



Polyethers and polyamide-3 synthesis by monomer activated anionic polymerization

Kevin Roos

► To cite this version:

Kevin Roos. Polyethers and polyamide-3 synthesis by monomer activated anionic polymerization. Polymers. Université de Bordeaux, 2015. English. ⟨NNT : 2015BORD0331⟩. ⟨tel-01291657⟩

HAL Id: tel-01291657

<https://theses.hal.science/tel-01291657v1>

Submitted on 21 Mar 2016

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

THÈSE PRÉSENTÉE
POUR OBTENIR LE GRADE DE
DOCTEUR DE
L'UNIVERSITÉ DE BORDEAUX

ÉCOLE DOCTORALE DES SCIENCES CHIMIQUES

SPÉCIALITÉ : POLYMÈRES

Par Kévin ROOS

**Polyethers and polyamide-3 synthesis by monomer
activated anionic polymerization**

Sous la direction de : Pr. Stéphane CARLOTTI

Soutenue le 15 décembre 2015

Membres du jury :

Mme GUILLAUME, Sophie
M. LECOMTE, Philippe
M. CAILLOL Sylvain
M. PENELLE, Jacques
M. TATON, Daniel
M. GADENNE, Benoît
M. CARLOTTI, Stéphane

Directeur de Recherche, Université de Rennes 1
Chercheur qualifié FNSR, Université de Liège
Chargé de Recherche, Université de Montpellier
Directeur de Recherche, Université Paris Est
Professeur, Université de Bordeaux
Docteur, Michelin (MFPM)
Professeur, Bordeaux INP

Rapporteur
Rapporteur
Examineur
Examineur
Président du jury
Invité
Directeur de thèse

Remerciements

Ce mémoire de thèse est le fruit de 3 années de recherche au sein du Laboratoire de Chimie des Polymères Organiques (LCPO). Au-delà des efforts fournis pour le mettre en forme je sais pertinemment que tout cela n'aurait été possible sans ces nombreuses personnes que j'ai pu côtoyer plus ou moins quotidiennement tout au long de cette aventure.

Ainsi, je tiens avant toute chose, exprimer toute ma gratitude et ma sympathie la plus sincère à mon directeur de thèse, le professeur Stéphane Carlotti. Je lui suis reconnaissant pour la confiance qu'il m'a accordée durant la réalisation de mes travaux ainsi que pour ses conseils avisés qu'il a toujours su me prodiguer. J'ai appris bien plus que les préceptes de la polymérisation anionique à vos côtés. Votre disponibilité, votre humilité ainsi que votre force de caractère font de vous un boss de haut vol. En plus d'un grand merci je vous dirai également que « tous les voyants sont au vert ». D'autre part je tiens à remercier le docteur Sylvain Caillol ainsi que sa doctorante Elena Dolci pour la collaboration fructueuse que nous avons pu établir.

Ensuite, je suis très reconnaissant au professeur Sophie Guillaume et au professeur Philippe Lecomte d'avoir accepté d'être les rapporteurs de cette thèse ainsi qu'au professeur Jacques Penelle et au professeur Sylvain Caillol d'avoir accepté d'examiner l'ensemble de ces travaux. Je remercie également le professeur Daniel Taton pour la qualité de sa présidence lors de cette soutenance et le docteur Benoit Gadenne d'avoir accepté mon invitation. Enfin j'adresse un grand merci à l'ensemble de ce jury de thèse pour la qualité et la pertinence de la discussion qui a animé la suite de ma présentation.

Pour en revenir au laboratoire, je souhaite exprimer ma reconnaissance à ceux qui en assurent le bon fonctionnement quotidien: Catherine, Dominique, Claude, Nicole, Bernadette, Corinne et Loïc. Vous nous facilitez grandement la vie.

A mes yeux, il est aussi indispensable de remercier des experts techniques qui nous permettent d'appréhender et utiliser un large panel d'appareils de mesures. Mes pensées vont alors à Anne-Laure, Gérard, Cédric, Eric, Emmanuelle, Nicolas, Amélie, Adrien, Patricia, Christelle. Vous avez des compétences certaines et ce fut un véritable plaisir de vous côtoyer.

Enfin un grand merci à tous les post doctorants, ex doctorants, doctorants et stagiaires que j'ai rencontré au LCPO pendant mes 3 années de thèse : Feifei, Christos, Efty, Dimitrios, Prakash, Mathieu, Maréva, Carine, Jules, Chrystilla, Charlotte, Deniz, Camille, Paul, Winnie, Thomas, Lise, Déborah, Elise, Estelle, Blandine, Edgar, Brandi, Alex, Geoffrey, Océane, Guillaume, Laurie, Yuki, Tapas, Dam, Arthur, Pierre-Luc, Pierre, Dounia, Julie, Jérémie, Etienne, Enrique et bien d'autres encore...

Une mention toute particulière à mes amis/collègues qui ont vécu cette aventure avec moi et qui ont été d'un soutien inconditionnel et ce bien au-delà des portes du laboratoire. C'est avec émotion que je vais me contenter de vous citer mais vous savez vous-même tout ce qui a pu être partagé. Ainsi Olivia, Mikael, Audrey, Romain, Clément, je tiens à vous remercier chaleureusement pour l'ensemble des expériences vécues et il ne fait nul doute dans mon esprit que de nombreuses sont à venir.

Je remercie aussi très sincèrement mes amis bordelais ou non qui ont fait de cette période de ma vie une période mémorable, Nico, Thom, Céline, Mamat, Bertrand, Mimich, Julien, Barbara, Kévin, Maxime, Mathilde, Maéva, Claire, Merci à vous !

Enfin, j'adresse à ma mère, mon père et ma sœur, mes plus sincères remerciements puisqu'ils m'ont épaulé sans relâche et ce durant toutes ces années. Sans hésitations je vous dédie ce manuscrit.

Kévin.

Résumé en français

Depuis que le monde est monde, les besoins des êtres humains ne cessent de croître tout en ne souhaitant considérer que des modifications mineures à leur mode de vie. Ainsi, dans de nombreux domaines, la recherche scientifique se focalise sur le futur et cela sur une vaste échelle de temps. Beaucoup de sujets à la mode, notamment ceux concernant les enjeux environnementaux sont au cœur de l'actualité. La réduction des consommations énergétiques, le développement de nouvelles technologies pour la production d'énergies « vertes » sont maintenant et fort heureusement devenus des priorités pour quasiment tous les gouvernements du monde. Cependant, même si certains projets deviennent de plus en plus matures, la plupart d'entre eux ne sont pas encore prêts à être assimilés par nos sociétés de consommations. Cette réalité implique alors aussi de développer des solutions techniques disponibles à courts ou moyens termes. Certains domaines peuvent alors apparaître comme étant moins séduisants mais en demeurent tout aussi stimulants. Ainsi, en sciences des polymères, notamment à l'échelle industrielle, il s'agit d'améliorer les performances des matériaux polymères dans le but d'étendre le champ des possibles. Mais, quand la formulation et/ou la mise en œuvre des matériaux actuels sont complètement optimisées, la chimie vient à être envisagée afin de lever certains verrous technologiques.

Ces travaux de thèse se focalisent alors sur la synthèse de polymères par polymérisation anionique au travers de méthodologies d'activation de monomères. En dépit, des conditions « drastiques » requises par ce type de polymérisation (atmosphères inertes, milieux anhydres ...), la polymérisation anionique est une remarquable voie de polymérisation en chaîne. En effet, la réactivité des espèces actives, le caractère vivant/contrôlé de cette méthode, la diversité des monomères polymérisables, font de la polymérisation anionique l'une des méthodes de choix pour la synthèse de matériaux fonctionnels ou de copolymères à blocs, d'architectures variées[1]. Combiné à des approches impliquant l'activation des monomères, l'enjeu principal de ma thèse est de promouvoir et contrôler la réactivité des espèces actives et des monomères pour le développement des voies de synthèse de certains polymères.

1. Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. Polymers with Complex Architecture by Living Anionic Polymerization. *Chem. Rev.* 2001, 101, 3747–3792.

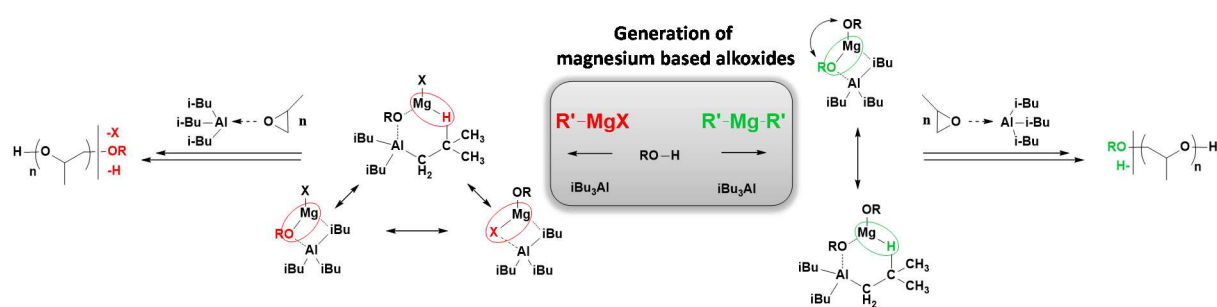
Dans une première partie je me suis intéressé à la synthèse de polyéthers aliphatiques. Ces polymères représentent une part non négligeable des tonnages annuels des polymères dits techniques. Ils présentent des propriétés intéressantes puisqu'en fonction de leurs structures chimiques ils peuvent être amorphes ou semi-cristallins et leur caractère hydrophile peut-être façonnable. Comparable à certains polydiènes, ce type de polymères présente habituellement de faibles températures de transition vitreuse, mais présente en revanche un squelette macromoléculaire riche en atomes d'oxygènes. Par conséquent les polyéthers trouvent des applications dans de nombreux domaines de notre vie quotidienne tels que l'industrie automobile et du papier ou encore pour des applications cosmétiques et biomédicales. Dans ce manuscrit leur synthèse est alors épluchée notamment par polymérisation anionique par ouverture de cycle (AROP) des époxydes substitués. La tension de cycle de ces monomères est la force motrice de leur polymérisation. Dans la littérature, divers systèmes ont été développés pour la polymérisation de l'oxyde d'éthylène mais celle des époxydes substitués reste encore problématique de par la présence de réactions de transfert au monomère sur le substituant qui entraîne une limitation des masses molaires. De plus, les cinétiques de polymérisation sont primordiales et dépendantes des paires d'ions mises en jeu.

Le chapitre I comporte alors une revue de la littérature portant sur l'AROP des époxydes qui est essentiellement axée sur l'utilisation de systèmes dits activés. Les composés à base de magnésium sont enfin abordés puisqu'ils ont, dans le cadre de mes travaux, été envisagés comme des agents de déprotonation pour générer des espèces actives en polymérisation des époxydes.

Généralement employés comme précurseurs d'alkylation, de simples réactifs de Grignard type RMgX ont été étudiés comme agents de déprotonation d'alcool pour générer des alcoolates d'halogénure de magnésium de plus faible basicité. Les espèces ainsi formées ont démontré une aptitude à amorcer la polymérisation de l'oxyde de propylène en présence de triisobutylaluminium ($\text{i-Bu}_3\text{Al}$) utilisé comme agent complexant et activant. En présence d'un excès d' $\text{i-Bu}_3\text{Al}$ l'oxyde de propylène est totalement converti en quelques heures. Les masses molaires sont contrôlées par le rapport molaire $[\text{Monomère}]/[\text{dérivés de Mg}]$ jusqu'à hauteur de 10 000 g/mol avec des valeurs de dispersité relativement faibles. Une analyse méthodique des bouts de chaînes permet de mettre en évidence différents types d'amorçage

via i) l'alcoolate d'halogénure de magnésium désiré ($\text{RO}^- + \text{MgX}$) à hauteur de 30%, ii) un hydruure provenant du triisobutylaluminium ($\text{H}^- + \text{MgX}$), et iii) l'halogène porté par l'alcoolate d'halogénure de magnésium ($\text{X}^- + \text{MgOR}$).

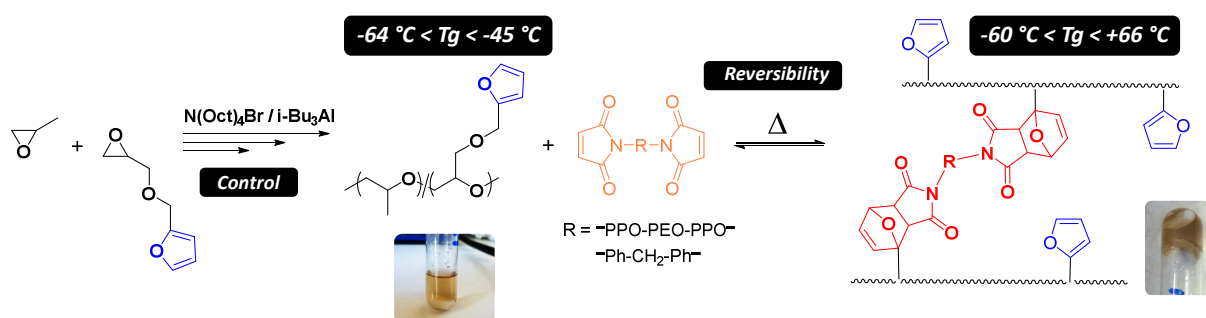
Sur la base des résultats obtenus avec les réactifs de Grignard, des composés de type dialkylmagnésium (R_2Mg) ont ensuite été étudiés pour palier à l'amorçage via l'halogène. Ils se sont révélés être de bons agents de déprotonation de molécules protiques utilisées ensuite pour la polymérisation d'éthers cycliques en présence de triisobutylaluminium. La formation d'un complexe « ate » Mg/Al est admise et permet d'augmenter l'efficacité d'amorçage via l'alcoolate (alcool comme précurseur) désiré à hauteur de 70-80%. L'ensemble de l'étude permet également de déterminer la provenance des amorçages résiduels. Des précurseurs protiques de types amine primaire, thiol, alcyne furent également étudiés ainsi que des macroamorceurs obtenus par déprotonation de polymères terminés par une fonction alcool et permettant la synthèse de copolymères à blocs (ex polydimethylsiloxane-bloc- poly(oxyde de propylène) PDMS-b-PPO).



