density, the later the retro-DA reaction. The slope of the curve corresponding to the rDA is also less steep meaning that the rDA reaction is slower.

Gel content and swelling ratio of the cross-linked materials provide information about the cross-linking density. A high gel content combined with a low swelling ratio indicates that the material is highly cross-linked.

Gel content and swelling ratio were determined under the same conditions than the ones previously detailed (Equation 1 and Equation 2). The gel contents and the equilibrium swelling ratios values of the networks are given in Table 5. The effect of the pendent furan content on the polymer can be clearly seen. The resulting polycarbonate networks had greatly increased gel

contents and decreased swelling ratios with increasing pendent furan rings content. Indeed, the gel content of the network increases from 71% to 96.5% for 31 mol.% and 88 mol.% of pendent furan content respectively. Simultaneously, the swelling ratio of the network decreased from 765% to 238% with the above-mentioned pendent furan content. As expected, the cross-linking density is thus higher when high furan content is grafted on P(**NH-Und-6CC**).

To conclude on this part, several furan-containing polycarbonates were synthesized *via* the thiol-ene reaction between P(**NH-Und-6CC**) and furfuryl mercaptan. The content of pendent furan rings grafted on the polymer structure can be tuned by monitoring the reaction time. Such furan-functionalized polycarbonates were then cross-linked thanks to the Diels-Alder reaction with a bis-maleimide as cross-linking agent. The reversibility of the cross-linking reaction was proved by FT-IR analyses. Moreover, cross-linked polycarbonate materials have been reprocessed twice without altering their mechanical properties. Finally, the thermo-reversible DA reaction affords the preparation of reversible cross-linked polycarbonate materials with tuneable properties as a function of the pendent furan content grafted on the polycarbonate backbone.

However, the poor thermal stability of the furan-functionalized cross-linked polycarbonates represents a hindrance for further applications. In order to free the cross-linking method from temperature, another stimulus was used, i.e. UV irradiation, as it is discussed in the next part.

2.3 Photo-reversible networks ([2+2] cycloaddition of cinnamoyl moieties)

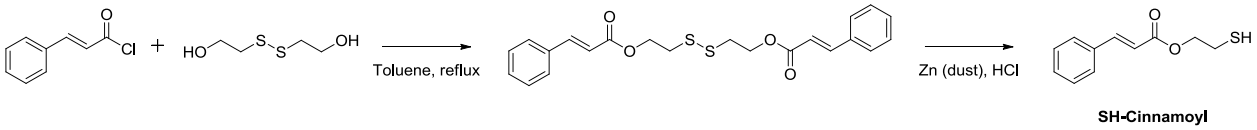
The above-mentioned strategy exploited the Diels-Alder reaction as a thermally mediated reversible cross-linking reaction towards self-healing material. Such reaction paved the way for the investigation of other types of reversible cyclo-additions for the design of self-healing polymers. In particular, dimerization consisting of photochemically allowed [2+2] or [4+4] cyclo-additions naturally appeared especially promising. Such cyclo-addition leads to a cyclobutane dimer which combines thermal stability[60,61] and photosensitivity.[62] Moreover, photo-responsive polymers have attracted much attention due to their responses upon application of light.[63,64]

In this context, this part is devoted to the design of photo-reversible polycarbonate materials.

2.3.1 Synthesis and grafting of the thio-cinnamoyl moiety to the polymer

Among photosensitive moieties, the photo-reactive cinnamoyl group dimerization, occurring through the [2+2] photochemical cyclo-addition reaction, was implemented for polymerization reactions and for cross-linking purposes.[58] Using the photo-sensitive cinnamoyl group, the reversibility of the cross-linking was, for instance, nicely exploited for the synthesis of self-healing polymers[57,65,66] and tuneable shape-memory materials.[67]

In a similar manner to the synthesis of thermo-reversible polycarbonate networks, the post-functionalization of P(**NH-Und-6CC**) was selected in this study as a strategy for the design of photo-reversible polycarbonate networks.



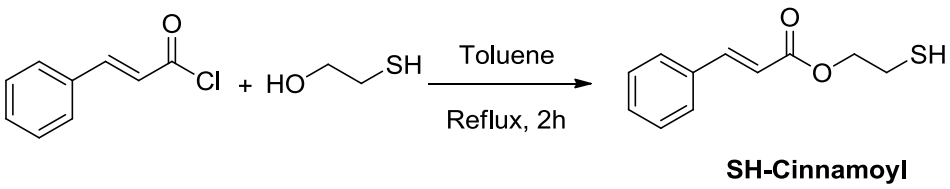
Scheme 3: First synthetic method for the synthesis of the thio-cinnamate derivative

Therefore, the first step of this work is the synthesis of cinnamoyl moieties which would be able to be grafted on P(**NH-Und-6CC**). Again, the thiol-ene reaction between the terminal unsaturation of P(**NH-Und-6CC**) and a thio-cinnamate derivative appears to be the most suitable option. Indeed, the easy and fast click-reaction combined with the fact that the cinnamoyl content grafted on the polymer is controllable by monitoring the reaction time are advantages.

Consequently, a thio-cinnamate derivative was synthesized. Two synthetic routes have been investigated. The first one, developed by Hartman and Rose,[68] involves the coupling of cinnamic acid chloride with hydroxyethyl disulfide to give a disulphide (Scheme 3). Subsequent reduction of the latter compound by treatment with zinc/HCl yields the corresponding thiol **SH-Cinnamoyl**.

This easy route enables the synthesis of cinnamate containing disulphide in a large scale (20 g). However, the reduction of the disulphide by Zinc failed several times. The quality of the dust or the poor activation process is a potential explanation.

This unsatisfying result led us to a second synthetic route, which is the direct reaction of cinnamic acid chloride with the 2-mercaptoethanol (Scheme 4).



Scheme 4: Second synthetic method for the synthesis of the thio-cinnamate derivative

This reaction was performed in stoichiometric conditions with complete conversion and very high yield (95%). No multi purification steps were necessary.

The structure of **SH-Cinnamoyl** was confirmed by ^{1}H, ^{13}C and 2D NMR analysis (Figure 32 and Figure 34). Cinnamoyl aromatic protons appeared between 7.3 and 7.6 ppm whereas cinnamoyl alkene protons were shown at 6.5 and 7.7 ppm. Methylene protons in alpha postion of the carbonyl shifted from 3.2 ppm (2-mercaptoethanol) to 4.3 ppm (attached to the cinnamoyl moieties). Few impurities were observed at 3.4, 4.4 and 6.8 ppm, which may come from the formation of the thioester as by-product.

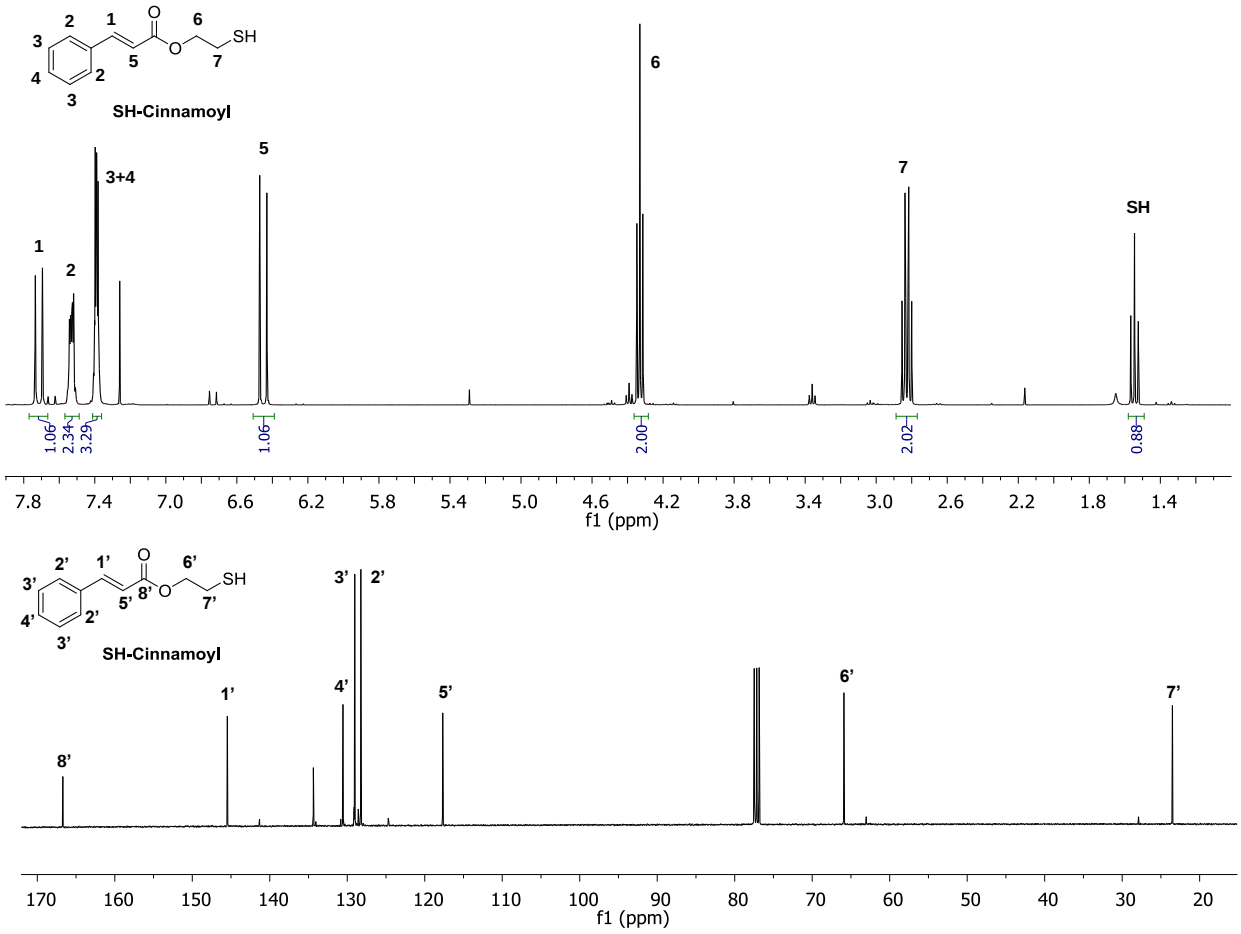


Figure 32: (Top) ^{1}H NMR spectra of SH-Cinnamoyl and (bottom) ^{13}C NMR spectra of SH-Cinnamoyl in $CDCl_3$