Sur la base des caractéristiques attrayantes que les thermodurcissables présentent (résistance au fluage, insolubilité, propriétés thermomécaniques accrues...) et les propriétés avantageuses des polyéthers tels que leur comportement flexible (basse T_g), l'attention du chapitre II est portée sur la synthèse de polyéthers réticulables. La première partie est consacrée à une revue de la littérature sur les matériaux réticulés mettant en jeu les polyethers. Sur cette base bibliographique, deux approches distinctes furent étudiées pour obtenir des polyethers réticulables.

Une approche réversible, dans laquelle des copolyéthers statistiques d'oxyde de propylène (PO) et furfuryl glycidyl ether (FGE) de différentes compositions (95/5, 90/10, 75/25, 50/50, and 25/75 (PO/FGE mol%)) ont été synthétisés par AROP d'époxydes activés via

l'utilisation de bromure de tétraoctylammonium et de triisobutylaluminium. Ces copolymères statistiques de masses molaires d'environ 10 000 g/mol et de Tg comprises entre -60°C et -40°C ont été obtenus en quelques heures. Ils ont ensuite été mis en présence d'agents de réticulation de type bismaléimides aliphatiques ou aromatiques afin de permettre une réaction de Diels-Alder entre les motifs maléimides et les motifs furanes des polymères. Des réseaux tridimensionnels furent obtenus et caractérisés par des mesures de taux de gonflement et fractions insolubles. Les copolymères riches en fonctions furanes donnent lieu à la formation de réseaux plus denses et de Tg plus élevées (jusqu'à 66°C). Les analyses par calorimétrie différentielle nous permettent d'observer la réaction de retro Diels-Alder comme un phénomène endothermique visible aux alentours de 100°C. Enfin l'aptitude de nos réseaux 3D à dé-réticuler a été mise en évidence par une étude de solubilité et un suivi quantitatif en RMN du proton. Cette étude à 110°C a montré que le bismaléimide aromatique accélère le processus de dé-réticulation et que les gels se reforment à 20°C conduisant ainsi à des polyéthers réticulables de façon réversible.

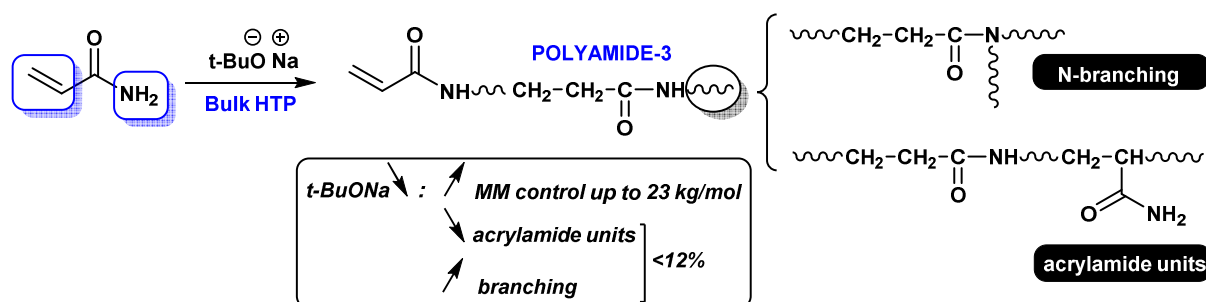


Dans le chapitre III, la synthèse de polyamides a été étudiée et plus précisément celle de polyamide-3 (PA-3). Tout comme les polyéthers, les polyamides représentent une large part des polymères techniques. Avec une production annuelle d'environ 6.5 millions de tonnes, ces polymères trouvent des intérêts dans les domaines du textile et des matériaux de constructions de par leurs propriétés remarquables telles que leur grande cohésion et leurs excellentes propriétés mécaniques et de résistance à l'usure. Avec une demande à la hausse cette classe de matériaux subit toujours une importante phase de développement dans le but d'améliorer leurs voies de synthèse et/ou leurs propriétés thermomécaniques. En effet, en

dépit de leurs remarquables caractéristiques, les polyamides aliphatiques, notamment le polyamide-6, souffrent de faibles valeurs de T_g (comprises entre 40 et 60°C) intrinsèques à leurs structures chimiques. L'augmentation de la quantité de liaisons hydrogènes au sein du matériau est proposé comme un moyen pour monter les valeurs de T_g . La synthèse de structures « plus courtes » de type polyamide-3 apparaît alors intéressante puisque le PA-3 présente une T_g déjà mesurée à 126°C attribuée à une densité accrue en fonctions amides et donc en liaisons hydrogène. Cependant, bien que la synthèse de PA-3 fut étudiée selon plusieurs méthodes, elle est associée à un certain nombre de limitations telles que des masses molaires trop faibles, des conversions en monomères incomplètes, des temps de réaction trop longs ou encore l'utilisation de solvants toxiques, principalement attribuée à la réactivité des monomères ou bien aux méthodes de polymérisation elles-mêmes.

Le chapitre III fait alors état de toutes les approches permettant la synthèse de polyamide-3. Sur cette base, une attention toute particulière est portée sur la polymérisation par transfert d'hydrogène (HTP) de l'acrylamide. En effet, bien que ce monomère soit réputé comme toxique, l'acrylamide est intrinsèquement fortement activé puisqu'il est composé d'une double liaison et d'une amine primaire, chacune activée par un carbonyle.

Un procédé de synthèse du PA-3 en masse a alors été proposé basé sur l'HTP de l'acrylamide et amorcé par le tert-butanolate de sodium t-BuONa. Des polyamides-3 ont été synthétisés en quelques minutes avec des masses molaires contrôlées atteignant 23 000 g/mol. Les caractérisations RMN et DSC révèlent la présence d'unités PA-3 branchées de 2.5 à 11%mol et d'unités polyacrylamide de 12 à 1%mol le long des squelettes PA-3, toutes dépendantes de la quantité d'amorceur. Un équilibre entre les réactions de branchement et de déprotonation est alors proposé. D'un point de vue thermique, la température de dégradation de nos polymères s'avère être principalement dépendante de la quantité d'unités acrylamide que de la quantité d'unités PA-3 branchées. Les valeurs de T_g comprises entre 80 et 90°C sont supérieures à celle d'un polyamide-6.



GENERAL TABLE OF CONTENTS

Scientific production	5
List of abbreviations.....	7
General Introduction	9

CHAPTER I. Mg/Al systems for the synthesis of polyethers by anionic ring- opening polymerization of epoxides

1. Introduction	17
2. Conventional anionic polymerization of epoxides.....	18
2.1. Basic principles	18
2.2. Transfer reactions.....	19
2.3. Propagation step	21
3. Anionic polymerization using activated systems	22
3.1. Alkali metal with additives	22
3.1.1. Addition of crown ethers	22
3.1.2. Addition of phosphazene bases	23
3.2. Phosphazanium counter-ion	23
3.3. Aluminium-based systems.....	24
3.3.1. Bulky aluminium.....	24
3.3.2. Triisobutylaluminum	27

4. Polymerization systems using magnesium derivatives.....	30
4.1. Lactams.....	30
4.2. Cyclic esters	31
4.2.1. With ethylmagnesium bromide	31
4.2.2. With dialkylmagnesium.....	32
5. Grignard-based anionic ring-opening polymerization of propylene oxide activated by triisobutylaluminum	35
6. Dialkylmagnesium-promoted deprotonation of protic precursors for the activated anionic ring-opening polymerization of epoxides.....	47
SUPPORTING INFORMATION.....	66
REFERENCES.....	69

CHAPTER II. Synthesis of cross-linkable polyethers by anionic polymerization

1. Introduction	83
2. Cross-linking via Diels-Alder chemistry: furan/maleimide.....	84
2.1. In-chain approach.....	85
2.1.1. Polymerization by DA reactions	85
2.1.2. Polymerization of the DA adducts.....	86
2.2. Side-chain approach	87
2.2.1. Post-functionalization	88
2.2.2. Copolymerization	88
3. Ring-opening polymerization of Maleic Anhydride	91

3.1. Coordinative approach	92
3.2. Anionic approach.....	94
3.3. Radical polymerization	96
4. Examples of cross-linked polyether-based materials.....	96
4.1. Polycondensation approach	96
4.1.1. For proton exchange membrane fuel cells	97
4.1.2. For gas separation membranes.....	98
4.1.3. Epoxy resins.....	99
4.1.4. Polymers for blood-interfacing applications.....	100
4.2. Cationic approach.....	101
4.3. Radical approach	103
4.4. Anionic polymerization approach of epoxide monomers.....	103
5. Activated anionic ring-opening polymerization for the synthesis of reversibly cross-linkable poly(propylene oxide) based on furan/maleimide chemistry	109
6. Activated copolymerization of propylene oxide with maleic anhydride for the synthesis of cross-linkable poly(propylene oxide)	127
REFERENCES.....	130

CHAPTER III. Synthesis of polyamide-3 by anionic polymerization

1. Introduction	142
2. Synthesis of aliphatic polyamides by polycondensation.....	143

2.1. Common polyamides	143
2.2. Polyamide-3 by polycondensation of β -alanine and its derivatives	144
3. Anionic ring-opening polymerization of cyclic amides (lactams)	146
3.1. Mechanism of the anionic polymerization of lactams	147
3.1.1. Initiating and activating systems.....	147
3.1.2. Propagation reaction.....	150
3.1.3. Side reactions	151
3.2. Polymerization of β -lactams.....	154
3.2.1. Substituted β -lactams	154
3.2.2. Unsubstituted β -lactam	155
4. Hydrogen-Transfer Polymerization	158
4.1. Polymerization of acrylamide.....	158
4.1.1. Initiation and propagation steps.....	158
4.1.2. Sides reactions.....	162
4.2. Polymerization of other precursors.....	164
5. Solvent-free anionic polymerization of acrylamide, a mechanistic study for the rapid and controlled synthesis of polyamide-3	169
SUPPORTING INFORMATION.....	185
REFERENCES.....	188
 General Conclusion & Perspectives	 195

Scientific production

❖ Publication

- Roos, K.; Carlotti, S. Grignard-based anionic ring-opening polymerization of propylene oxide activated by triisobutylaluminum. *Eur. Polym. J.* **2015**, *70*, 240–246.

❖ Poster

- Controlled synthesis of polyethers by simple Mg/Al systems Activation & Functionalization
→ Michelin award, during the Bordeaux doctoral school journey, April 17th 2014
- Solvent free anionic polymerization of acrylamide: toward the rapid & controlled synthesis of Polyamide-3
→ 1st poster prize at the International Symposium on Ionic Polymerization (IP'15), July 5-10th, Bordeaux, FRANCE.

❖ Oral communication

- MACRO IUPAC, Chiang Mai, Thailand, July 6-11th (2014)
“Anionic polymerization as a tool box for the controlled synthesis of polyethers: Activation & Functionalization”
- 250th ACS congress, Boston, United States of America, August 16-20th (2015)
“Grignard-based anionic ring-opening polymerization of propylene oxide activated by triisobutylaluminum”

List of abbreviations

AAm: acrylamide
AGE: allyglycidylether, PAGE: poly(allyl glycidyl ether)
AROP: anionic ring-opening polymerization
ATRP: atom transfer radical polymerization
BM: bismaleimide
Bu₂Mg: dibutylmagnesium
BuOH: 1-butanol
BO: butylene oxide, PBO poly(butylene oxide)
CaH₂: calcium hydride
CsOH: cesium hydroxide
CTA: chain transfer agent
Đ: dispersity
DA: Diels–Alder
DEPT: distortionless enhancement by polarization transfer
DGEBA: diglycidylether of bisphenol-A
DIT: 1,8,-anthracentriol
DMF: dimethylformamide
DMP: 2,4-dimethyl-3-pentanol
DMSO: dimethylsulfoxide
DOSY: diffusion ordered spectroscopy
dPhbm: 1,1'-(methylene-di-4,1-phenylene)bismaleimide
DPMK: diphenylmethylpotassium
 $\overline{DP_n}$: average degree of polymerization
DSC: differential scanning calorimetry
ε-CL: ε-caprolactam
EDG: electron donating group
EO: ethylene oxide, PEO: polyethylene oxide, PEG: polyethylene glycol
EtMgBr: ethylmagnesium bromide
Et₂Mg: diethylmagnesium
Et₂O: diethylether
EWG: electron withdrawing group
FMA: furfuryl methacrylate, PFMA: poly(furfuryl methacrylate)
FGE: furfuryl glycidyl ether, PFGE: poly(furfuryl glycidyl ether)
GMA: glycidyl methacrylate, PGMA: poly(glycidyl methacrylate)
GME: glycidyl methyl ether
HFIP: hexafluoroisopropanol
HTP: hydrogen transfer polymerization
HSQC: heteronuclear single quantum coherence spectroscopy
i-Bu₃Al: triisobutylaluminum
IF: insoluble fraction
iPrOH: isopropanol
iPrMgBr: isopropylmagnesium bromide
KOH: potassium hydroxide
 k_p : propagation rate

l-LA: l-lactide, PLA: poly(l-lactide)
 LiCl: lithium chloride
 MA: maleic anhydride
 MALDI-ToFMS: matrix-assisted laser desorption/ionization time-of-flight mass spectrometry
 MgBr₂: magnesium bromide
 MeOH: methanol
 MeTHF: 2-methyltetrahydrofuran
 MeMgBr: methylmagnesium bromide
 MeMgCl: methylmagnesium chloride
 \overline{Mn} : average number molar mass
 MMA: methyl methacrylate, PMMA: poly(methyl methacrylate)
 NaH: sodium hydride
 NaI: sodium iodide
 NMR: nuclear magnetic resonance
 NOct₄Br: tetraoctylammonium bromide
 PA: polyamide
 PAAm: polyacrylamide
 PEMFC: proton exchange membrane fuel cells
 PES: poly(ether sulfone)
 PDMS: poly(dimethylsiloxane)
 PGPMs: poly(glycidoxypropyl methyl siloxane)
 PhCH₂OH: benzyl alcohol
 Ph₂CHOH: diphenyl ethanol
 Ph₃COH: triphenyl methanol
 PMHS: polymethylhydrosiloxane
 PO: propylene oxide, PPO: polypropylene oxide, PPG: polypropylene glycol
 PS: polystyrene
 PTMO: poly(tetramethylene oxide)
 rDA: retro Diels-Alder
 RI: refractive index
 R₂Mg: dialkylmagnesium
 ROP: ring-opening polymerization
 R_p: polymerization rate
 RT: room temperature
 SEC: Size Exclusion Chromatography
 SR: swelling ratio
 t-BuGE: *tert*-butyl glycidyl ether
 t-BuOK: potassium *tert*-butoxide
 t-BuOLi: lithium *tert*-butoxide
 t-BuONa: sodium *tert*-butoxide
 t-BuP₄: 1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylideneamino]-2λ⁵,4λ⁵-catenadi(phosphazene)
 T_g: glass transition temperature
 TGA: thermogravimetric analysis
 THF: tetrahydrofuran
 UV: ultra-violet

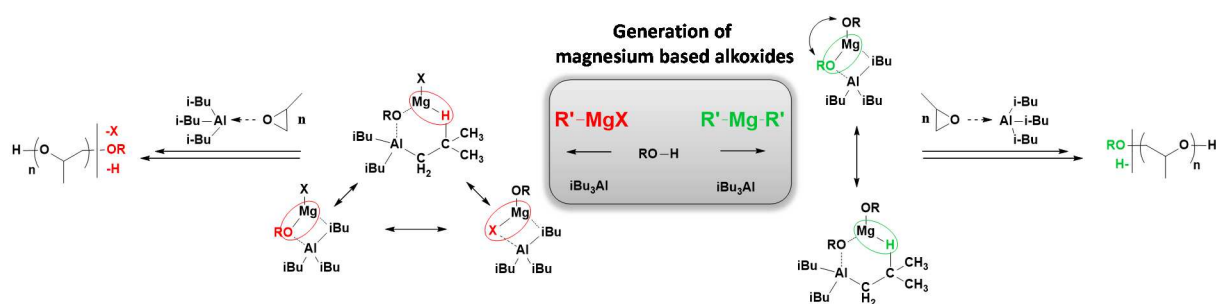
General introduction

Since the world was created, the human needs never stopped to increase. Always expecting more with only minor changes in our daily life, scientific research in every field is focused on the future in a broad timescale. In this world in full expansion many fields of research are challenging and trendy to provide solutions for our sustainable development. Indeed, the environmental concerns are in the heart of the debate. The reduction of the energy consumption, the implementation of new technologies for the production of green energy are nowadays and hopefully major priorities for governments almost all around the world. However, even if some projects are becoming more and more mature, most of them are not readily acceptable in all minds at this time. This reality involves to also develop short or mid-term solutions in order to face the demand. Some development may therefore appear less appealing but still remain challenging as well. Thus, in the polymer science, notably at the industrial scale, it appears important to enhance the polymer material performances in order to explore other limits. But, when the formulation, the compounding, or the processing of actual materials are fully optimized, the chemistry comes to be envisaged intending to circumvent some limitations.

This project is thus focused on the polymer synthesis by anionic polymerization through monomer activation methodologies. Despite the “drastic” conditions that this polymerization method requires (i.e. inert atmosphere, anhydrous components) the anionic polymerization is a remarkable chain growth polymerization pathway. Indeed the reactivity of the actives species, the living and controlled character of this method, the versatility of polymerizable monomers make the anionic polymerization one of the best candidate for the synthesis of functionalized polymers and block copolymers of various architectures[1]. Combined with the monomer activation approach, the key idea of my thesis is to promote and control the reactivity of the growing species and of the monomers to enhance some polymerization pathways.

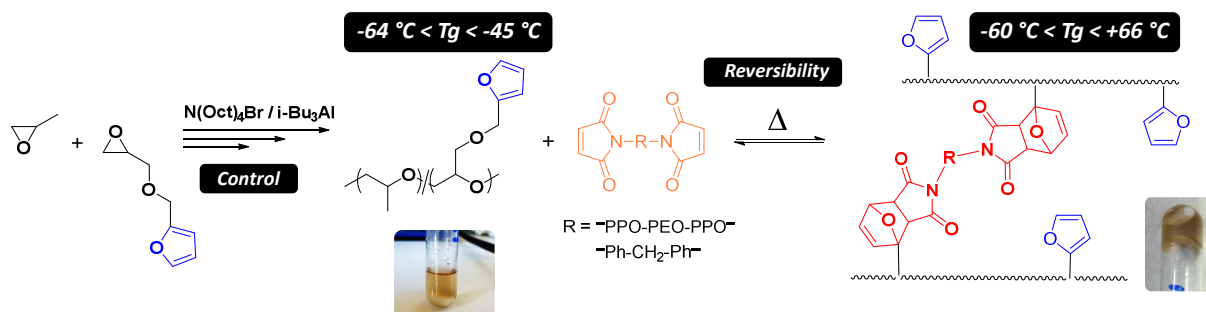
1. Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. Polymers with Complex Architecture by Living Anionic Polymerization. *Chem. Rev.* 2001, 101, 3747–3792.

In a first part, I paid attention on the synthesis of aliphatic polyethers. These polymers have interesting properties. Depending on their chemical structures they can be semi-crystalline or amorphous and their hydrophilicity can be tuned. Similar to elastomer, this kind of polymer usually presents low glass transition temperatures and exhibits an oxygen-rich backbone in contrary to polyolefins. As a consequence, polyethers find applications in many field of our daily life, for automotive and paper industry to cosmetics and biomedical applications. Here after, their synthesis was investigated especially by anionic ring-opening polymerization (AROP) of substituted epoxides. The ring strain of such monomers is the driving force of their polymerization. In the literature, many systems have been developed to polymerize epoxides but the polymerization of the substituted ones remains a big issue as transfer to monomer can occur on the pendant moieties thus limiting the molar masses. Polymerisation kinetic is also challenging as it was shown to be dependent on the ion pairs involved. The chapter I. is so a literature review toward the AROP of epoxides mainly focused on activated anionic systems. Magnesium compounds are evoked as they were envisaged as potential good candidates for a use as deprotonating agents, initiating and growing species in the epoxide chemistry. The context being given, I then present my work in this domain involving the use of magnesium-based precursors for the preparation of various initiators. Their ability to polymerize activated substituted epoxides is studied and attention is given to the initiation step.



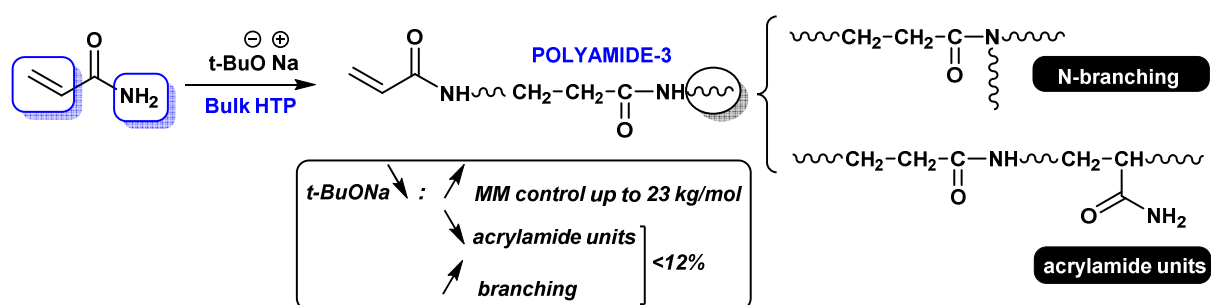
Based on the attractive features that crosslinked materials exhibit (limited creep, insolubility, improved thermo-mechanical properties) and the interesting properties of polyethers such as an elastomeric behaviour, the chapter II. then focus on the synthesis of cross-linkable polyethers. The first part is devoted to a literature review toward cross-linked

polyether-based materials. On this basis, two approaches were studied, a reversible one using a furan/maleimide chemistry (side-chain approach) and a permanent one using the curing of double bond directly introduced within the polyether backbone (in-chain approach).



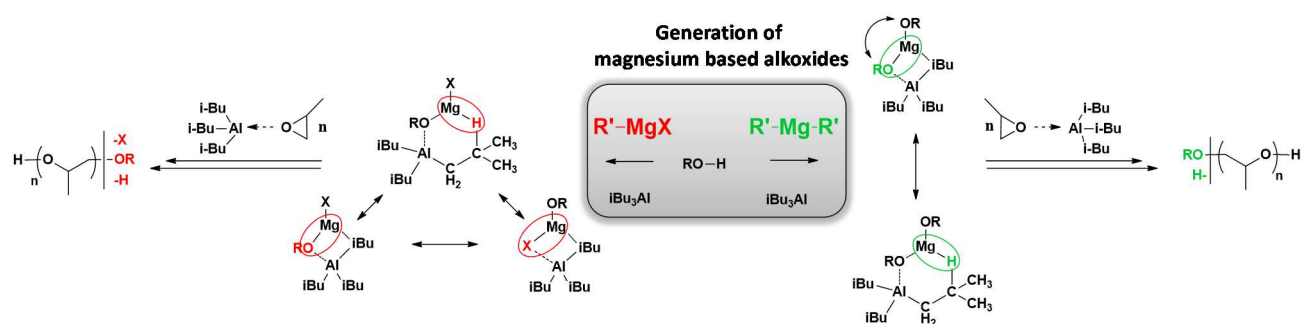
In a latter part, the synthesis of polyamide was investigated and especially the polyamide-3 (PA-3). Polyamides are parts of a broad family of engineering plastics. With an annual global production reaching more than 6.5 million tons they gained interest in textile, building construction, electronic devices and packaging areas by offering toughness and strength as well as chemical resistance. Undergoing an increasing demand, this kind of material is still under investigation in order to improve its synthesis process or its thermomechanical properties. Indeed, despite all their interesting features, aliphatic polyamides, in particular common polyamide-6, still suffer from relatively low T_g values (between 40 to $60\text{ }^\circ\text{C}$) intrinsic to their chemical structures. As a mean to increase the T_g , the increase of the hydrogen bonding amount in the material is proposed. The synthesis of shorter structures such as polyamide-3 therefore appears interesting due its higher T_g (up to $126\text{ }^\circ\text{C}$) provided by more numerous amide groups in its chemical structure as compared to its longer homologs such as polyamide-6, polyamide 12, etc. However, even if polyamide-3 synthesis was investigated using various methods, its polymerization is still an issue as it is facing to several limitations such as low molar masses, incomplete conversions, long reaction times, or the need and use of toxic solvents mainly attributed to the monomer reactivity or the polymerization method itself. The chapter III. is so reviewing all the possible approaches to get polyamide-3. On this basis, the focus is done on the hydrogen-transfer polymerization (HTP) of acrylamide as we consider it to be the most sustainable approach to develop even if the monomer is known as toxic. Indeed, acrylamide is intrinsically highly reactive because it is composed of a double bond and a secondary amine both activated by a carbonyl group. This anionic polymerization

was studied in bulk intending to circumvent some drawbacks but also to understand the growing mechanism in such conditions. As compared to the polyether synthesis using a monomer activation methodology and an active chain end (ACE) mechanism, the PA-3 synthesis is based on an activated monomer (AM) mechanism, i.e. the monomer carries the anionic charge.



CHAPTER I.

Mg/Al systems for the synthesis of polyethers by anionic ring-opening polymerization of epoxides



CHAPTER I. Mg/Al systems for the synthesis of polyethers by anionic ring-opening polymerization of epoxides

1. Introduction	17
2. Conventional anionic polymerization of epoxides.....	18
2.1. Basic principles	18
2.2. Transfer reactions.....	19
2.3. Propagation step	21
3. Anionic polymerization using activated systems	22
3.1. Alkali metal with additives	22
3.1.1. Addition of crown ethers	22
3.1.2. Addition of phosphazene bases	23
3.2. Phosphazanium counter-ion	23
3.3. Aluminium-based systems.....	24
3.3.1. Bulky aluminium.....	24
3.3.2. Triisobutylaluminum	27
4. Polymerization systems using magnesium derivatives.....	30
4.1. Lactams.....	30
4.2. Cyclic esters	31
4.2.1. With ethylmagnesium bromide	31
4.2.2. With dialkylmagnesium.....	32
5. Grignard-based anionic ring-opening polymerization of propylene oxide activated by triisobutylaluminum.....	35

6. Dialkylmagnesium-promoted deprotonation of protic precursors for the activated anionic ring-opening polymerization of epoxides.....	47
SUPPORTING INFORMATION.....	66
REFERENCES	69

1. Introduction

Polyethers like poly(ethylene oxide) and poly(propylene oxide) often referred to poly(ethylene glycol) and poly(propylene glycol) respectively, are obtained by polycondensation of alcohols but more predominantly from the ring-opening polymerization (ROP) of epoxides. Those monomers also called oxiranes, are the smallest cyclic ethers that can be produced. They are typically ring-opened due to their high ring strain (112 kJ/mol for ethylene oxide as example) and can be variously substituted. Polyethers are produced worldwide in several million tons per year for commodity or high performance applications. These polymers are mainly used as precursors for polyurethanes, surfactants and lubricants, but also in the biomedical domain, cosmetics, or nutritional applications, and in more specialized areas like lithium-ion batteries[1,2].

The most convenient chemistry which can enable the synthesis of polyethers is mainly based on the ring-opening of epoxides by ionic or coordination mechanism. Here, the focus will be given on the anionic polymerization due to its efficiency in terms of functionalisation (through the initiation step or by the nature of the monomer involved) and control of molecular features (molar mass, dispersity, stereochemistry ...). Nucleophiles can initiate the polymerization leading to alkoxides able to attack a new monomer enabling the propagation step, and constitute the attributes of the conventional anionic polymerization of epoxides. But, this chemistry suffers from limitations intrinsic to the active species and monomer structures. Thus, in order to circumvent for example long polymerization times and undesirable transfer reactions decreasing the molar masses, many systems have been investigated. The development of metallic but also organic systems is depicted below. A preliminary complexation of the monomer or the active species by specific additives (an electrophile) can be considered as an anionic-related mechanism and consequently refers to the so-called activated anionic polymerization. Based on this chemistry, as well as organic synthetic tools, many substituted epoxide monomers are able to be polymerized, opening pathways for well-defined polyether structures and functionalities and allowing the preparation of materials with various properties.

Supported by the thesis of Brocas[3] and the book chapter of Carlotti and Peruch[4] the following literature part will thus present the main outlines regarding the epoxide ring-opening by conventional anionic polymerization and most of all by activated systems. Finally, this bibliographic part will be also dedicated to magnesium compounds used for my researches.