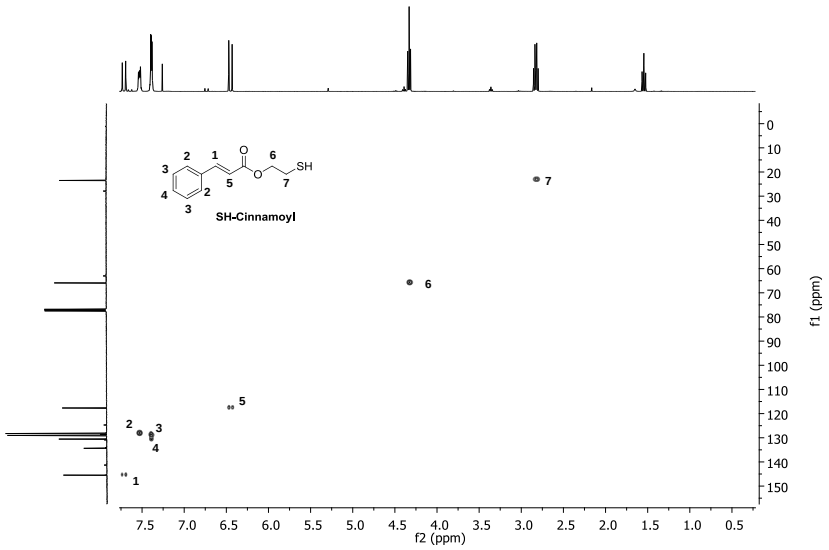


Figure 33: HSQC NMR spectrum of SH-Cinnamoyl in $CDCl_3$

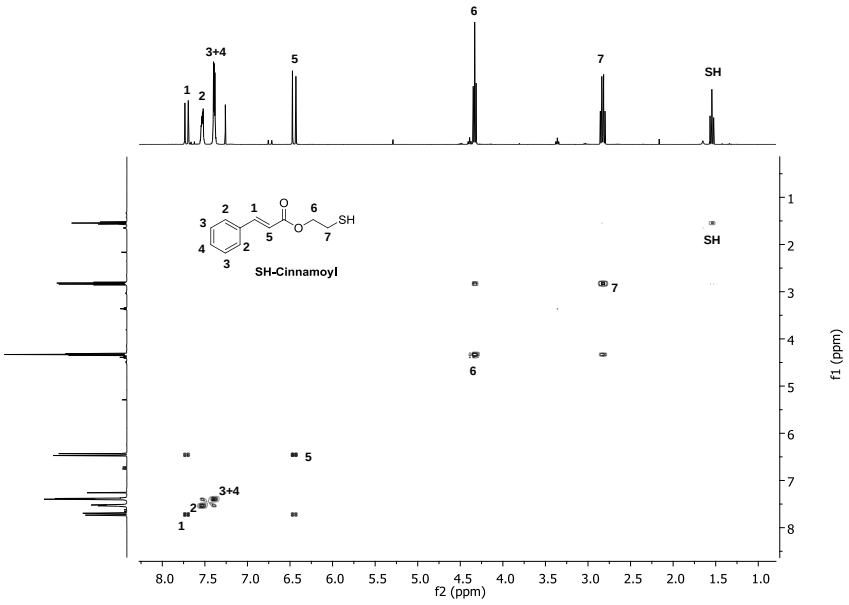
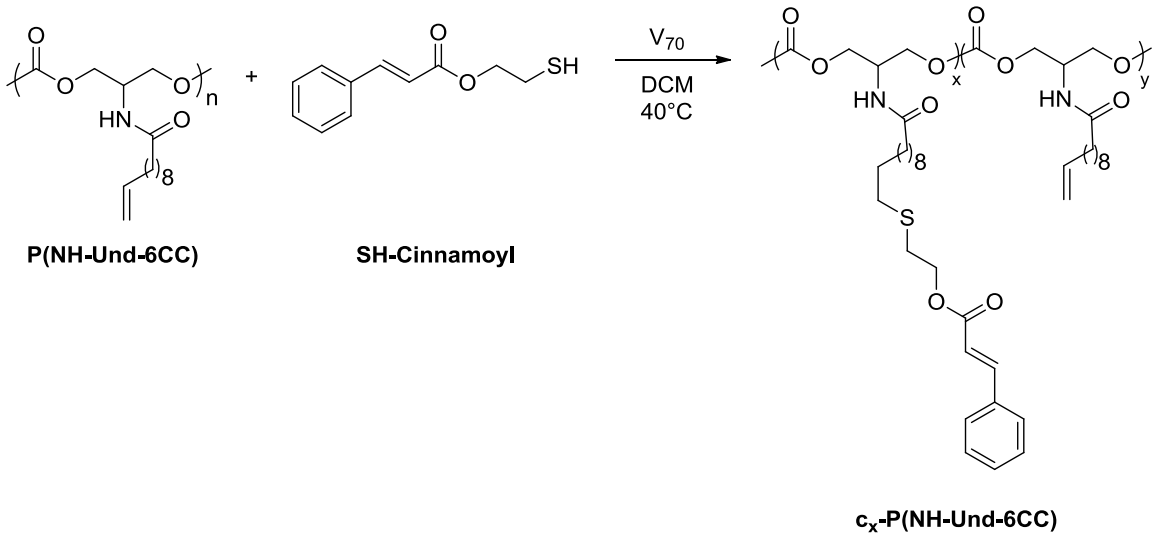


Figure 34: COSY NMR spectrum of SH-Cinnamoyl in $CDCl_3$

The next step towards the design of photo-responsive polycarbonate material is the grafting of **SH-Cinnamoyl** on P(**NH-Und-6CC**). As above-mentioned, the thiol-ene reaction was used to link these two entities. Nevertheless, since **SH-Cinnamoyl** is sensitive to UV irradiation, a radical initiator which decomposes thermally (V70), was used to initiate the thiol-ene reaction. The grafting reaction is illustrated Scheme 5. 3 equivalents of **SH-Cinnamoyl** were added and

the cinnamoyl content was controlled by the reaction time. After the grafting step, all obtained copolymers were purified by dialysis in methanol to remove unreacted **SH-Cinnamoyl**.



Scheme 5: Experimental procedure for the preparation of cinnamoyl-functionalized P(NH-Und-6CC)

Syntheses of polycarbonates bearing different amount of pendent cinnamoyl moieties were conducted. Cinnamoyl content was calculated with the Equation 3 involving the integration of characteristic signals of cinnamoyl units (H_{11}) and olefin units (H_7). The ^{1}H NMR spectrum of c_{30}-P(**NH-Und-6CC**) confirms the structure of the functional polycarbonate (Figure 35).

$$\%\ \boldsymbol{Cinnamoyl} = \frac{\int \boldsymbol{H_{11}}}{\int \boldsymbol{H_7} + \int \boldsymbol{H_{11}}}$$

Equation 3: Formula used for the calculation of cinnamoyl percentage grafted after the thiol-ene reaction using ^{1}H NMR integrations of characteristic protons (H_{11} and H_7) in $CDCl_3$

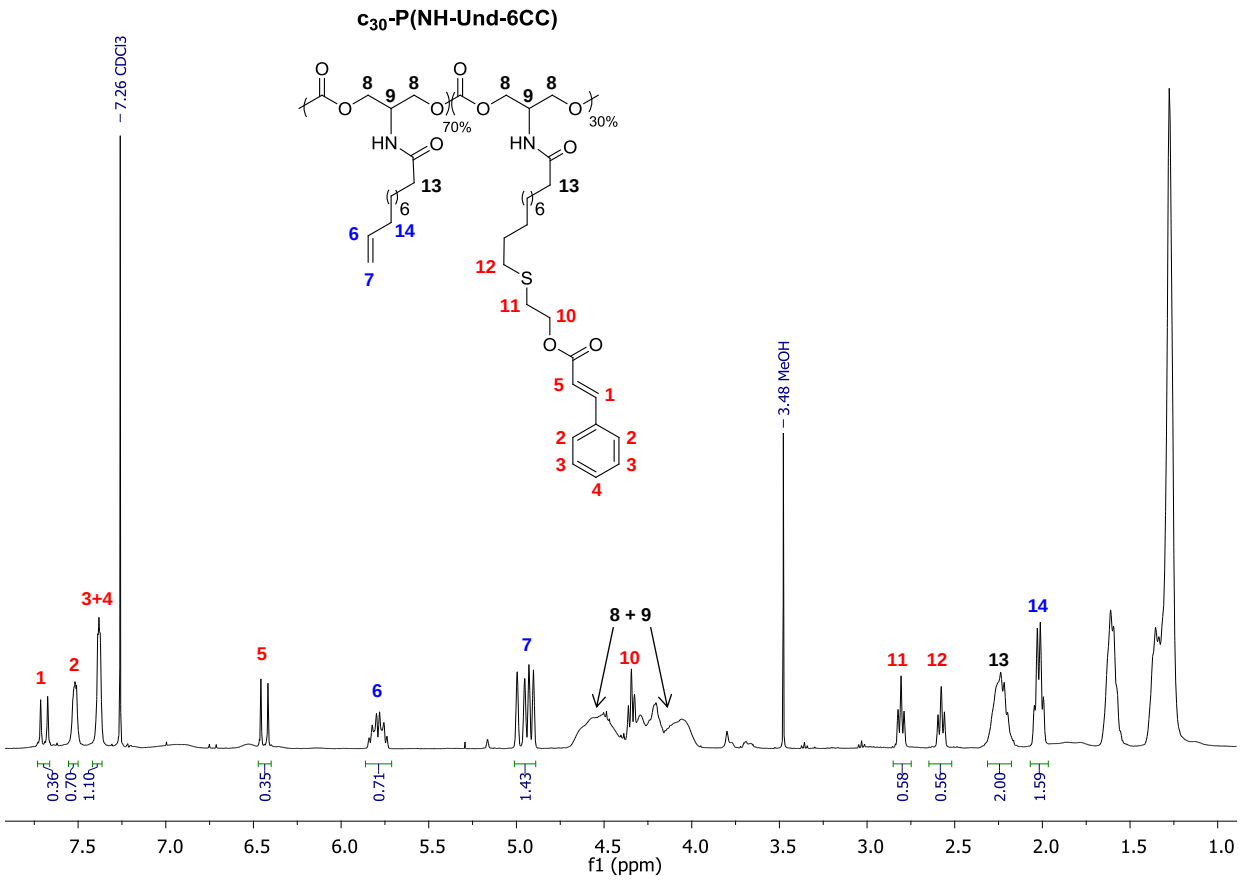


Figure 35: ^{1}H NMR spectrum of c_{30}-P(NH-Und-6CC) in $CDCl_3$

Some characteristics of the different so-formed functional polycarbonates are presented in Table 6 and their stacked ^{1}H NMR in $CDCl_3$ spectra are depicted in Figure 36.