2. Conventional anionic polymerization of epoxides

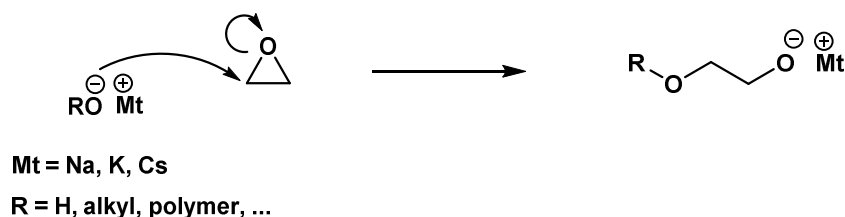
2.1. Basic principles

There are three predominant classes of epoxide polymerization mechanisms: (1) cationic, (2) anionic, and (3) coordination or metal-mediated. In general, cationic epoxide polymerizations afford limited control. Anionic and coordination polymerizations are related, as their active species are typically of the form L_nM-OR (with L_n an optional ligand, M the metal, and OR the alkoxide). The nature of the metal determines the ionic nature of the $M-O$ bond. In general, group I and II metal alkoxides are considered anionic initiators, whereas other metals (transition, lanthanide, and main group) alkoxides are “more” covalent in nature[5].

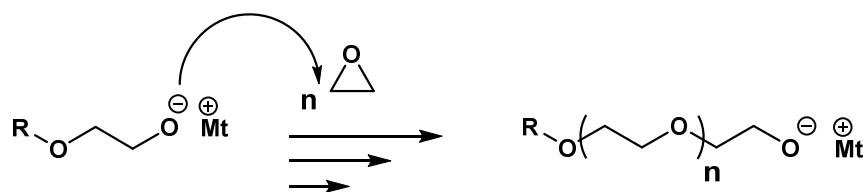
Thus, in the following attention will be given to the conventional anionic polymerization generally performed using sodium (Na^+), potassium (K^+), and cesium (Cs^+) cations. Usually hydrides, alkyls, aryls, amides, and mainly alkoxides of those alkali metals are the most common initiators used for the AROP of epoxides [6–11]. As an exception, lithium alkoxides do not generally lead to the polymerization of such monomers due to strong aggregation between lithium species after insertion of the first epoxide unit[12,13]. With the other alkali metals, propagation may proceed without side reaction in anionic polymerization of ethylene oxide or non-substituted epoxide[14]. Polymerizations can be carried out in aprotic and apolar media but polar solvents are usually preferred like dimethylsulfoxide (DMSO) or dimethylformamide (DMF) in order to enhance the reactivity of the growing alkoxides by dissociation of the active species. The driving force for the ring-opening reaction is the relief of the strain energy of the epoxide ring. High temperatures are therefore needed to perform the AROP of for example, long-chain alkylene oxides.

The different steps of conventional AROP of ethylene oxide are depicted Scheme I-1. The initiation step consists of a nucleophilic substitution -SN2 type- of the alkoxide species leading to the formation of new alkoxides able to further attack the monomer molecules resulting in polyether chains with an atactic structure. The termination step is achieved by addition of an acidic compound with labile hydrogen. Alcohols and water are the most commonly used termination agents in order to obtain hydroxyl end-groups.

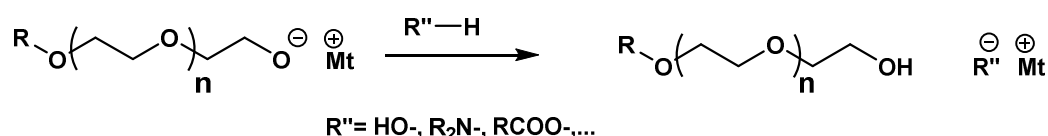
INITIATION



PROPAGATION



TERMINATION

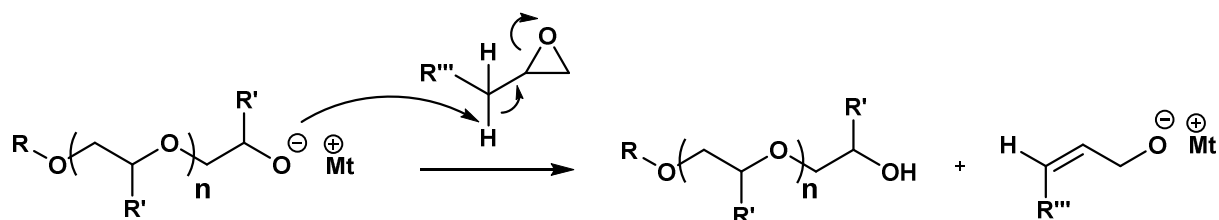


Scheme I-1: Anionic ring-opening polymerization of ethylene oxide initiated by alkali metal alkoxides

2.2. Transfer reactions

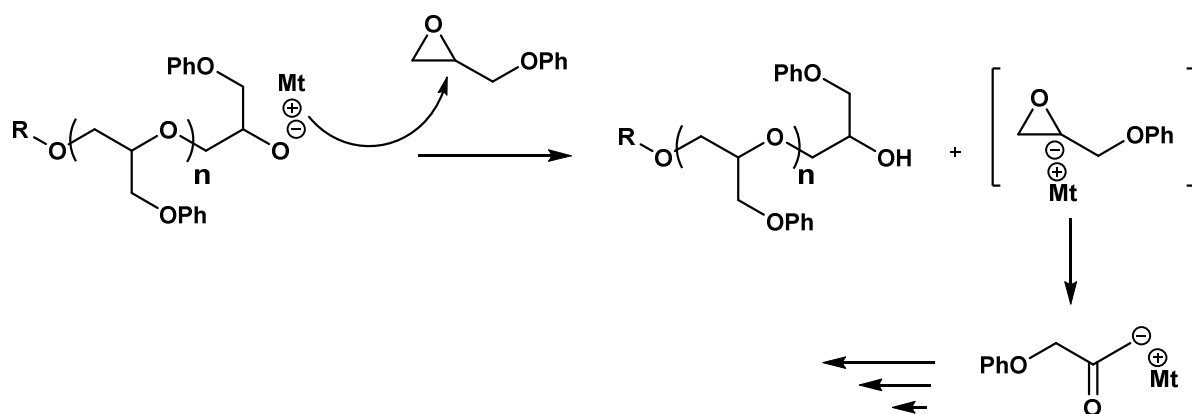
However, epoxides are known to be versatile monomers due to the wide range of substituent they can bear. But even if ethylene oxide polymerization in presence of alkali metal precursors is a sustainable method, it appears to be much less efficient since a substituent is present onto the epoxide ring. With substituted epoxides, the polymerization loses its living character and becomes more prone to transfer to monomer. Indeed, as alkoxides species are relatively strong bases, the abstraction of a proton from the substituent can occur. This side reaction

leads to the formation of unsaturation (Scheme I-2) at the polymer chain end limiting hereby the molar masses[15,16].



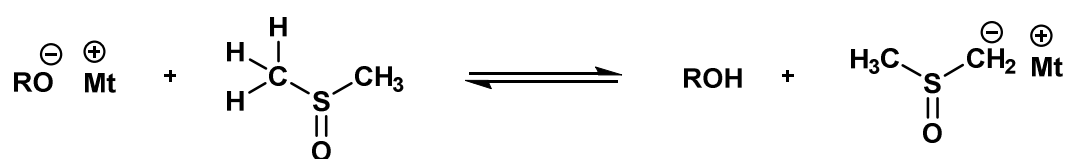
Scheme I-2: General mechanism of a transfer reaction to monomer occurring in the AROP of substituted epoxides

In the case of AROP of glycidyl ethers, another kind of transfer reaction was observed involving a proton abstraction from the epoxide ring[17]. This kind of reaction is not excluded for other substituted monomer but rarely mentioned in the literature (Scheme I-3).



Scheme I-3: Proposed mechanism for the transfer reaction to phenyl glycidyl ether

Transfer reactions involving the solvent were also observed, which can even more limit the molar masses of the growing polymer[18]. The case of DMSO is given in the following Scheme I-4.



Scheme I-4: Transfer reaction to DMSO in presence of alkali metal alkoxides

2.3. Propagation step

Similarly to ethylene oxide, the size of the counter-ion and the temperature were shown to influence the polymerization rate of mono-substituted epoxides. Increasing the size of the counter-ion leads to more dissociated active species and thus to higher polymerization rate. Faster polymerizations were observed with cesium counter-ion. Higher temperatures can also increase the polymerization rate[6,13] but the polymerizations still require several hours to days to reach high yields.

As an example, using potassium as counter-ion (t-BuOK as initiator), the reactivity of propylene (PO) oxide in hexamethylphosphoramide (HMPA) at 40 °C is about 4 times lower than that of ethylene oxide on the basis of overall polymerization rates[18]. The reactivity of other mono-substituted epoxides depends on both electronic (electron withdrawing or electron donating character) and steric factors induced by the substituent attached to the epoxide ring[19]. For instance, the reactivity of 2,2-dimethyloxirane is 10 times lower than that of PO, whereas glycidyl ethers, such as *tert*-butyl glycidyl ether (t-BuGE), are more readily polymerized than PO.

To sum up, conventional anionic ring-opening polymerization suffers in general from slow kinetics and, especially for substituted epoxides, of transfer reactions. Other systems were therefore developed intending to circumvent some of these recurrent drawbacks.

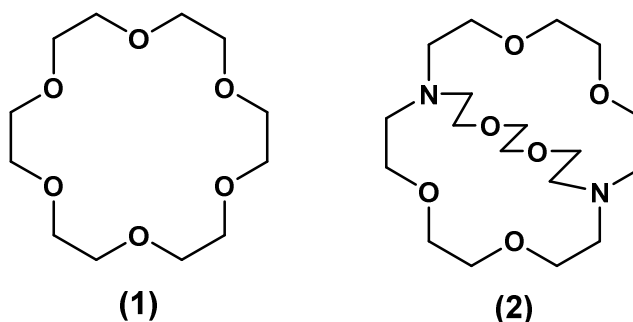
3. Anionic polymerization using activated systems

3.1. Alkali metal with additives

3.1.1. Addition of crown ethers

The addition of complexing agents to alkali metal cations, such as crown ethers or cryptands (Scheme I-5) enabled to increase the solubility of the reactive species, to decrease the aggregation phenomena and also to enhance the polymerization kinetics of epoxides thanks to a better dissociation of the ion pairs.[20–27]

For example, the dissociation constant of PEO^-K^+ at 20 °C in THF is 1700 times higher when K^+ is complexed by cryptand 222. In this system, the reactivity of free ions is about 60 times higher than that of cryptated ion-pairs.

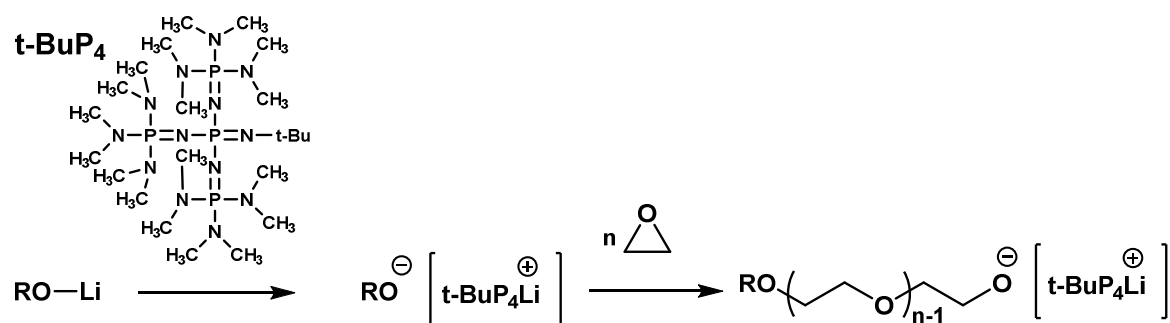


Scheme I-5: Crown ether 18C6 (1), Cryptand 222 (2) used to complex alkali metal cations in epoxide polymerization

Crown ether 18C6 is commonly used to complex potassium cation and was also shown to increase the polymerizability of substituted epoxides. But the breakthrough using these additives was associated with a decrease of the polymerization temperatures enabling to minimize transfer reaction to monomer. Various 2-alkyleneoxides could be polymerized at 0°C almost without side reactions and higher molar masses could be obtained. However, very long reaction times were still required in those conditions, i.e. 4 to 8 days without reaching full monomer conversion.[13]

3.1.2. Addition of phosphazene bases

As mentioned in paragraph 2.1 lithium does not generally allow epoxides polymerization due to strong aggregation phenomena. However, since phosphazene bases were developed by Schwesinger and coll. in 1987[28], they were also used to complex lithium alkoxides. This enabled the polymerization of ethylene oxide and ethoxyethyl glycidyl ether[29]. The base behaves as a cryptand for Li^+ cations via polar amino groups located inside the globular molecule dissociating the ion pairs and allowing polymerization (Scheme I-6). Copolymers based on polystyrene and polyethers were prepared without the need of cation exchange. However, the presence of residual transfer reactions and an induction period, resulting from the slow disaggregation of the lithium alkoxide species, still complicated the epoxide polymerization[30].

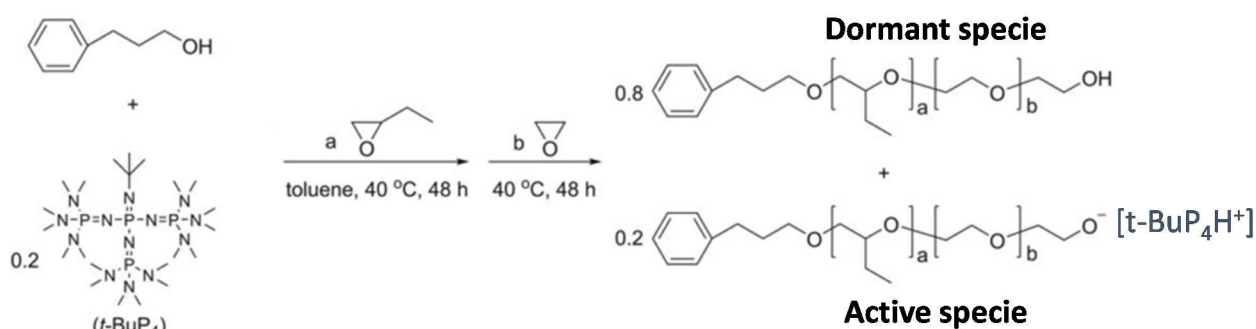


Scheme I-6: Ethylene oxide polymerization initiated by lithium alkoxide in the presence of phosphazene base t-BuP_4

3.2. Phosphazanium counter-ion

As phosphazene compounds are also strong bases, they were also involved for the deprotonation of protic compounds to generate phosphazanium alkoxides. Here, the focus is given on t-BuP_4 due to its demonstrated efficiency in various polymerizations. Indeed, this strong, bulky and non-metallic base is still largely investigated[31]. Lactones[32,33], lactams[34], cyclopropanes[35–37] and epoxides[38–41] are shown to be polymerizable with such a counter-ion. Regarding the epoxide polymerization, t-BuP_4 is usually involved to deprotonate alcohols below stoichiometry. Indeed an equilibrium is suggested involving growing and dormant species enabling to minimize transfer reactions. The polymer molar masses are thus controlled by the ratio $[\text{monomer}]/[\text{OH}]$ to some extent. Using this methodology, the syntheses of α -functionalized-polymers[42], copolymers[41,43], and

grafted copolymers[44] are possible but long reaction times are still needed (Scheme I-7). As $t\text{-BuP}_4$ is a strong base, transfer to monomer is still reported[15]. Moreover, its cost being frequently evoked $t\text{-BuP}_4$ appears to be as expensive as bulky.



Scheme I-7: Synthesis of block copolymers by AROP of butylene oxide and ethylene oxide in presence of partially deprotonated alcohol with $t\text{-BuP}_4$.

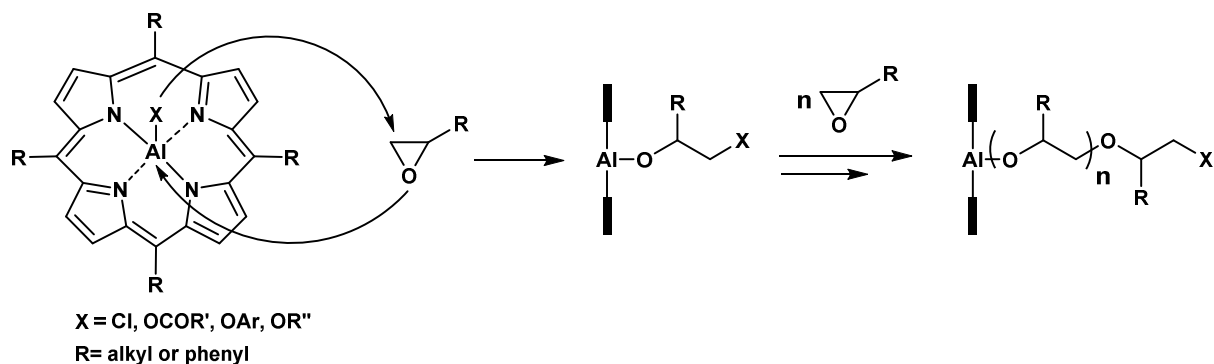
On this basis, even if efforts have been done toward the tunability of the growing alkoxides, the polymerization rates still appeared to be a limitation. Another approach was investigated mainly focused on the enhancement of epoxides reactivity. Inspired from coordination mechanisms, aluminium-based systems were developed.

3.3. Aluminium-based systems

3.3.1. Bulky aluminium

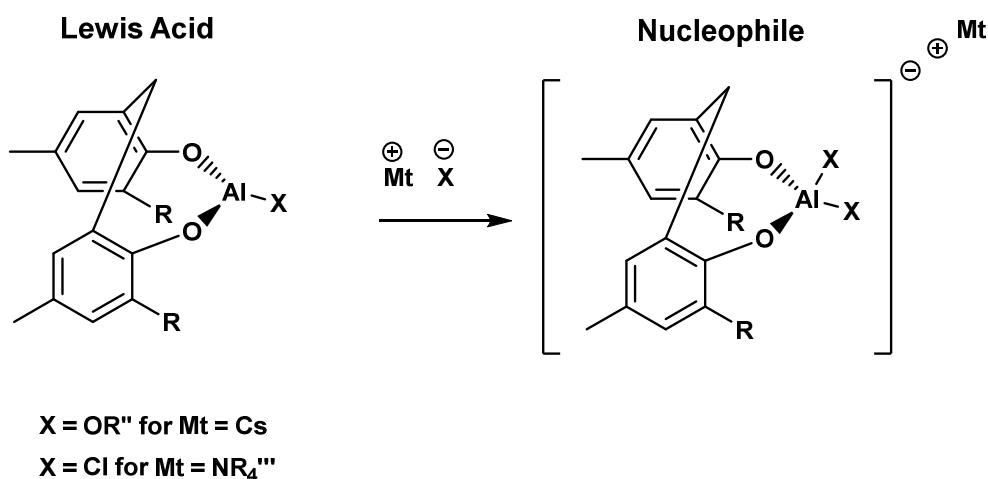
In the 1980s, Inoue et al. used metalloporphyrin as catalyst, in particular aluminum-based porphyrin, for the polymerization of methacrylates[45,46], lactones[47] and epoxides[48,49]. The equimolar combination between diethylaluminum chloride and $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrine (TPPAlCl) led to a high catalytic activity in the polymerization of propylene oxide. As seen paragraph 2.1, the covalent nature of the Al-Cl bond suggested a polymerization via a coordination mechanism. Synthesized poly(ethylene oxide), by the so called “immortal” polymerization, reached molar masses up to 70 000 g/mol with a narrow distribution. A monomer molecule is first inserted between the Al-Cl bond of the initiator (Scheme I-8). Aluminum porphyrin, due to its nucleophilic character, was used as initiator enabling coordination with epoxide. Although EO polymerization could be rapidly achieved (half-time reaction is about 30 min at room temperature for $[\text{EO}]/[\text{TPPAlCl}] = 400$), other

epoxides exhibited a lower reactivity. In similar conditions, several hours were required for the polymerization of propylene oxide and butylene oxide in order to reach complete conversion.



Scheme I-8: Polymerization mechanism of epoxides initiated by aluminium porphyrin

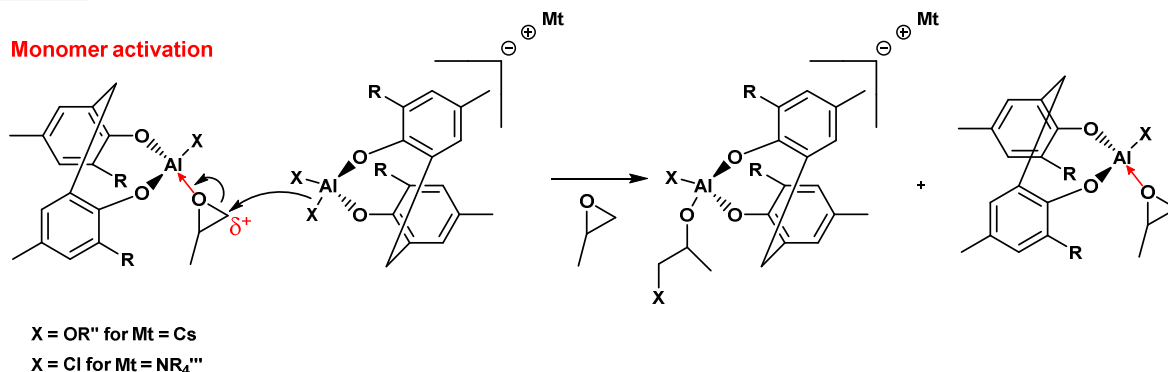
Based on this approach, several attempts to increase the polymerization rate of propylene oxide, and bi-components were investigated. A complementary bulky Lewis acid was involved to coordinate the epoxide and to activate the monomer through an electrophilic interaction favouring a nucleophilic attack. The catalytic species and the initiator were independent due to their bulkiness. Polymerization rates of propylene oxide were strongly enhanced due to the presence of the bulky Lewis Acid. Few minutes could be enough to get poly(propylene oxide) of 12 000 g/mol with 86% conversion.[50] Finally, in 2003, Braune and Okuda used porphyrin-free bulky aluminate complexes capable of acting as Lewis acid and as nucleophile[51]. The nucleophilic species were obtained by reaction of the aluminium compound under its Lewis acid form with a cesium alkoxide or an ammonium salt (Scheme I-9).



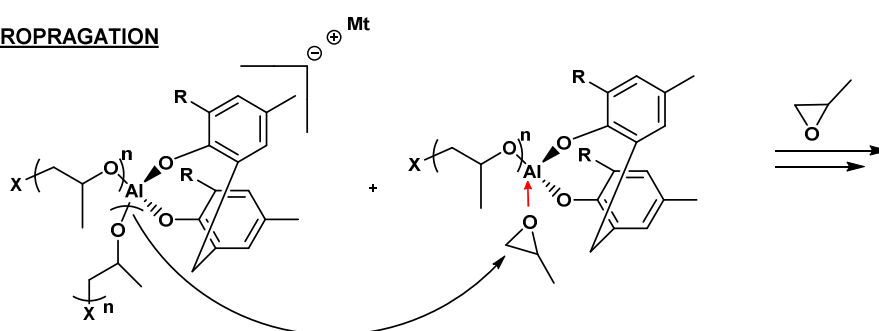
Scheme I-9: Initiating systems developed by Braune and Okuda for the propylene oxide polymerization

With such a system, the ring-opening polymerization proceeds under the synergic interaction of a phenolate-aluminum-oxirane complex forming an activated monomer with the corresponding “ate” complex which initiates the reaction (Scheme I-10). Ring-opening takes place by transfer of an alkoxy group from the “ate” complex, regenerating an aluminate able to activate a new monomer. The synthesis of poly(propylene oxide) with molar masses up to 4 000 g/mol was proposed to follow an anionic (or coordinative) mechanism because of exclusive head-to-tail linkages.

INITIATION



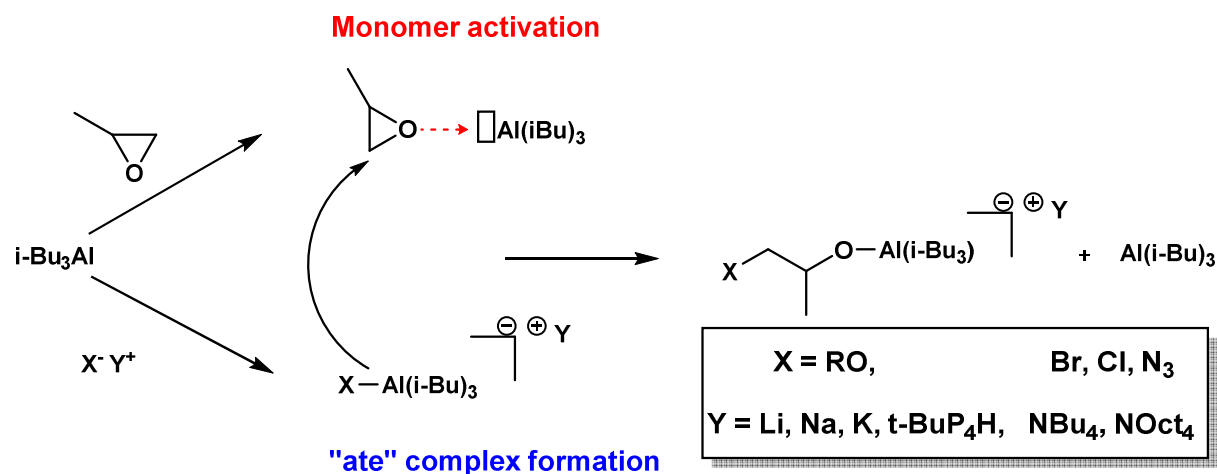
PROPAGATION



Scheme I-10: Initiation and propagation steps involved in the propylene oxide polymerization with a bulky aluminum complex

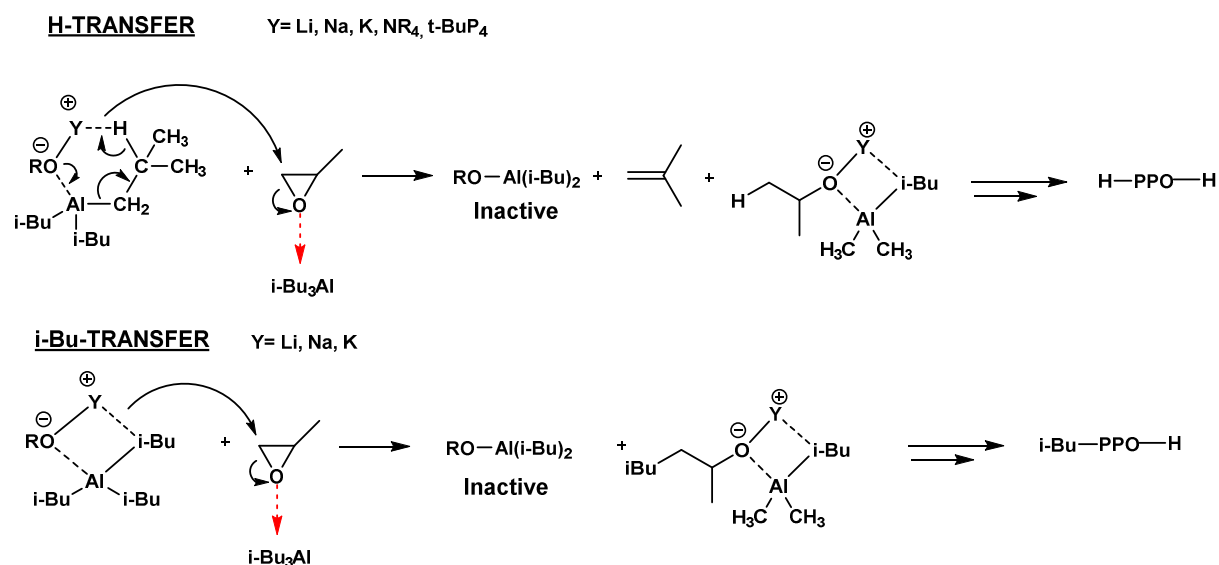
3.3.2. Triisobutylaluminum

Using epoxide monomers and combinations of a simple Lewis acid, mostly triisobutylaluminum ($i\text{-Bu}_3\text{Al}$), and alkali metal alkoxides[52–54] or onium salts(NR_4X)[55–60], Carlotti and Deffieux developed efficient synthesis of various polyethers. An excess of Lewis acid with respect to the initiator was required. The formation of an “ate” complex, which was able to ring-open the activated epoxide by the excess of Lewis acid, was observed (Scheme I-11). Propylene oxide polymerization, based on a monomer-activated anionic polymerization, occurs at room or lower temperature. Control over the polymerization was strongly dependant on the nature of the counter-ion. Sodium and potassium enabled the polymerization in a few hours, resulting to controlled poly(propylene oxide) chains, up to 20 000 g/mol. Lithium was also shown to enable polymerization. The presence of triisobutylaluminum used in excess permitted the disaggregation of lithium alkoxides species by complex formation. However, slow deactivation of the growing species was observed, therefore limiting the molar masses at 9 000 g/mol for a PEO in toluene.