Table 6: Characterization of P(NH-Und-6CC) with pendent cinnamoyl moieties

Polymer	Reaction time (min)	Cinnamoyl content [a] (mol. %)	M_n [b] (g.mol^{-1})	[Đ] [b]	T_g (°C) [c]
P(NH-Und-6CC)	0	0	5 700	1.07	23
c_{10}-P(NH-Und-6CC)	0.5	10	5 800	1.10	11
c_{30}-P(NH-Und-6CC)	2	30	5 900	1.18	5
c_{55}-P(NH-Und-6CC)	6	55	6 500	1.25	-1
c_{70}-P(NH-Und-6CC)	15	70	8 500	1.29	-12
c_{100}-P(NH-Und-6CC)	30	100	9 400	1.31	-20

[a]: Determined by ^{1}H NMR; [b]: Determined by SEC in THF (PS Std); [c]: Determined by DSC at 10°C.min^{-1} from the second cycle.

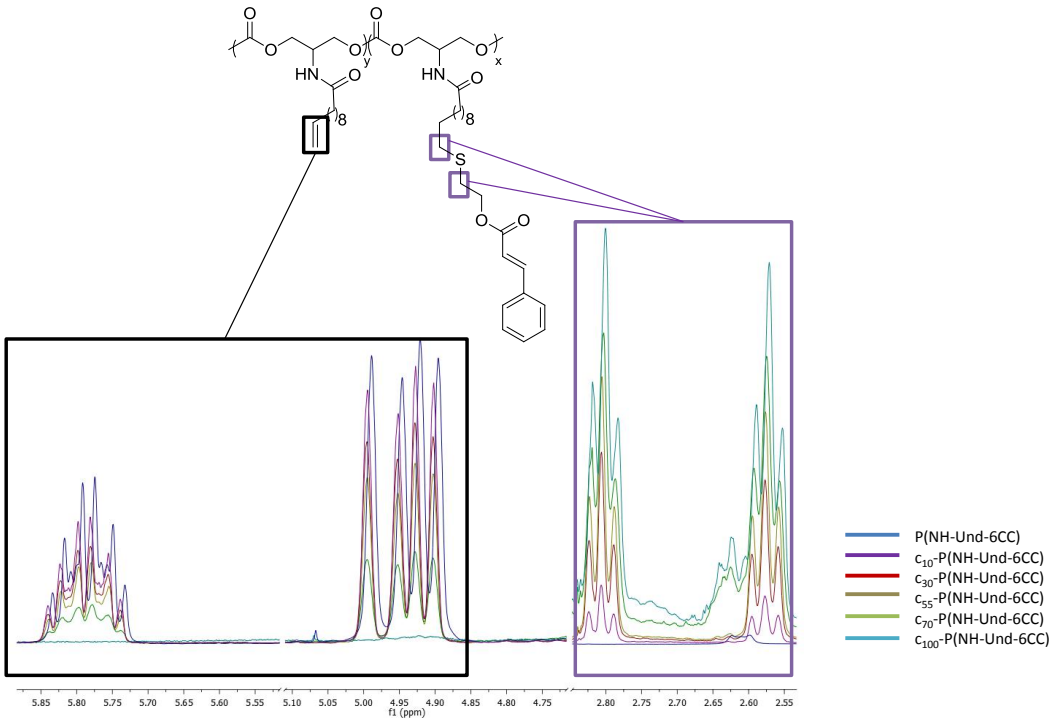


Figure 36: Stacked ^{1}H NMR monitoring the reaction between SH-Cinnamoyl and P(NH-Und-6CC) in $CDCl_3$

As expected, an increase of the polymer molar mass values associated to a decrease of the T_g are observed when a higher cinnamoyl content is grafted on the polymer side chains. Such phenomena are similar than those observed when furan groups were grafted to P(**NH-Und-6CC**). However, interestingly, contrary to all other amorphous polymers, a melting point at 0°C is observed for the fully cinnamoyl-functionalized polycarbonate (ESI Figure 5). The π-stacking of the pendent aromatic rings could be the reason of such chain arrangements.

2.3.2 Reversibility of the cross-linking

Polycarbonate networks can be obtained by UV cross-linking using the pendent cinnamate groups on the polymer chains. With UV light at λ = 365 nm, the cinnamate group switches from the trans to the cis conformation. When two cis cinnamate groups react together, they undergo a [2+2] cyclo-addition reaction leading to the formation of a cyclobutane ring (Figure 37). This reaction is used to cross-link all cinnamoyl-functionalized c_x-P(**NH-Und-6CC**).

Cross-linked polycarbonate materials were obtained as follows. The polymer c_{55}-P(**NH-Und-6CC**) was dissolved in chloroform ($CHCl_3$) at 1 $g.mL^{-1}$ in a vial and transferred into a Teflon mold. After evaporation of the solvent, the films were exposed to UV light at a distance of 9 cm from the UV lamp, wavelength λ = 365 nm, for 12 h on each side to ensure uniform curing, thus leading to the formation of a network structure.

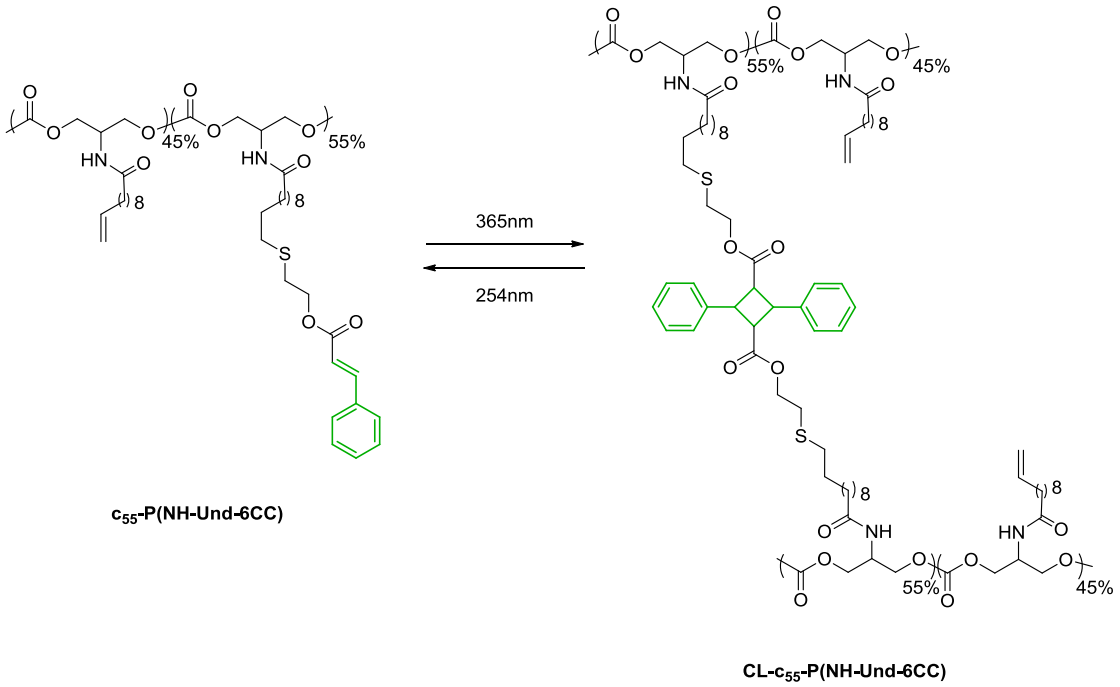


Figure 37: Photo-reversible cross-linking of c_{55}-P(NH-Und-6CC)

The curing kinetics were studied using UV−vis spectrophotometry by monitoring the absorption maximum at 280 nm, which relates to the double bonds adjacent to carbonyl group of the cinnamate functionality (Figure 38-(a)). As seen in the UV−vis spectrum, a decrease in intensity of the peaks at 280 nm was observed within 6 h, meaning that almost 100% of the cinnamate groups have undergone the [2+2] cyclo-addition reaction.

The fast initial absorbance decrease is characteristic of the polymer cross-linking through irradiation because the concentration of cinnamate groups is higher in the initial stages. As the cross-linking increases, concentration and mobility of the chains decreases leading to a plateau. For the cyclo-addition to occur, two cinnamate groups must be in close proximity to each other. This is the reason why polymers bearing photosensitive groups show a higher photo-reactivity in solution than in a solid-state coated film.[69] Consequently, in our case, the cross-linking reaction

was performed within 6h in solution whereas it takes 24h in a solid-state. Besides, the efficiency of the dimerization reaction of pendent cinnamoyl groups decreases when the chain length increases due to a lower mobility.[70]

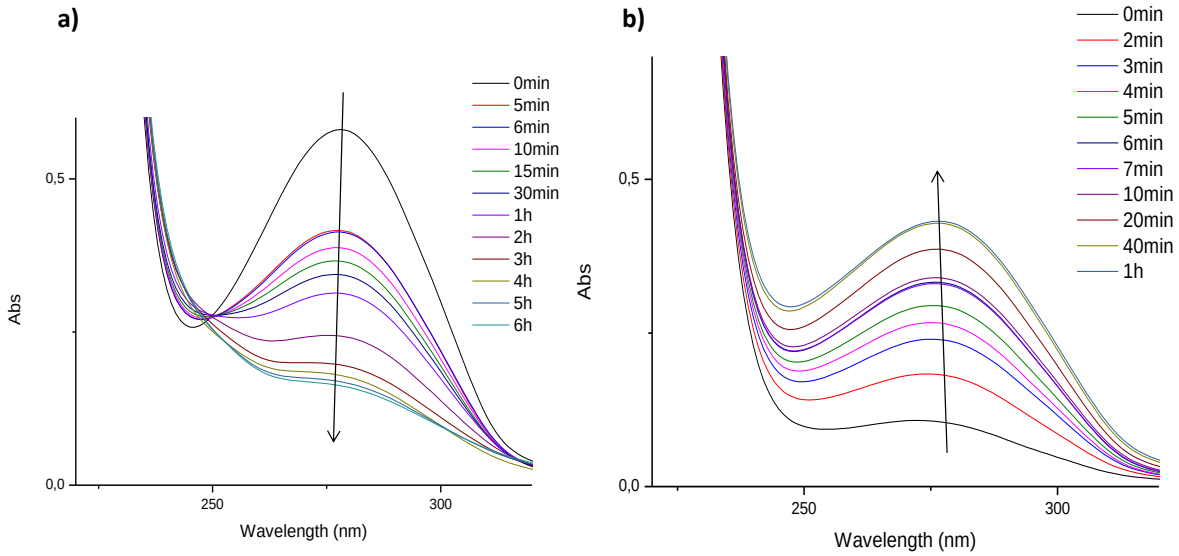


Figure 38: a) Cross-linking kinetic under 365 nm and b) de-cross-linking kinetic under 254 nm in solution (DCM)

Subsequently, upon exposing the cross-linked polycarbonate to 254 nm light irradiation, the de-cross-linking of the polycarbonate material occurs. This phenomenon was followed by monitoring the maximum absorbance increase at 280 nm (Figure 38-(b)). The decross-linking reaction is relatively fast but the absorbance doesn't reach its former value before cross-linking. Thus, the decross-linking is not complete probably due to the poor power of the UV lamp. Nevertheless, Figure 38 demonstrates the reversible feature of the photo-mediated cross-linked polycarbonate.