Scheme I-11: Nucleophilic attack of alkali metal alkoxide or ammonium salts or phosphazanium in the presence of triisobutylaluminum on activated propylene oxide

The presence of some residual transfer reactions were observed using alkali derivatives, i.e. transfer to monomer leading to allyloxy groups in the α -position (see paragraph 2.2), but also transfer to triisobutylaluminum (i-Bu₃Al), which could generate either an initiation with an hydride[58] or an isobutyl group[54] (Scheme I-12).



Scheme I-12: Mechanism proposed for the occurrence of hydride and isobutyl-transfer reactions

Ammonium salts were more successful in the sense that much higher molar masses could be achieved in a controlled manner, especially at -30 °C (\overline{Mn} = 170 000 g/mol, \mathcal{D} = 1.34).[58] A strong decrease of transfer reactions was observed and explained by the decrease of basicity of the active bi-component complex. The exclusive preparation of regioregular polymers (head-to-tail) was indicative of an anionic/coordination type mechanism. Polymerization proceeded at $[Al]_0/[Initiator]_0$ ratio higher than 1, indicating that only complexed propylene oxide molecules were susceptible to ring-open, thanks to significant electron-withdrawing effect making the ring carbon atoms much more electrophilic. Increasing triisobutylaluminum concentration, at constant monomer and initiator concentrations, was shown to yield a drastic increase in polymerization rate whereas the number of PPO chains remained unchanged. As compared to conventional anionic polymerization using alkali metal initiators, the tetraoctylammonium bromide/ triisobutylaluminum (NOct₄Br/i-Bu₃Al) initiating system strongly enhanced the rate of ethylene oxide and substituted epoxides polymerization, while retaining the living character of the reaction. Thus, these initiating systems were also applied to the polymerization of a broad family of epoxides including several alkylene oxides[61] and glycidyl ethers[57,62,63], epichlorohydrin[64], etc. enabling to bring different functionalities along the polyether chains. This approach still suffers from some drawbacks, such as the use of one equivalent of initiating species per growing chain (inherent to the anionic polymerization), but also from the amphiphilic character that ammonium salts exhibit. Indeed the removal of the remaining ammonium hydroxide after polymerization termination can be an issue for some applications. Moreover the use of a macroinitiator such as an hydroxyl-terminated prepolymer cannot be envisaged as ammonium salts do not present a deprotonating character.

Phosphazene base t-BuP₄ was still used as deprotonating agent in combination with triisobutylaluminum for the synthesis of polyhydroxy-telechelic poly(propylene oxide)[65]. Based on the monomer activation methodology presented previously, high molar mass polyethers were obtained (up to 80 000 g/mol with low dispersity) in a few hours, at room temperature in hydrocarbon solvents with a low contribution of side reactions. The bulkiness of the counter-ion is believed to play a key role in such a control. This system was therefore a

breakthrough regarding the preparation of well-defined polyethers. But, from an industrial point of view, mixing $t\text{-BuP}_4$ with $i\text{-Bu}_3\text{Al}$ does not reduce the cost of the general process.

Other deprotonating agents were therefore envisaged and magnesium derivatives were proposed in replacement of alkali metals or phosphazene base in my researches. The following literature part is so dedicated to the presentation of magnesium based-compounds involved as active species in anionic polymerization.

4. Polymerization systems using magnesium derivatives

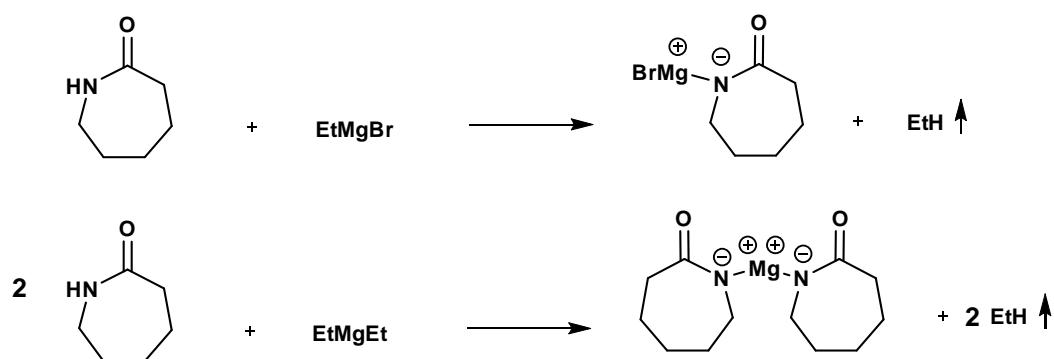
At the molecular level, magnesium-based compounds can be directly associated to Grignard reagents since they are widely used in various organic reactions in academia or industry.

Reactions and applications of Grignard reagents include asymmetric syntheses using Grignard reagents, Grignard reactions with inorganic chlorides, Grignard reagents as bases, metal-assisted modified Grignard reactions, intramolecular Grignard reactions, and Grignard reagents as supports for the Ziegler-Natta process.[66]

Such magnesium compounds were also reported to be reactive in anionic polymerization of lactams, lactones and lactides directly under the form of Grignard reagents or derivatives. The most important heterocycle polymerizations are presented below.

4.1. Lactams

In the polyamide chemistry, lactamate of magnesium bromide or even magnesium dilactamate are common catalysts in the activated or non-activated AROP of lactames[67–69]. This chemistry is well-described in chapter III paragraph 3.1.1, but in a nutshell, taking ϵ -caprolactam as an example, ϵ -caprolactamate is obtained by deprotonation of ϵ -caprolactam in presence of ethylmagnesium bromide to generate a mono-active center or by diethylmagnesium, a bis-active center (Scheme I-13). The remarkable point in this chemistry is that the monomer is bearing the charge. The growth of the polymer is therefore occurring by an activated monomer mechanism (AM) whereas in the epoxides chemistry the polymer is growing by the terminal alkoxides bearing the active specie (activated chain end mechanism (ACE)).

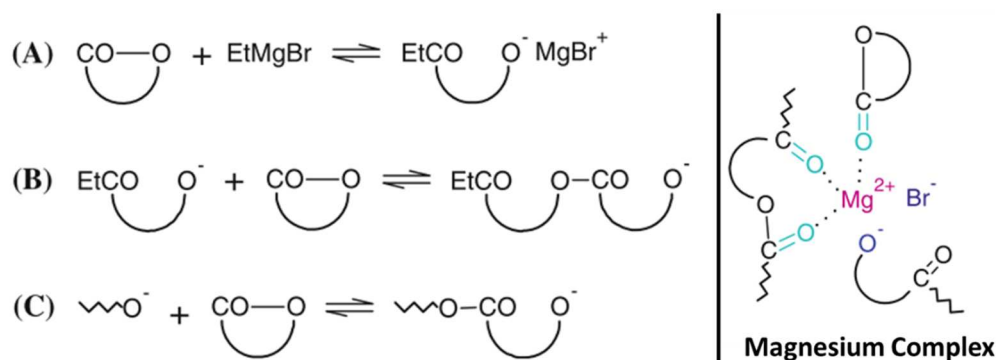


Scheme I-13: Deprotonation of ϵ -caprolactam in presence of EtMgBr or Et₂Mg for the formation of the corresponding ϵ -caprolactamate

4.2. Cyclic esters

4.2.1. With ethylmagnesium bromide

In the case of cyclic esters, Brozek and coll. reported in 2014 the use of ethylmagnesium bromide (EtMgBr) as an efficient initiator for the controlled polymerization of ϵ -caprolactone (ϵ -CLO)[70]. The molar masses were controlled by the ratio ϵ -CLO/EtMgBr. Polymer growth is proposed to occur by a sterically hindered magnesium alkoxide complex, formed through the interactions between the magnesium atom and the carbonyl groups of either the lactone and/or the polyester (Scheme I-14).



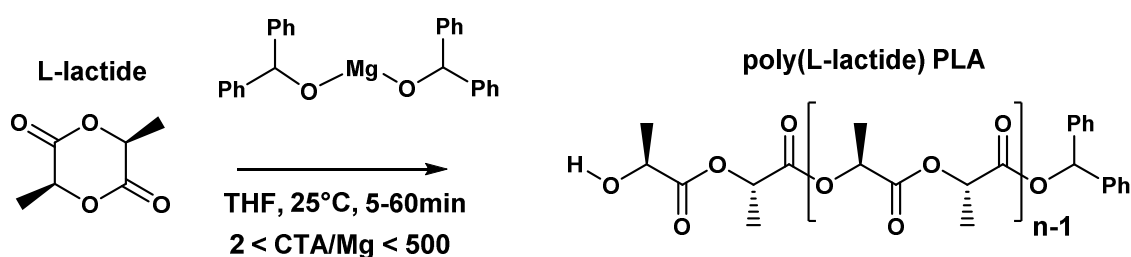
Scheme I-14: Proposed ring-opening polymerization of ϵ -caprolactone, (A) initiation, (B & C) propagation by magnesium complex.

It is also believed that this complex suppressed the intra- and intermolecular transesterification reactions that could lead to cyclic oligomers and to the broadening of the

disperty. The authors confirmed their assumption by the isolation and characterization of a stable complex of ϵ -caprolactone with magnesium bromide (MgBr_2).

4.2.2. With dialkylmagnesium

Contrary to ϵ -caprolactone with EtMgBr , lactones and lactides were largely investigated with the use of dialkylmagnesium such as Bu_2Mg . Both kind of monomer were shown to be initiated, but their ring-opening polymerization occurred with an uncontrolled manner. The resulting polyesters had molar masses higher than the theoretical values, coupled with very broad distributions, due to transesterification reactions. With the discover of the so-called “immortal” ring opening polymerization in the epoxide chemistry (see paragraph 3.3.1), this polymerization method was investigated toward lactones, lactides and cyclic carbonates[71,72]. Since then, many efforts were devoted to the design of various bulky magnesium, aluminum, calcium, zinc, rare-earth metals complexes. Some of them were found to be efficient in lactide ROP, but limited success were reported for the “immortal” one which is characterized by control of molar masses, low dispersity values and the simultaneous chain end-capping thanks to a suitable chain transfer agent (CTA). In 2012 Chen and coll. reported the use of simple Bu_2Mg with various CTAs and afforded the “immortal” ROP of L-lactide[73]. Alcohols with different steric bulkiness and acidity, including $i\text{PrOH}$, PhCH_2OH , Ph_2CHOH , and Ph_3COH , were employed to “activate” Bu_2Mg . Indeed, in equimolar proportion (alcohol/ Bu_2Mg) no improvement in the polymerization control was observed (Scheme I-15). But when a higher alcohol content was used in diluted solutions the control was achieved. Such a system was also found to be efficient regarding ϵ -caprolactone[74], ω -pentadecalactone[75,76] and other lactones.



Scheme I-15: L-lactide “immortal” polymerization in presence of Bu_2Mg and an excess of biphenylmethanol

This finding therefore provided a low cost and nontoxic catalytic systems which could be envisaged in a large-scale industrial approach toward the production of poly(L-lactide)-based materials.

Aware of the available tools for the synthesis of polyethers by AROP of substituted epoxides and due to the predispositions of magnesium-based compounds to enable several polymerizations, either through an activated monomer mechanism or an activated chain end mechanism or due to its basic character, we decided to investigate the use of magnesium based compounds in the epoxides chemistry for functionalization and control purposes.

5. Grignard-based anionic ring-opening polymerization of propylene oxide activated by triisobutylaluminum

Roos, K.; Carlotti, S. *Eur. Polym. J.* **2015**, *70*, 240–246.[77]

ABSTRACT

Better known as alkylating agent, Grignard reagents are investigated as deprotonating agent of an alcohol to generate magnesium alkoxides for the initiation and propagation of the anionic ring-opening polymerization of propylene oxide. By using an excess of triisobutylaluminum, this magnesium-aluminum system enables a full conversion polymerization in a few hours yielding controlled poly(propylene oxide) up to 10 000 g/mol with relatively low dispersity. Characterizations by NMR and MALDI-ToF-mass spectrometry allowed the determination of the chain-ends and therefore the associated initiation mechanisms. This study revealed that propylene oxide can be polymerized in presence of a magnesium-based counter-ion. Concomitant initiations by alkoxide, halide and hydride are discussed. The absence of transfer to monomer is also highlighted.

KEYWORDS

Grignard reagent, deprotonation, monomer activation, anionic ring-opening polymerization, poly(propylene oxide), polyethers, magnesium counterion

INTRODUCTION

Polyethers are conventionally prepared by anionic ring-opening polymerization using alkali metal derivatives.[6,7] Potassium or cesium hydroxides or alkoxides are well-known candidates as initiators for the synthesis of polyether.[8–11,63] This method is of interest for the controlled functionalization of polymers,[1,78] especially to introduce reactive functions at both chain-ends. However, polymerization of substituted epoxides initiated by alkoxides of alkali metals suffers generally from several drawbacks like transfer reactions to the monomer, sometimes to solvent, slow kinetics and a strong aggregation phenomenon in the case of lithium derivatives.[12,13,18] Transfer to monomer leads to the formation of allylic unsaturations limiting molar masses and functionalization of the prepared polyethers.[15,16] In order to increase the reactivity of the nucleophilic species, crown ethers were added to alkali metal alkoxides to increase the degree of ion-pair separation.[13,22,26] This association enables the preparation of higher molar masses for propylene oxide,[22] tert-butyl glycidyl ether[23,25] and various alkylene oxides,[25] as well as an increase of their polymerization rates which still remain low. Bulky and strong organic bases, called aminophosphazenes, were used as deprotonating agents of alcohols to obtain higher polymerization rates of epoxides.[29,31,79] *t*-BuP₄ was the most used base for this purpose.[38,39,42–44,80] Polymerization systems based on monomer activation developed first by Inoue on propylene oxide were shown to strongly increase the polymerization rates.[48,49] The combination of an aluminum porphyrin as the initiator and a bulky organoaluminum compound such as methylaluminum bis-(2,4,6-tri-*tert*-butylphenolate)[81] allowed the polymerization rate to be multiplied by a factor of 460 compared to the non-activated system initiated by the same porphyrin. We have also shown that the combination of simple alkali metal alkoxides or ammonium salts with triisobutylaluminum allowed the rapid and controlled polymerization of propylene oxide, and other epoxides, for various molar masses at 20°C.[57–59,62] This system presents the specificity to strongly increase the rates of the polymerization due to the monomer activation and to minimize transfer reactions thanks to the weak basicity of the “ate” complex formed as initiating and propagating species.

During the past 100 years Grignard reagents were one of the most widely used organometallic reagents. They are known as strong nucleophiles and react with a broad range of electrophilic substrates. The reaction with aldehydes, ketones, esters, acids and amides are the most useful reactions in organic chemistry for the formation of C-C-bonds.[82,83] Grignard reagents are also valuable bases and can deprotonate a variety of acidic compounds such as water, alcohols and amines to form the corresponding alkane (R-H) and magnesium hydroxides, alkoxides or amides.[84,85] The basicity of Grignard reagents is comparable with organolithium-reagents, although the latter are stronger and more widely used for this purpose. Grignard reagents are particularly known to be used in the polymerization of ϵ -Caprolactam (CL). Obtained from the deprotonation of CL by an alkyl magnesium bromide, ϵ -caprolactamate of magnesium bromide constitutes part of a fast catalytic system for the synthesis of polyamide 6 by “reaction injection molding”[69]. Recently, ethyl magnesium bromide was used as an anionic initiator for the controlled polymerization of ϵ -caprolactone[70]. The polymerization abilities of magnesium systems seem to be not enough explored in particular with epoxide monomers.

In this study, we report the use of Grignard reagents as deprotonating agent of an alcohol to generate initiators and growing centers, in combination with triisobutylaluminum, for the synthesis of poly(propylene oxide).

Experimental Section

Material

Propylene oxide (PO, 99%, Sigma Aldrich) was purified over CaH_2 , distilled and stored under vacuum at room temperature in graduated glass tubes until use. 2-Methyltetrahydrofuran (MeTHF, 98%, Sigma Aldrich) was stored over sodium/benzophenone mixture and kept under vacuum for further distillation until use. Triisobutylaluminum ($i\text{-Bu}_3\text{Al}$, 1 M in toluene, Aldrich), anhydrous 1-butanol (But-OH, 99.8%, Sigma Aldrich), methylmagnesium bromide (MeMgBr, 1.4M in THF/Toluene (1:3)), isopropylmagnesium bromide (iPrMgBr, 2.9M in MeTHF, Sigma Aldrich), methylmagnesium chloride (MeMgCl, 3M in THF, Sigma Aldrich), were used without further purification.

Analysis

Polymer molar masses were determined by Size Exclusion Chromatography (SEC) using THF as the eluent. Measurements in THF were performed on a PL GPC50 integrated system with RI and UV detectors and three TSK columns: G4000HXL (particles of 5 mm, pore size of 200A, and exclusion limit of 400 000 g/mol), G3000HXL (particles of 5 mm, pore size of 75A, and exclusion limit of 60 000 g/mol), G2000HXL (particles of 5 mm, pore size of 20A, and exclusion limit of 10 000 g/mol) at an elution rate of 1mL/min. Polystyrene was used as the standard.

^1H and ^{13}C NMR analyses of the polymers were performed on a Bruker Avance 400 spectrometer in CDCl_3 at room temperature.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToFMS) was performed by the CESAMO (Bordeaux, France) on a Voyager mass spectrometer (Applied Biosystems). The instrument is equipped with a pulsed N_2 laser (337 nm) and a time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron and with an accelerating voltage of 20 kV. Samples were dissolved in CH_2Cl_2 at 10 mg/mL. The DIT matrix (1,8-Anthracenetriol) solution was prepared by dissolving 10 mg in 1 mL of CH_2Cl_2 . A MeOH solution of cationisation agent (NaI, 10 mg/mL) was also prepared. The solutions were combined in a 10:1:1 volume ratio of matrix to sample to cationisation agent. One to two microliters of the obtained solution was deposited onto the sample target and vacuum-dried.

General Procedure for propylene oxide polymerization

Initiator 1-butanol was deprotonated by an alkylmagnesium halide base (1 eq. of RMgX by hydroxyl group) in dried MeTHF. All polymerizations were initiated at $-30\text{ }^\circ\text{C}$ under argon in a glass reactor equipped with a magnetic stirrer and fitted with Teflon stopcocks. As an example, a polymerization reactor was flamed under vacuum and cooled down prior to the introduction of 5.4 mL of dried MeTHF. Then 0.82 mL (0.4 mmol) of a solution ($C = 0.49\text{ M}$) of deprotonated 1-butanol with MeMgBr followed by 1.5 eq of $i\text{-Bu}_3\text{Al}$ (0.6mmol, 0.6 mL, 1 M) were added via syringes under dynamic argon flow. Finally 1.2 mL of dried PO was added through a connected glass tube. The polymerization was started at $-30\text{ }^\circ\text{C}$ and let to go to $20\text{ }^\circ\text{C}$ for 16 h. Methanol was used to stop the reaction. The monomer conversion (100 %) was determined

gravimetrically after complete drying of the polymer under vacuum at 50 °C. Conversion: 100 %. Theoretical \overline{Mn} =2 500 g/mol and SEC \overline{Mn} =5 400 g/mol. \overline{D} =1.24.

RESULTS & DISCUSSION

One of the main drawbacks of magnesium species is their poor solubility in apolar media. Indeed they are usually prepared in ethereal solvents such as THF or diethylether. They are soluble in numbers of aprotic solvents, when oxygen or nitrogen electron-rich-atoms enable the formation of complexes with magnesium. Preliminary experiments revealed that THF could not be used in epoxide polymerization in presence of triisobutylaluminum due to competitive complexation, making aluminum compound no more available for epoxide activation and thus yielding no polymerization. Because of these solubility issues and undesired aluminum complexation by THF, 2-methyltetrahydrofuran (MeTHF) was used. MeTHF is being increasingly used both in organic chemistry and biocatalysis. Although it is an ether-type solvent, it resembles to toluene in terms of physical properties.[86] It was therefore used to dissolve magnesium derivatives and to conduct polymerization of propylene oxide.

Table 1 attests of propylene oxide polymerizability initiated by different magnesium alkoxides in presence of triisobutylaluminum used as an activator. Always starting from 1-butanol, various alkylmagnesium halides were tested to investigate the deprotonation and the initiation step. All the polymers obtained present a monomodal size exclusion chromatography (SEC) distribution. Entries 1 and 2 confirm the key role of aluminum derivative on the polymerization time. As compared to ammonium salts in previous articles, it has been shown that an excess of triisobutylaluminum was needed to achieve the polymerization.[58] But differently, the use of a default of the aluminum compound as compared to the magnesium one enabled the polymerization characterized by long reaction time. This suggests a residual activation ability of the aluminum derivative complexed with the chain end. The formation of an alkoxide/Mg/Al complex is believed to exist as no or limited transfer to monomer is observed. This point will be discussed further. Comparison between entries 2, 3 and 4 does not reveal any effect by varying the Grignard nature. Alkoxides of

magnesium-bromide or magnesium-chloride by alcohol deprotonation are expected. Conversion, distribution, and molar mass remain similar.

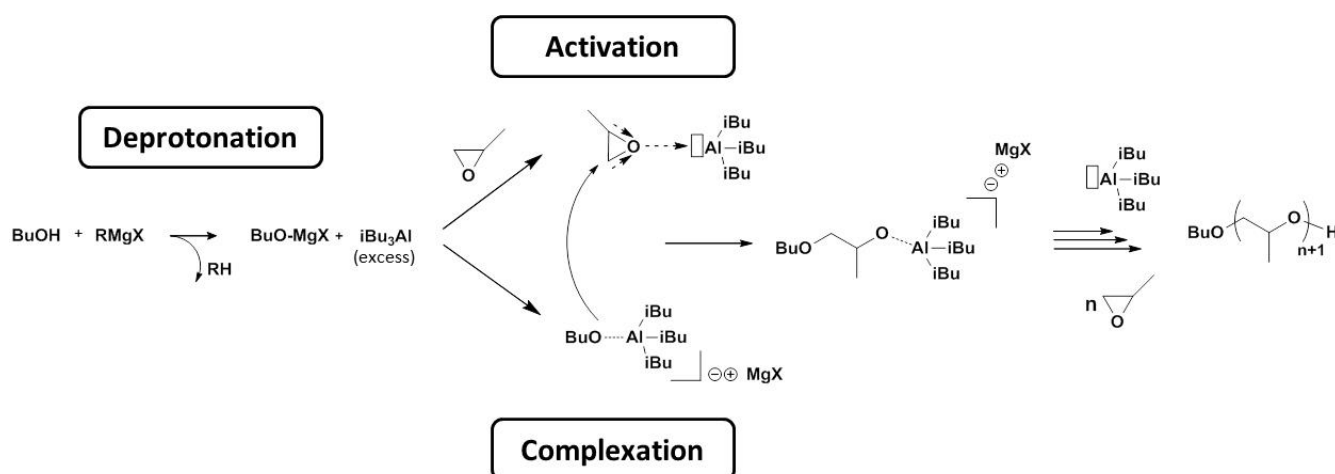
Table 1: Polymerization of propylene oxide initiated by 1-butanol deprotonated by RMgX and in the presence of *i*-Bu₃Al in MeTHF ([ROMgX] = 0.055 mol/L, conversion = 100 %)

Run	Deprotonating agent	OH/RMgX/ <i>i</i> -Bu ₃ Al	[PO] mol/L	Time (h)	\overline{Mn}_{th} (g/mol)	\overline{Mn}_{exp}^a (g/mol)	\overline{D}^a
1	Me-MgBr	1/1/0.5	2.36	67	2 500	3 400	1.20
2	Me-MgBr	1/1/1.5	2.36	16	2 500	5 400	1.23
3	<i>i</i> Pr-MgBr	1/1/1.5	2.36	16	2 500	4 900	1.20
4	Me-MgCl	1/1/1.5	2.36	16	2 500	5 100	1.24
5	Me-MgBr	1/1/1.5	4.75	24	5 000	9 800	1.39
6	Me-MgBr	1/1/2.0	9.47	24	10 000	18130	1.37

^adetermined by size exclusion chromatography in tetrahydrofuran using a calibration with polystyrene standards.

Regarding the evolution of molar masses, it is in agreement with the variation of the feed ratio [PO]/[ROMgX], see runs 4 to 6, Table 1. A difference is generally observed between theoretical and experimental molar mass obtained from SEC (RI detector) with PS standards. This finding supposes also a somewhat incomplete initiation efficiency. The use of a viscosimetric detector for selected samples confirmed higher molar masses than theoretical ones. This finding supposes a somewhat incomplete efficiency. In addition, it was observed that propylene oxide concentration must be increased for a given magnesium alkoxide concentration to get polymerization and full monomer conversion.

Concerning the main mechanism involved in the polymerization, the first step suggests the deprotonation of the starting alcohol by a Grignard reagent, releasing the corresponding alkane (Scheme 1). Then, 1 equivalent of *i*-Bu₃Al is used to generate an “ate” complex with the magnesium-based alkoxide. The so-generated complex is then available to ring open propylene oxide units activated by an excess of *i*-Bu₃Al.



Scheme 1: Main mechanism of the anionic ring-opening polymerization of propylene oxide initiated by the system $\text{BuOH/RMgX/i-Bu}_3\text{Al}$

^{13}C DEPT135 and ^1H NMR characterizations were first proposed to identify the initiation step (Figures 1 and 2). (a), (b), (c), (d) Labels can be assigned to carbons and protons of butoxy end groups. (e), (f), (g) are assigned to carbons and protons of propylene oxide repeating units. The carbon (d) from the butoxy group is shifted to higher chemical shifts as compared to its homolog in butanol. Moreover, a zoom on the area of allylic carbons and protons does not reveal any trace of unsaturated species indicating no contribution of transfer to monomer usually observed in conventional anionic ring-opening polymerization of substituted epoxides.[15,16] Peaks labelled with asterisk are assigned to other types of initiation instead of the expected alkoxide one. This point is discussed with the following MALDI-ToF characterization.

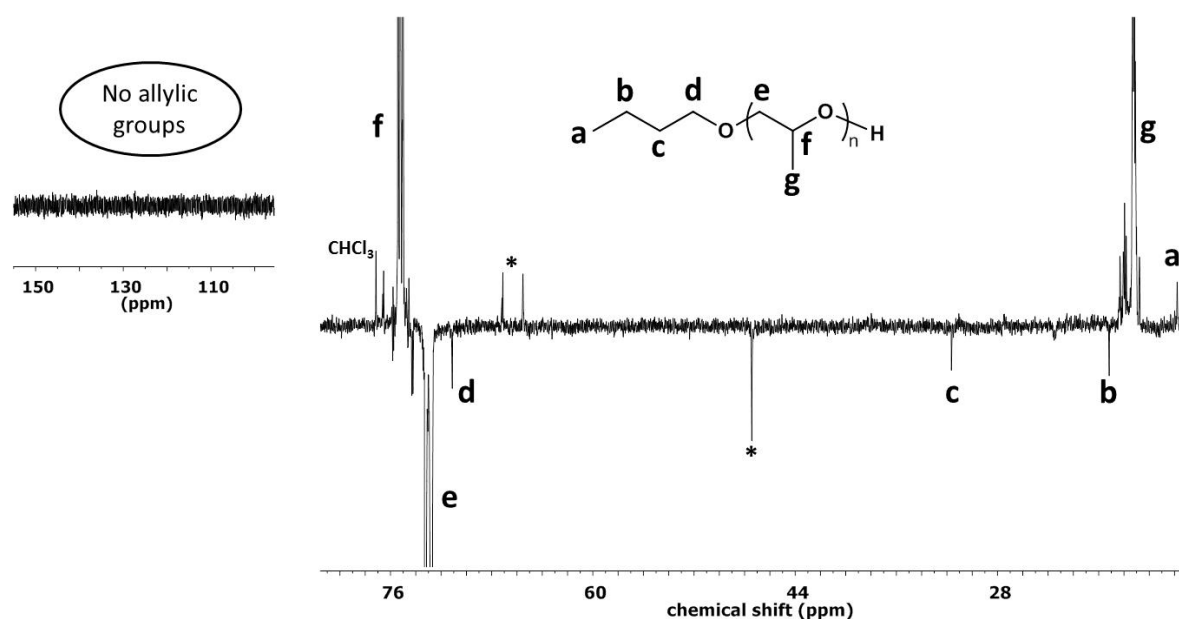


Figure 1: ^{13}C DEPT135 NMR spectrum of poly(propylene oxide) (from run 4) in CDCl_3 . The material was prepared using deprotonated 1-butanol with MeMgCl in presence of 1.5eq $i\text{-Bu}_3\text{Al}$. Zoom on the area of allylic carbons