Since the reversibility of the photo-cross-linking has been proven, the influence of the cross-linking density on the thermo-mechanical properties of the polycarbonate networks was investigated.

2.3.3 Tuneable properties with respect to the cross-linking density

All functional polycarbonates presented in Table 6 bearing different contents of pendent cinnamoyl moieties were cross-linked by the [2+2] photochemical cyclo-addition of cinnamoyl units to form solid films.

Thermal and mechanical characterizations of such cross-linked films were investigated by differential scanning calorimetry (DSC), thermogravimetry (TGA) and dynamic mechanical analysis (DMA). All results are summarized in Table 7. Non-functionalized P(**NH-Und-6CC**) does not exhibit mechanical properties and do not undergo cross-linking under irradiation due to the absence of photo-responsive groups in its structure.

Table 7: Thermo-mechanical properties of photo-cross-linked cinnamoyl containing polycarbonates

Cinnamoyl functionality[a]	T_g network (°C)[b]	Young modulus (MPa)[c]	Elongation at break (%)[c]	Max stress (MPa)[c]	Gel content (%)	Swelling ratio (%)
100%	17	1266	3	35	94.0	57.1
70%	24	622	6	29	99.8	48.4
55%	13	110	15	6	84.5	62.1
30%	11	39	49	2.4	63.6	153
10%	8	1.3	156	0.5	6.4	69.0

[a]:Calculated from ^{1}H NMR; [b]: Determined by DSC at 10°C.min^{-1} from the second cycle.; [c]:Calculated from tensile tests

To evaluate the network cross-linking density, swelling tests have been performed. The same procedure than the one used for testing swelling properties of previous networks was used. It can be noted from Table 7 that very low gel content (6.4%) was observed when only 10 mol.% of cinnamoyl units were grafted to P(**NH-Und-6CC**). The poor photoreactivity in a solid-state coated film explains this low gel content. However, the gel content increases significantly when the pendent cinammoyl content increases in the polymer to almost reach 100%. At the same time, the swelling ratio decreases when the cross-linking increases. This feature shows that the cross-linking density can be controlled by adjusting the polycarbonate cinnamoyl content.

Such cross-linked materials demonstrated slight increase in T_g with an increase of cross-linking density (Table 7). It is due to a decrease of the chain mobility related to numerous cross-linking points. The temperature stability also increases slightly with the cross-linking density.

More interestingly, mechanical properties of the networks strongly depend on the cross-linking density. Indeed, CL-c_{10}-P(**NH-Und-6CC**) and CL-c_{30}-P(**NH-Und-6CC**) are transparent and flexible materials at room temperature as shown in Figure 39. However, when high cinnamoyl content was used, the polymer chains became more rigid. Consequently, the fully functionalized cross-linked polymer was very brittle.

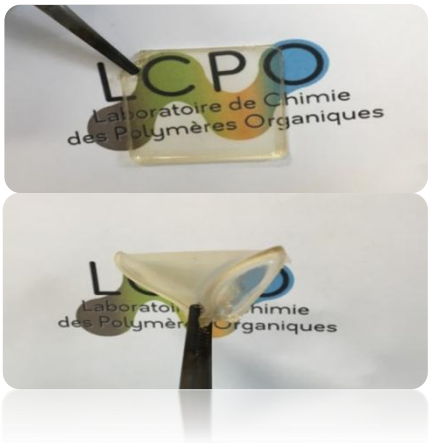


Figure 39: Pictures of flexible CL-c_{30}-P(NH-Und-6CC)

This observation was confirmed by tensile tests and DMA analyses. Tensile tests at room temperature were performed with a strain rate of 50 mm/min on 3 samples. The representative stress−strain curves of the networks are shown in Figure 40.

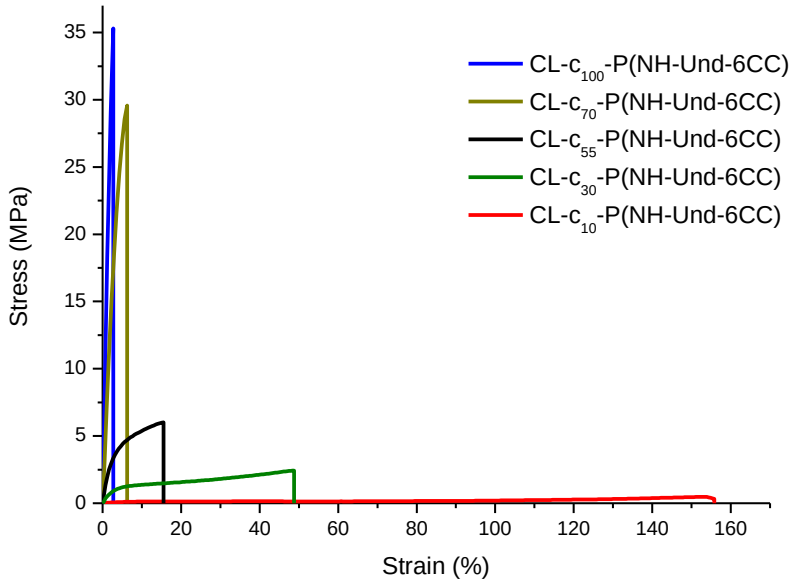


Figure 40: Stress−strain curves at room temperature of the polycarbonate networks prepared with the [2+2] photochemical cyclo-addition of pendent cinnamoyl units

The influence of the cross-linking density on the polycarbonate mechanical properties can be clearly seen. The poorly cross-linked CL-c_{10}-P(**NH-Und-6CC**) displays very low Young modulus calculated from the initial slope of the stress−strain curve (1.3 MPa) while the highly cross-linked CL-c_{100}-P(**NH-Und-6CC**) exhibits a Young modulus 1 000 times higher. In between these values, the higher the cross-linking density, the higher the Young modulus. Max stress at break values follow the same trend. However, the elongation at break of poorly cross-linked polycarbonate materials is 50 times higher than the most densely cross-linked ones. Therefore, the mechanical properties of the networks are significantly affected by the cinnamoyl content grafted on P(**NH-Und-6CC**).

DMA analyses were also performed on the polycarbonate materials (Figure 41). The moduli of the samples were measured, while heating and cooling at a controlled rate (4°C/min) with an oscillation frequency of 1 Hz, and a strain of 0.03%.

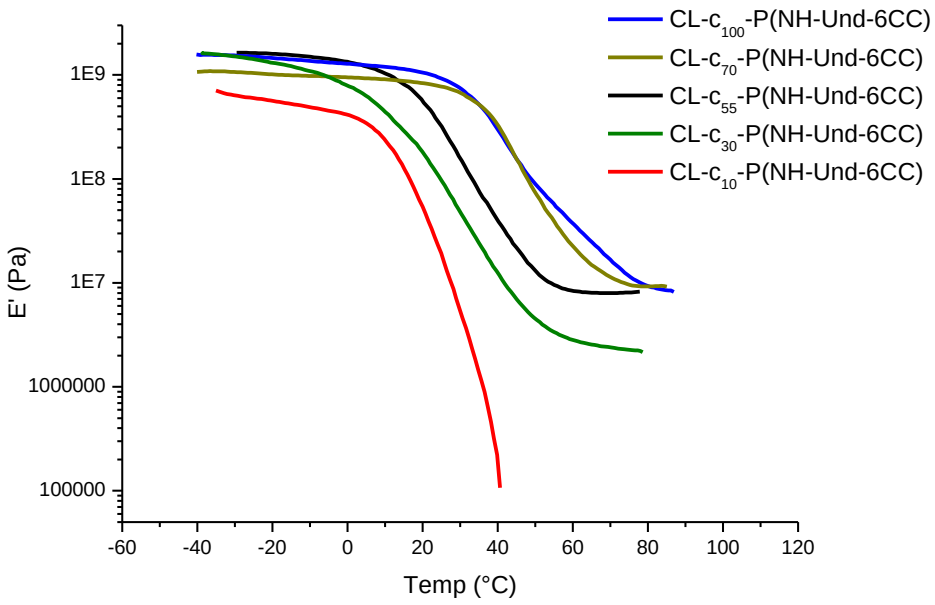


Figure 41: Thermomechanical experiments showing the tensile storage modulus (E′) measured using DMA at an oscillation frequency of 1 Hz

As indicated in Figure 41, the poorly cross-linked CL-c_{10}-P(**NH-Und-6CC**) is not mechanically stable after 40°C. However, all other cross-linked polycarbonate materials display an elastic plateau (E' remains constant while the temperature is increasing). The elastic modulus (E′) measured after T_g by DMA exhibited an increase up to 9.5 MPa for the most highly cross-linked polycarbonate. Moreover, in agreement with the results obtained by DSC, we observe that the T_α increases with the increasing of the cross-linking density.

To conclude on this part, several cinnamoyl-containing polycarbonates were synthesized *via* the thiol-ene reaction between P(**NH-Und-6CC**) and a synthesized thio-functionalized cinnamoyl. Photo-reversible polycarbonate networks were prepared thanks to the photo-induced [2+2] cyclo-addition reaction between two cinnamoyl moieties. Among the advantages of this synthetic approach, is the use of the cinnamate functionality to control the cross-linking density *via* UV light without requiring any initiators or chemical cross-linkers that can remain in the final polymer. Although the degradation products of these bio-based polycarbonate networks are expected to be biocompatible, subsequent studies should focus on their biodegradation and biocompatibility.

Conclusion

In conclusion of this chapter, fatty-acid based aliphatic polycarbonates have been successfully cross-linked using several cross-linking methods, reversible or not.

First, thanks to preliminary studies, the thiol-ene coupling appeared to be the most suitable cross-linking method in terms of convenience and processability. As a consequence, this method was used to prepare polycarbonate materials in a larger scale with P(**NH-Und-6CC**) as starting polymer. In addition, the properties of the cross-linked polycarbonates were controllable ranging from tough to elastomeric materials.

In a second part, self-healed polycarbonate materials were synthesized. The reversibility of the cross-linking of such materials involves either temperature or UV irradiation as stimulus.

On the one hand, several pendent furan-containing polycarbonates have been successfully synthesized from P(**NH-Und-6CC**) and furfuryl mercaptan. Furan content grafted by thiol-ene coupling ranged from 31 to 88 mol.% and can be adjusted by varying the reaction time. The furan-functionalized polycarbonates were then cross-linked thanks to the Diels-Alder reaction with a bis-maleimide as cross-linking agent. The so-formed networks exhibit tuneable properties depending on the furan content on the functional polycarbonate and can be recycled at least 3 times without losing their mechanical properties

On the other hand, a photo-responsive cinnamate moieties have been grafted on P(**NH-Und-6CC**) in a control manner. Consequently, the photo-induced [2+2] cyclo-addition reaction between two cinnamate groups afforded the formation of photo-reversible polycarbonate networks. The reversibility has been proven by UV-Vis spectrophotometry.

Therefore, this chapter has demonstrated the possibility of synthesizing bio-based polycarbonate networks. Nonetheless, this study requires further investigations, especially in terms of polymer properties in order to find suitable applications where the numerous synthetic steps and the use of solvent would not be a limitation.

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Experimental methods and Appendices

Experimental Methods

1. Molecular synthesis:

1.1 Procedure for the synthesis of SH-Cinnamoyl

In a round-bottom flask equipped with magnetic stirrer, acid chloride of cinnamic acid (20 g, 120 mmol) was dissolved in toluene (300 mL). 2-mercaptoethanol (9.3 g, 120 mmol, 1 equiv.) was added and the mixture was stirred under reflux for 2 hours. The solvent was removed on rotary evaporator yielding to **SH-Cinnamoyl** as viscous liquid without further purification. Yield= 90%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.73 (d, 1H), 7.53 (m, 2H), 7.38 (m, 3H), 6.47 (d, 1H), 4.33 (t, 2H), 2.82 (q, 2H), 1.55 (t, SH).

2. Post-polymerization functionalization:

2.1 Procedure for the epoxidation of P(TMC-co-Und-6CC)

In a round-bottom flask equipped with magnetic stirrer, P(**TMC-*co*-Und-6CC**) containing 9.1 mol.% of Und-6CC units (0.1 g, 0.89 mmol) was solubilized in 5 mL of chloroform. M-CPBA (53.2 mg, 0.308, 4 equiv. to olefin groups) was added to the solution. The mixture was stirred under reflux for 12 hours. The acid form of m-CPBA was removed by filtration. The filtrate was washed twice with an aqueous solution of Na_2SO_3 (10 wt.%) and twice with $NaHCO_3$. 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. Viscous transparent oil was obtained after purification. Yield: 70%. ^{1}H NMR ($CDCl_3$, 400 MHz,) δ (ppm): 4.24 (t, 40H) 2.90 (m, 1H), 2.74 (m, 1H), 2.46 (m, 1H) , 2.05 (q, 18H), 1.35-1.31 (m, 14H).

2.2 General procedure for the synthesis of furan-functionalized fx-P(NH-Und-6CC)

In a round-bottom flask equipped with magnetic stirrer, P(**NH-Und-6CC**) (1 equiv.), furfuryl mercaptan (3 equiv.) and DMPA (1 mol.%) were dissolved in ethanol (2 $mol.L^{-1}$). The reaction was allowed to proceed at room temperature during the appropriate period of time under UV

irradiation through an optical fiber (365 nm). The solvent was removed to result in f_x-P(**NH-Und-6CC**) which was purified by precipitation in cold methanol (-63°C, mixture liquid nitrogen/chloroform). The functional polymer was obtained as waxy solid. Yield= 80-90% depending on the degree of functionalization.

2.3 General procedure for the synthesis of cinnamoyl-functionalized cx-P(NH-Und-6CC)

In a round-bottom flask equipped with magnetic stirrer, P(**NH-Und-6CC**) (1 equiv.), **SH-Cinnamoyl** (3 equiv.) and V70 (1 mol.%) were dissolved in DCM (1 mol.L^{-1}). The reaction was allowed to proceed at 40°C during the appropriate period of time. The solvent was removed to result in c_x-P(**NH-Und-6CC**) which was purified by dialysis in methanol (1L for 1g of polymer, 48h, and methanol was changed after 24h).

3. Cross-linking and decross-linking reactions:

3.1 General procedure for polycarbonates cross-linking by thiol-ene coupling

The polycarbonate (1 equiv.), the dithiol (0.8-0.1 equiv.) and **Irgacure 2959** (0.01 equiv.) were dissolved in 1mL of DCM and transferred to a Teflon mold. The solvent was gently evaporated overnight and residual DCM was removed under reduced pressure during 4h. The mixture was then irradiated under UV at 365 nm during 4 hours. The obtained cross-linked film was characterized by DSC, TGA, DMA and tensile tests.

3.2 General procedure for polycarbonates cross-linking by diels-alder reaction

The polymer f_x-P(**NH-Und-6CC**) was dissolved in chloroform ($CHCl_3$) at 1g.mL^{-1} in a vial. The bis-maleimide cross-linking agent was then added to the previous solution (0.5 equiv. with respect to furan groups) and the mixture was homogenized by vortex stirring until a clear yellow solution appeared. The vial was then closed tightly and heated up to 60°C for 10 minutes.

The warm solution was then poured in a Teflon mold, and the chloroform was allowed to gently evaporate overnight at room temperature. A cross-linked film CL-f_x-P(**NH-Und-6CC**) was

obtained and dried under reduced pressure for several hours to remove traces of chloroform. The obtained cross-linked film was characterized by DSC, TGA, DMA and tensile tests.

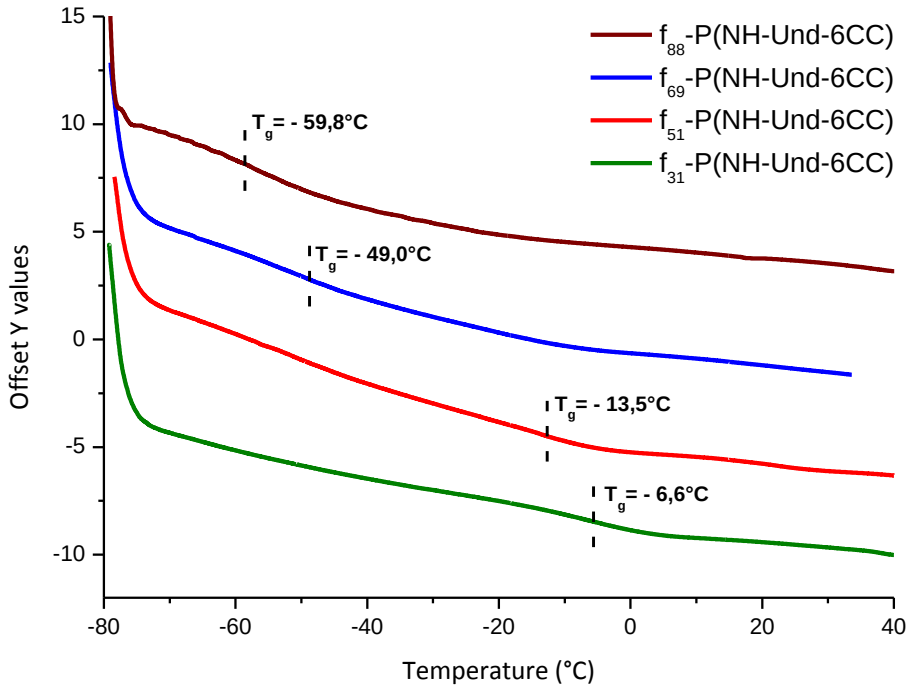
3.3 General procedure for polycarbonates decross-linking by retro-diels-alder reaction

Placed in chloroform, the cross-linked polycarbonate CL-f_x-P(**NH-Und-6CC**) was heating at 90°C for 10 min. The retro-DA reaction occurs and the polymer is dissolved in the chloroform. These transformations can be repeated several times without any decomposition of the polymer.

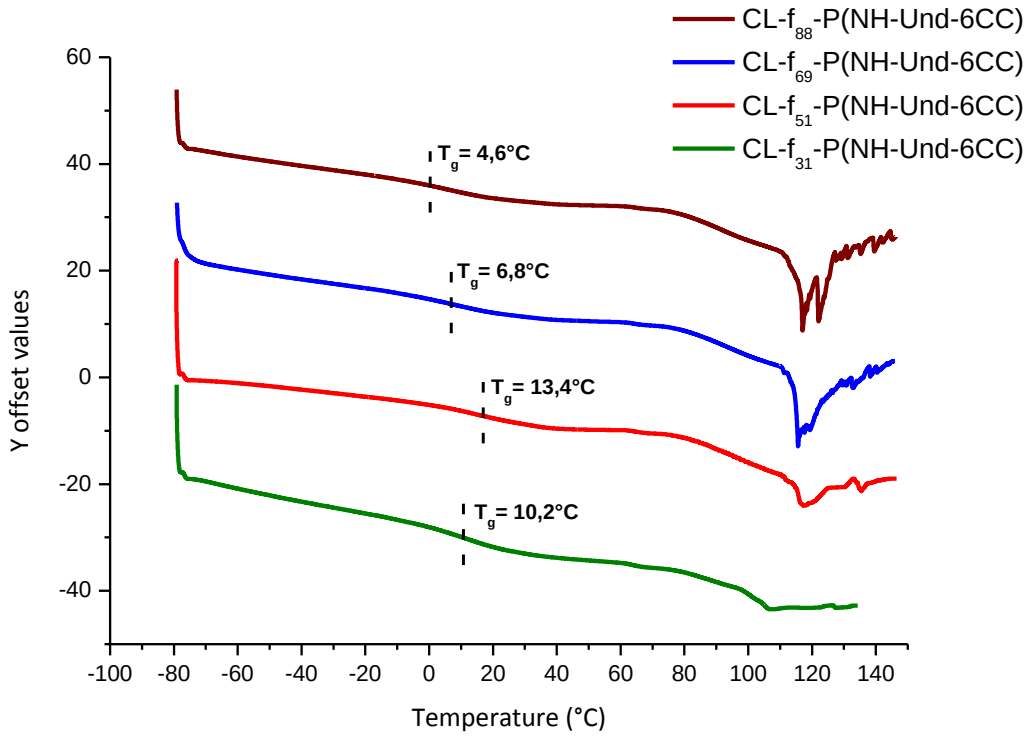
3.4 General procedure for polycarbonates cross-linking by [2+2] photochemical cycloaddition reaction

The polymer c_x-P(**NH-Und-6CC**) was dissolved in chloroform ($CHCl_3$) at 1g.mL^{-1} in a vial. After evaporation of the solvent, the films were exposed to UV light at a distance of 9 cm, wavelength λ = 365 nm, for 12 h on each side to form a network structure CL-c_x-P(**NH-Und-6CC**) and to ensure uniform curing.

Appendices

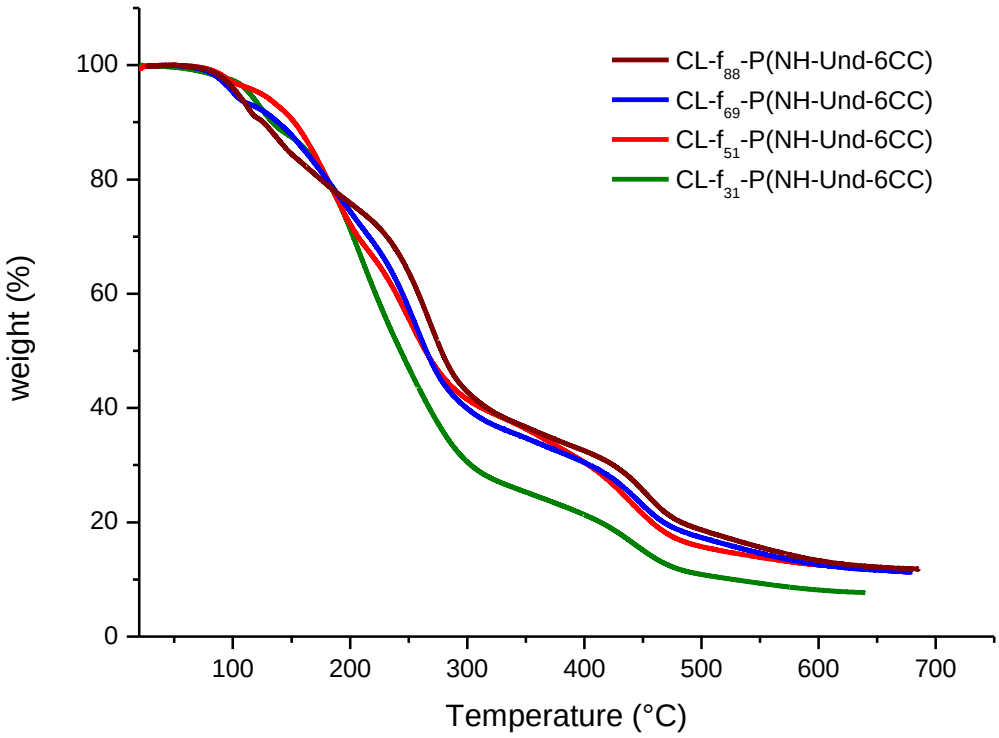


ESI Figure 1: DSC traces of furan-functionalized P(NH-Und-6CC)

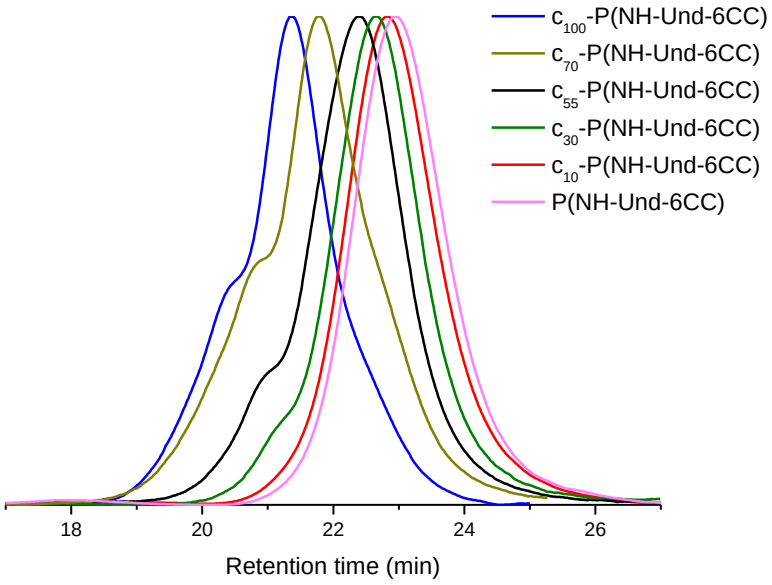


ESI Figure 2: DSC traces of cross-linked furan-functionalized P(NH-Und-6CC)

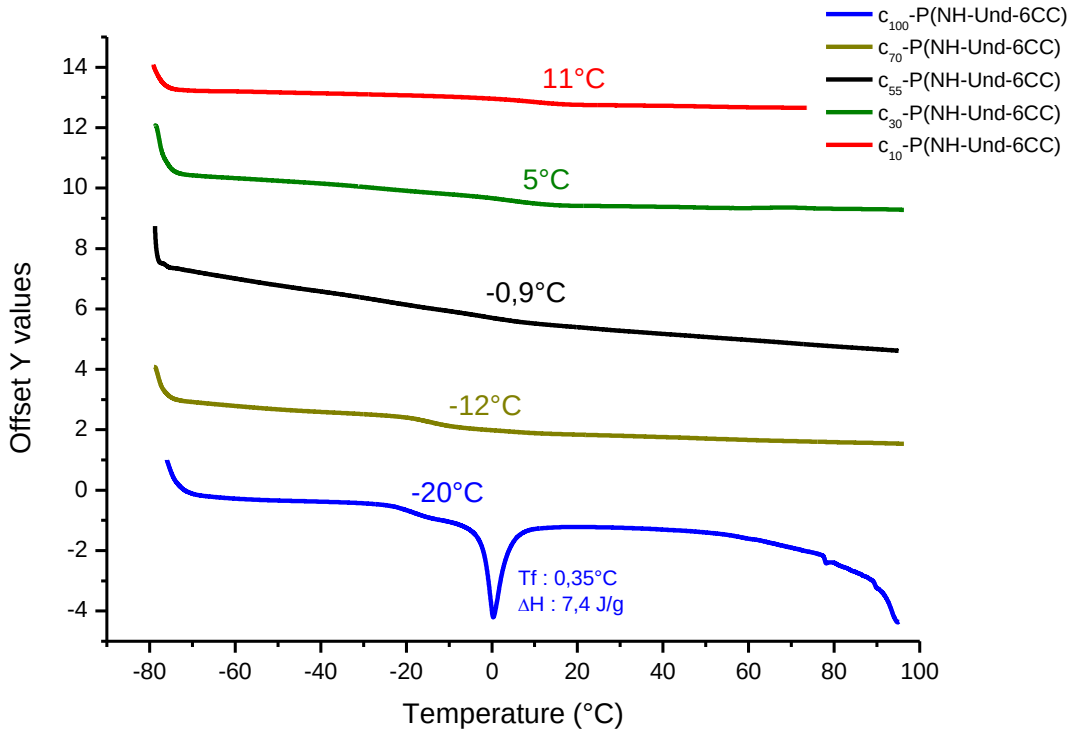
CONFIDENTIAL



ESI Figure 3: TGA traces of cross-linked furan-functionalized P(NH-Und-6CC)

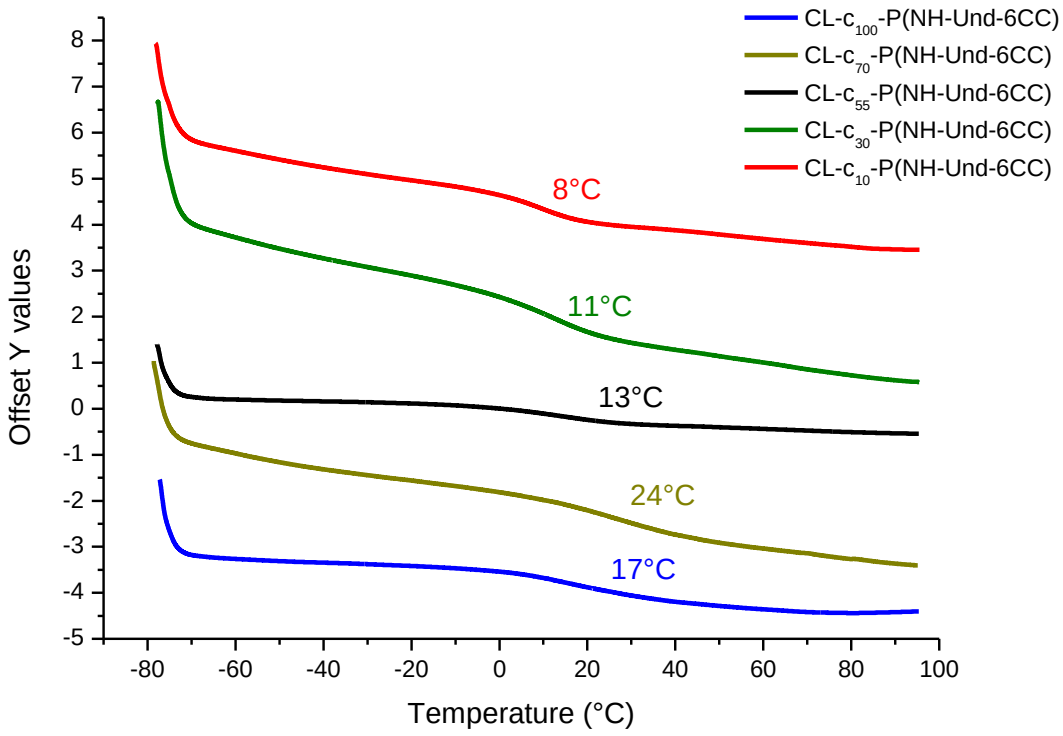


ESI Figure 4: SEC traces of cinnamoyl-functionalized P(NH-Und-6CC)

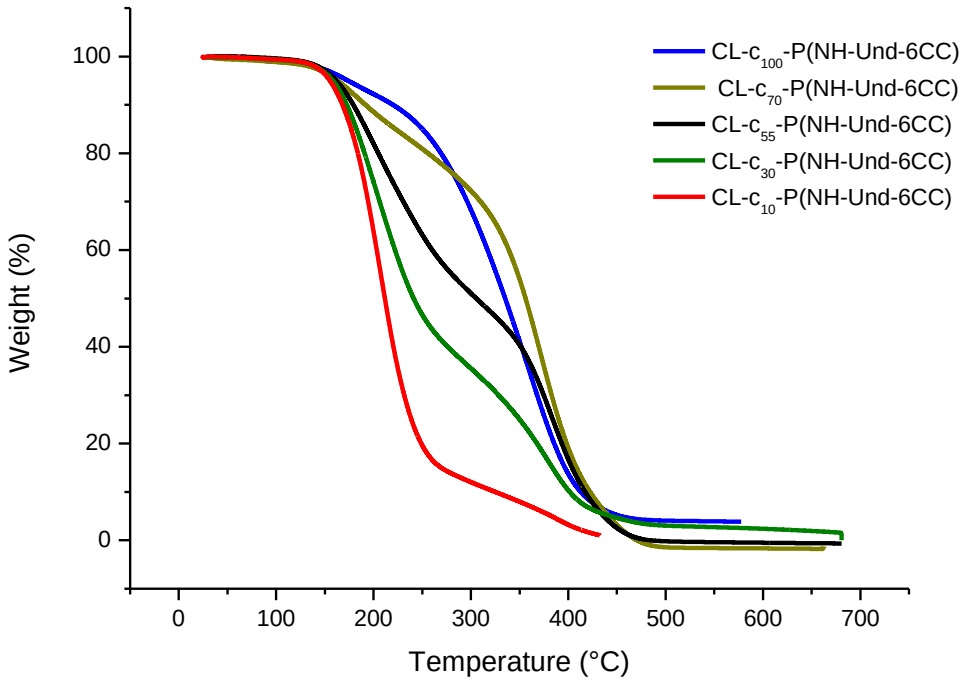


ESI Figure 5: DSC traces of cinnamoyl-functionalized P(NH-Und-6CC)

CONFIDENTIAL



ESI Figure 6: DSC traces of cross-linked cinnamoyl-functionalized P(NH-Und-6CC)



ESI Figure 7: TGA traces of cross-linked cinnamoyl-functionalized P(NH-Und-6CC)

General conclusion and perspectives

Aliphatic polycarbonates have regained interest in the recent years especially in the biomedical field due to their biocompatibility and biodegradability. Besides, petrol depletion and environmental concerns lead the chemical industry to consider renewable resources as source of building blocks for the synthesis of polymers. Among renewable resources, fatty acids appear as an interesting platform for the development of new polymers since the latter exhibit several functionalities such as unsaturation, ester or alcohol functions that can be directly used or derivatized for the design of new monomers and polymers thereof. In this context, the aim of this thesis was to investigate new lipidic aliphatic polycarbonate materials with versatile thermo-mechanical properties.

To that purpose, the ROP of bio-based cyclic carbonates has been chosen as polymerization method because it requires mild reaction conditions and allows the synthesis of well-controlled functional polymers. However, the ring size of the cyclic carbonate is a key parameter. Indeed, although 5CCs are easily synthesized from fatty acids, their homopolymerization do not afford true polycarbonates because of unfavourable thermodynamic features. On the contrary, despite their less direct synthesis from vegetable oils, 6CCs can be easily polymerized in a controlled manner by a ring-opening process. Not described in the literature, the copolymerization of ethylene carbonate (EC) and trimethylene carbonate (TMC) has been studied as a model reaction. The influence of various parameters such as the nature of the catalyst, the monomers ratio or the initiator to monomers ratio has been investigated. We were able to optimize the process affording the incorporation of 15.0 mol.% of EC units in a PTMC backbone without decarboxylation side-reaction. Such EC incorporation enhanced the thermal stability and increased the glass transition temperatures of the copolymers so-formed. However, the copolymerization of fatty acid-based 5CCs with TMC failed, affording only homoPTMC.

Consequently, the synthesis of more reactive lipidic 6-membered cyclic carbonates was then investigated. Two routes were studied to prepare these cyclic carbonates giving access to two platforms of lipidic 6CCs. The relatively high overall yield of the second route involving the coupling between a fatty acid and the 2-amino-1,3-propanediol is a major advantage with respect

to the first route. The ROP of these two families of cyclic carbonates has been then described. On the one hand, the first platform of 6CCs was polymerized in the presence of $Sn(Oct)_2$ catalyst, yielded low T_g aliphatic polycarbonates ranging from -60.8°C to -26.1°C as a result of long pendant side chains. On the other hand, the polymerization of the second platform of lipidic 6CCs was performed using DBU/Schreiner thiourea as catalytic system in a controlled fashion. The resulting polycarbonates displayed unexpected relatively high T_gs (above 20°C) explained by the presence of hydrogen bonding due to amide functions nearby the polymer.

Taking advantage of the functional bio-based APCs synthesized in chapter 3, original cross-linked polycarbonate materials were prepared by several cross-linking methods, reversible or not. We demonstrated that P(**NH-Und-6CC**) can be a source of numerous polycarbonate materials with tuneable thermo-mechanical properties (Figure 1).

First, the direct thiol-ene coupling between the terminal unsaturation of P(**NH-Und-6CC**) and a dithiol was used to prepare cross-linked polycarbonate materials in a large scale. In addition, the mechanical properties of the so-formed cross-linked polycarbonates were controllable, ranging from tough to elastomeric behaviour.

Then, self-healed polycarbonate materials have been developed involving either temperature or UV irradiation as stimulus. Indeed, thermo-responsive polycarbonate networks were synthesized from P(**NH-Und-6CC**) through a grafting of furan moieties on the polymer side chain and the subsequent DA reaction with a bis-maleimide cross-linker. Furan content grafted by thiol-ene coupling ranged from 31 to 88 mol.% and induced the thermo-mechanical properties of the resulting network. In addition, we could demonstrate that the so-formed networks could be recycled at least 3 times without losing their mechanical properties. Besides, a photo-responsive cinnamate moieties have been grafted by thiol-ene coupling on P(**NH-Und-6CC**) in a control manner. Consequently, the photo-induced [2+2] cyclo-addition reaction between two cinnamate groups afforded the formation of photo-reversible polycarbonate networks.

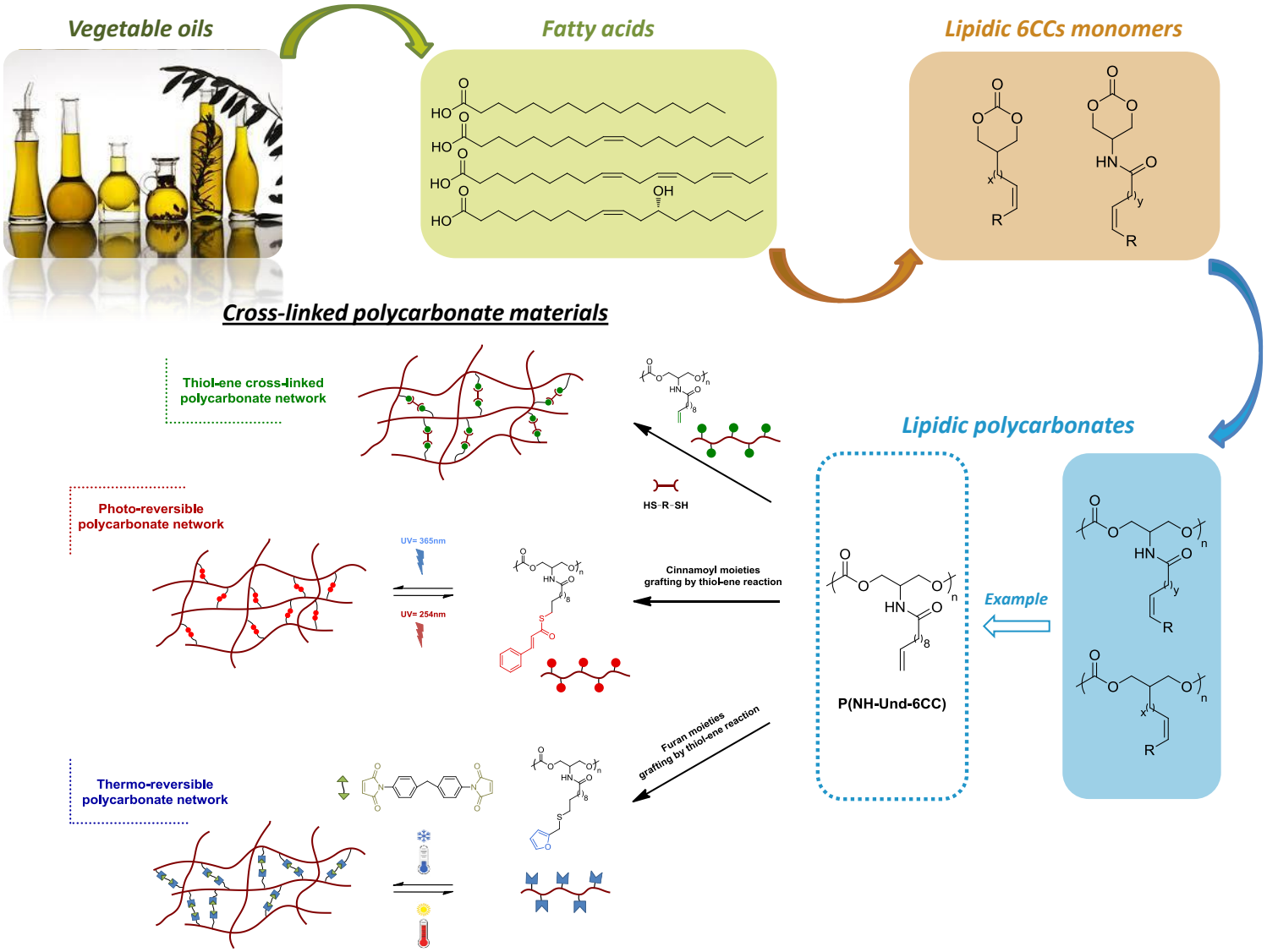


Figure 1: Global strategy developed in this PhD thesis towards new aliphatic polycarbonate materials from vegetable oils

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To summarize, new cross-linked aliphatic polycarbonate materials were designed from vegetables oils. Moreover, some of these networks were prepared with the idea to be recycled or reshaped thanks to the reversibility of some cross-linking reactions.

Since the synthesis of aliphatic polycarbonates is more and more studied, research perspectives in this subject are numerous. The major lines of potential developments are summarized below.

An important key-challenge in this field is the optimization of the polymerization process. Indeed, the use of solvents such as toluene, THF or DCM is an obstacle to the industrialization of the process. Bulk polymerizations at room temperature would circumvent the use of such toxic and heavy solvents and would enhance the reaction rate. However, when a bulk polymerization is conducted, the viscosity increases due to the rise of polymer molar masses and the important hydrogen-bonding (in the case of P(**NH-fatty acid-6CC**)). Therefore, progress in using specific tools such as reactive extruder or mechanical stirrers would be highly recommended for the development of such processes.

Taking advantage of the hydrophobicity of such cyclic carbonates with pendant alkyl chains, copolymerization with more hydrophilic monomers could be performed to broaden the application fields. In addition, APCs physico-chemical properties need to be deeply investigated. Indeed, the self-assembly properties of polycarbonates with lateral side chains deserves to be clarified. Such materials could behave as polymer brushes and being used for different applications.

Finally, from the perspective of using such materials in the biomedical field, the biocompatibility and the biodegradability of these polycarbonates networks need to be checked.

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Materials and Methods

Materials

Sodium hydrate (NaH) (60 % dispersion in mineral oil), sodium hydroxide (NaOH, pellet), ethyl chloroformate (97%), Grubbs 2nd generation metathesis catalyst, benzyl alcohol (BnOH), dimethyl carbonate (DMC, 99%), 1,5,7-triazabicyclodec-5-ene (TBD, 98%), 2,2-bis(hydroxymethyl)propionic acid (DMPA, 98%), sodium sulfate (Na_2SO_3, magnesium sulfate ($MgSO_4$), sodium carbonate ($NaHCO_3$), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,3-bis[3,5-bis(trifluoromethyl)phenyl]thiourea (Schreiner TU, >98.0%), 1,4-diazabicyclo[2.2.2]octane (DABCO, 98%), *meta*-chloroperbenzoic acid (mCPBA, 77%), Tin (II) (2-ethylhexanoate) ($Sn(Oct)_2$, 95%) were obtained from Sigma-Aldrich

1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (NHC-IPr) was purchased by Strem.

Triethylamine (Et_3N, 99%) was purchased from Alfa Aesar.

Ethylene carbonate, 1,3-dioxane-2-one (trimethylene carbonate, TMC, >98%), lithium aluminum hydride ($LiAlH_4$, 95%) were supplied by TCI, Europe.

Methyl 10-undecenoate, methyl oleate, methyl ricinoleate and methyl linoleate were obtained from Nu-Chek Prep, Inc.

ITERG kindly provided **NH-Und-1,3-diol, NH-Ole-1,3-diol and NH-Eru-1,3-diol**. 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

Methods

Nuclear Magnetic Resonance (NMR)

^{1}H and ^{13}C-NMR spectra were recorded on Bruker Avance 400 spectrometer (400.20 MHz or 400.33 MHz and 100.63 MHz for ^{1}H and ^{13}C, respectively) by using $CDCl_3$ as a solvent at room temperature, except otherwise mentioned. Two-dimensional analyses such as ^{1}H-^{1}H COSY (COrrelation SpectroscopY), ^{1}H-^{13}C HSQC (Heteronuclear Single Quantum Spectroscopy) and were also performed. All DOSY (Diffusion Ordered Spectroscopy) measurements were performed at 298K on a Bruker Avance III 400 spectrometer operating at 400.33 MHz and equipped with a 5mm Bruker multinuclear z-gradient direct cryoprobe-head capable of producing gradients in the z direction with strength 53.5 G cm^{-1}. For each sample, 2 mg was dissolved in 0.4 ml of DMSO-d6 for internal lock and spinning was used to minimize convection effects. The dosy spectra were acquired with the *ledbpgp2s* pulse program from Bruker topspin software. The duration of the pulse gradients and the diffusion time were adjusted in order to obtain full attenuation of the signals at 95 % of maximum gradient strength. The values were 3.0 ms for the duration of the gradient pulses and 100 ms for the diffusion time. The gradients strength was linearly incremented in 32 steps from 5% to 95% of the maximum gradient strength. A delay of 3s between echoes was used. The data were processed using 8192 points in the F2 dimension and 128 points in the F1 dimension with the Bruker topspin software. Field gradient calibration was accomplished at 25°C using the self-diffusion coefficient of H_2O+D_2O at 19.0 x 10^{-10} $m^2.s^{-1}$

Fourier Transformed Infra-Red-Attenuated Total Reflection (FTIR-ATR)

Infrared spectra were obtained on a Bruker-Tensor 27 spectrometer, equipped with a diamond crystal, using the attenuated total reflection mode. The spectra were acquired from 400 to 4000 nm^{-1} using 16 scans at a resolution of 4 wavenumbers.

Flash chromatography

Flash chromatography was performed on a Grace Reveleris apparatus, employing silica cartridges from Grace. Cyclohexane: ethyl acetate and dichloromethane: methanol gradients were

used as eluents depending on the products. The detection was performed through ELSD and UV detectors at 254 nm and 280 nm.

Size Exclusion Chromatography in THF (SEC)

Size Exclusion Chromatography analyses were performed in THF (25°C) on a PL GPC50 and with four TSK columns: HXL-L (guard column), G4000HXL (particles of 5 mm, pore size of 200A, and exclusion limit of 400000 g/mol), G3000HXL (particles of 5 mm, pore size of 75A, and exclusion limit of 60000 g/mol), G2000HXL (particles of 5 mm, pore size of 20 A, and exclusion limit of 10000 g/mol) at an elution rate of 1 mL/min.

The elution times of the filtered samples were monitored using UV and RI detectors and SEC were calibrated using polystyrene standards.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry thermograms were measured using a DSC Q100 apparatus from TA instruments. For each sample, two cycles from -80 to 100°C at 10°C.min^{-1} were performed and then the glass transition and melting temperatures were calculated from the second heating run.

Thermogravimetric analysis (TGA)

Thermogravimetric analyses 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.

Dynamic Mechanical Analysis (DMA)

DMA RSA 3 (TA instrument). The sample temperature was modulated from -50 °C to 150 °C, depending on the sample at a heating rate of 4°C.min^{-1}. The measurements were performed in a tension mode at a frequency of 1 Hz, an initial static force of 0.1 N and a strain sweep of 0.04%.

UV Cross-linking

Photo-crosslinking were performed using a UV lamp HAMAMATSU equipped with a LC8 lamp (full power of 4000 $mW.cm^{-1}$) and an A9616-03 filter transmitting in the range 280-400 nm, avoiding the heating of the mixture reaction. The samples were placed at a distance of 9 cm of the UV lamp.

Fatty acids as a source of original aliphatic polycarbonate materials

Abstract: Fatty acids were derivatized with the objective to design bio-based aliphatic polycarbonate (APC) materials. To that purpose, two platforms of lipidic 6-membered cyclic carbonates were prepared following synthetic routes either involving the ring-closure of a malonate intermediate or the coupling reaction between a fatty acid and 2-amino-1,3-propanediol. The ring-opening polymerization (ROP) of these cyclic carbonates was next investigated. The first platform of 6CCs was polymerized in the presence of $Sn(Oct)_2$ as catalyst, yielding low T_g aliphatic polycarbonates ranging from -61°C to -26°C with respect to the size of the pendant aliphatic side chains. The polymerization of the second lipidic 6CC platform was performed in a controlled fashion using DBU/Schreiner thiourea as catalytic system. Taking advantage of the presence of unsaturation functions on the linear bio-based APCs, cross-linked polycarbonate materials were then prepared. Several cross-linking methods were tested such as the irreversible thiol-ene coupling, the thermo-reversible Diels-Alder reaction and the photo-reversible [2+2] cyclo-addition reaction between two cinnamate moieties. Fatty acid-based cross-linked APCs were thus designed and characterized; the latter exhibit tunable physico-chemical properties as a function of the monomer structure and the cross-linking density.

Keywords: *Cyclic carbonates, Fatty acids, Ring-opening polymerization, Aliphatic polycarbonates, cross-linking.*

Les acides gras comme source de matériaux polycarbonates aliphatiques originaux

Résumé: Cette thèse porte sur la valorisation de dérivés d'acides gras dans l'objectif d'élaborer des matériaux polycarbonates aliphatiques (PCAs) bio-sourcés originaux. Dans cette optique, deux plateformes de carbonates cycliques à 6 chaînons (6CCs) ont été synthétisés en utilisant des voies d'accès impliquant soit la formation d'un intermédiaire de type malonate ou un couplage entre un acide gras et le 2-amino-1,3-propanediol. La polymérisation par ouverture de cycle de ces monomères a été étudiée. La première plateforme de 6CCs a été polymérisée en présence de $Sn(Oct)_2$ comme catalyseur, donnant accès à des polycarbonates de faible T_g allant de -61°C jusqu'à -26°C du fait de longues chaines latérales pendantes. La polymérisation de la seconde plateforme de 6CCs a été effectuée de manière contrôlée en utilisant un système catalytique composé de la DBU et d'une thio-urée. Tirant profit de ces polycarbonates aliphatiques bio-sourcés linéaires porteurs d'insaturations, des matériaux originaux réticulés ont été synthétisés. Plusieurs méthodes de réticulation ont été testées telles que le couplage thiol-ène irréversible, la réaction de Diels-Alder thermo-réversible et la cyclo-addition photo-réversible [2+2] entre deux groupements cinnamate. Ainsi, des PCAs réticulés issus d'acides gras ont été synthétisés et caractérisés; ces derniers possèdent des propriétés physico-chimiques modulables selon la nature des monomères de départ et la densité de réticulation des réseaux.

Mots clés: *Carbonates cycliques, Acides gras, Polymérisation par ouverture de cycle, Polycarbonates aliphatiques, Réticulation.*

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