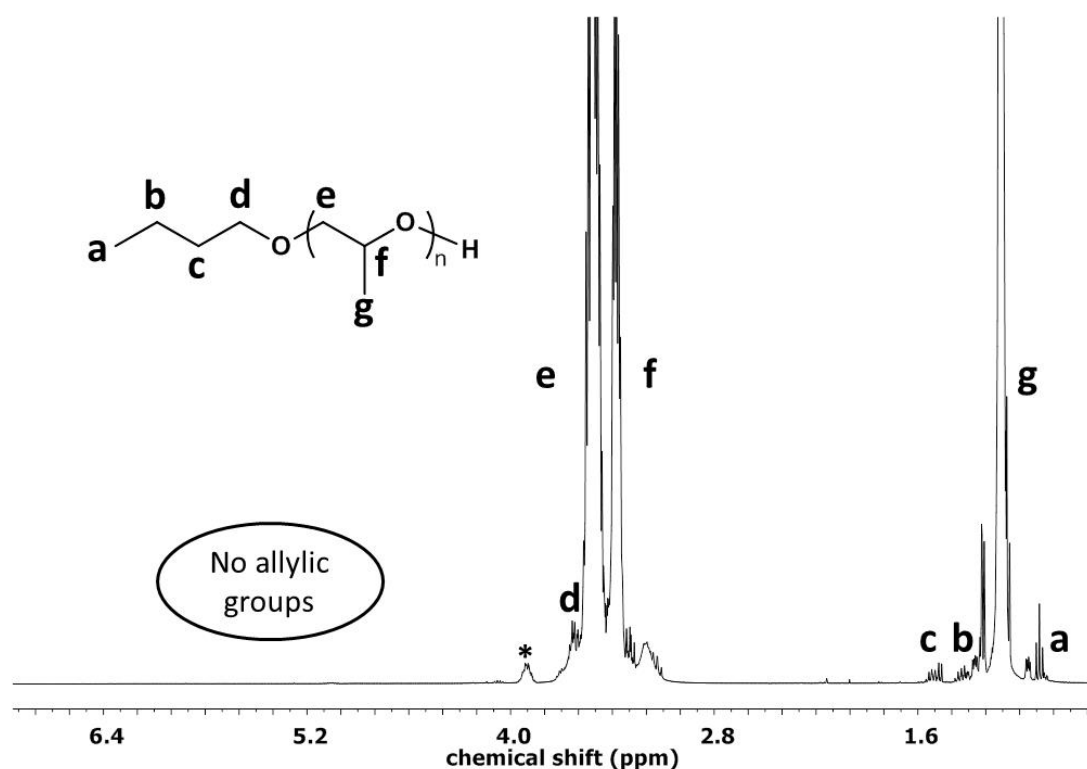


Figure 2: ^1H NMR spectrum of poly(propylene oxide) (from run 4) in CDCl_3 . The material was prepared using deprotonated 1-butanol with MeMgCl in presence of 1.5eq $i\text{-Bu}_3\text{Al}$.

NMR results confirm at first the synthesis of poly(propylene oxide). Question of chain ends needs to be investigated further in order to better understand the mechanism of the initiation step. MALDI-ToF-MS analyses were performed on PPO (entries 2 and 4 Table 1). The overall spectrum (Figure 3) illustrates a usual pattern of polyether and exhibits here the presence of different populations. A precise focus on peak series enables to distinguish three populations (Figures 3 and 4). Those two figures are differentiated by the nature of the halide of the Grignard used, i.e. bromide (Figure 3) or chloride (Figure 4).

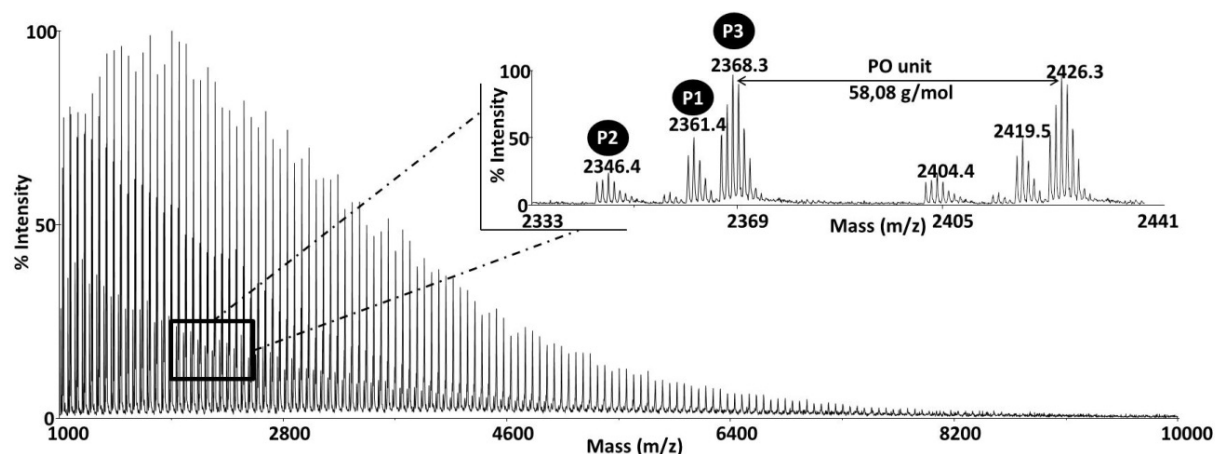


Figure 3: General and enlarged MALDI-TOF spectrum of PPO ($\overline{M}_n = 2500$ g/mol) initiated by BuOH/MeMgBr/*i*-Bu₃Al (1/1/1.5)

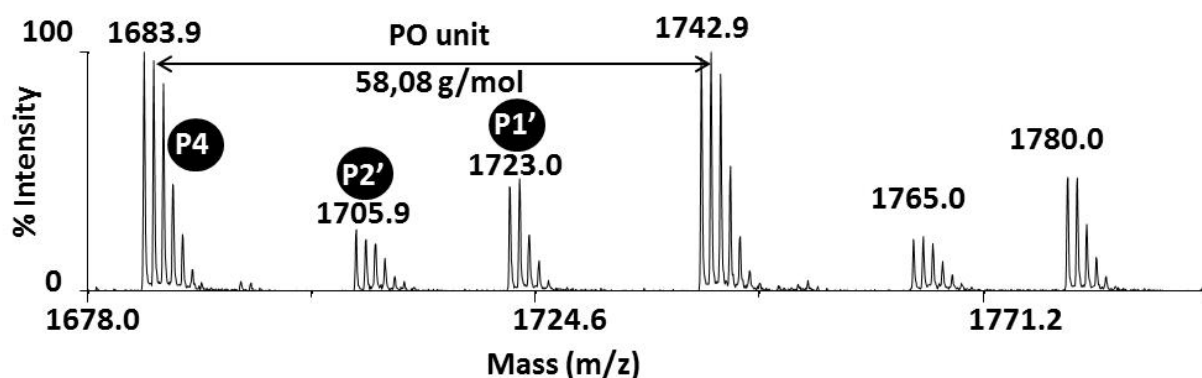


Figure 4: Enlarged MALDI-TOF spectrum of PPO ($\overline{M}_n = 2500$ g/mol) initiated by BuOH/MeMgCl/*i*-Bu₃Al (1/1/1.5)

The expected P1 and P1' peak series, for both polymers, with molar masses corresponding to PPO chains with deprotonated alcohol and hydroxide end groups, are observed in agreement with alkoxide initiation and proton termination.

$$P1 = 2361.4 \text{ g/mol} = M_{Na} + M_{C_4H_9O} + n \times M_{PO} + M_H \quad (M_{C_4H_9O} = 73.1 \text{ g/mol and } n = 39) \text{ and } P1' = 1723.0 \text{ g/mol} = M_{Na} + M_{C_4H_9O} + n \times M_{PO} + M_H \quad (M_{C_4H_9O} = 73.1 \text{ g/mol and } n = 28).$$

A second population P2 and P2' which appears in low proportion as compared to P1 can correspond to a PPO with an hydrogen in the α position (H-PPO-OH) coming from the transfer reaction to $i\text{-Bu}_3\text{Al}$. [58]

$$P2 = 2346.4 \text{ g/mol} = M_{Na} + n \times M_{PO} + 2 M_H \quad (n = 40) \text{ and } P2' = 1705.9 \text{ g/mol} = M_{Na} + n \times M_{PO} + 2 M_H \quad (n = 29).$$

According to calculations and literature, P2 and P2' could also be assigned to PPO chains with allyloxy and hydroxide end groups [15,16,87] or even to PPO chains with isobutyl and hydroxide end groups. [52,54] However, looking at the allylic and aliphatic regions of NMR spectra of those polymers, no peak characteristic of respectively transfer to monomer or isobutyl initiation is observed, as also shown in another work. [57] P2 and P2' were therefore mainly attributed to hydride initiation.

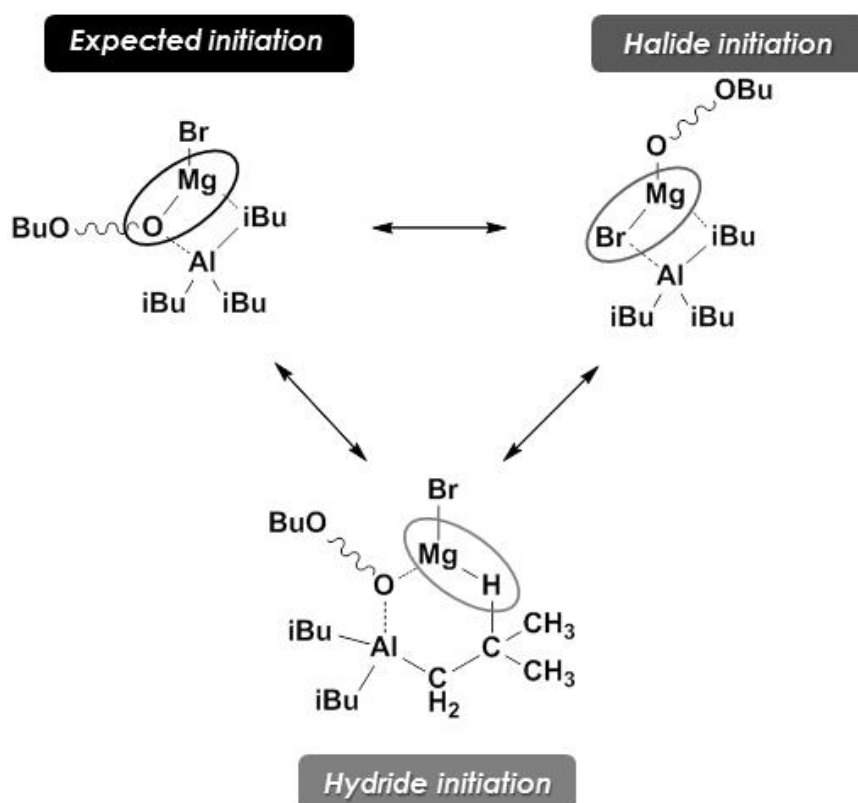
In both cases the major peaks P3 (Figure 3) and P4 (Figure 4) are assigned to a PPO with respectively bromine/hydroxide and chlorine/hydroxide end groups, in agreement with halide initiation and proton termination.

$$P3 = 2368.3 \text{ g/mol} = M_{Na} + M_{Br} + n \times M_{PO} + M_H \quad (n = 39) \text{ and } P4 = 1683.9 \text{ g/mol} = M_{Na} + M_{Cl} + n \times M_{PO} + M_H \quad (n = 28).$$

The functionalization quantification is then estimated by cumulated integrations of peak areas on the whole spectra. No matter the Grignard used, 50% of polyether chains are halide functionalized (P3 or P4), 30% are functionalized by alkoxide (P1 and P1') and 20% are hydride initiated (P2 and P2'). Moreover P1 or P1' and P4 population corroborates NMR results. Indeed, peaks at 47.60, 65.7 and 67.3 ppm labelled by asterisk are respectively assigned to $\text{Cl-}\underline{\text{C}}\text{H}_2\text{-CH}(\text{CH}_3)\text{-O-}$; $\text{H-CH}_2\text{-}\underline{\text{C}}\text{H}(\text{CH}_3)\text{-O-}$ and $\text{Cl-CH}_2\text{-}\underline{\text{C}}\text{H}(\text{CH}_3)\text{-O-}$ on the ^{13}C NMR spectrum (Figure

1). As well as ^1H NMR (Figure 2), the multiplet at 3.90 ppm is attributed to $\text{Cl}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O}-$. All these signals correspond to the initiated propylene oxide unit.

In the presence of onium salts it is assumed that hydride initiation comes from an hydride abstraction of an isobutyl group of triisobutylaluminum.[58] Here we can propose a similar six-membered specie involving hydride, and four membered species for growing magnesium alkoxide and magnesium halide. Considering this result, the polymerization mechanism (Scheme 1) can be extrapolated to suggest different initiating species (Scheme 2). Indeed, three active complexes involving Mg-heteroatom or Mg-hydride bonds are proposed. Monomodal SEC distributions and relatively low dispersities lead to think that all kinds of initiation are concomitant. Analogous pattern of the two MALDI-ToF spectra confirm results emphasized in table 1, bromine or chlorine-based Grignard reagents does not significantly influence the macromolecular dimensions neither the percentage of initiation by alkoxide.



Scheme 2: Proposed active species for different kind of initiation.

The less expected result comes from halide initiation. The experiments showed that halide end groups are present in the biggest proportion whatever the kind of Grignard used. In 1902, Blaise, obtained ethylene bromohydrin as the predominant product from the reaction of ethylene oxide and ethylmagnesium bromide.[88] To explain this product a method of cleavage of organomagnesium compounds was postulated: namely, instead of the usual dissociation into the groups R and MgBr, a splitting into RMg and Br occurred upon hydrolysis with water, giving the bromohydrin, $\text{BrCH}_2\text{CH}_2\text{OH}$. In the case of deprotonation, the R group is no longer present but this result indicates this splitting still occurs leading to a reactive complex involving halides.

Besides, Grignard reagents or even magnesium based compounds are also known to form polynuclear complexes [89–91] and can be expected to be formed in these experimental conditions which can explain an incomplete initiation efficiency. Nevertheless, the molar mass control and the chain-end functionalization remains the key features of this system.

CONCLUSION

Simple Grignard reagents were first used to deprotonate an alcohol. Then the so-formed magnesium alkoxides initiate the anionic ring-opening polymerization of propylene oxide in the presence of a trialkylaluminum as complexing and activating agent. Molar masses are shown to be dependent on the initial ratio $[\text{Monomer}]/[\text{Mg derivative}]$. Analysis of chain ends demonstrated the occurrence of several modes of initiation, from i) the expected alkoxide magnesium halide ($\text{RO}^- \text{MgX}$), ii) the hydride coming from the triisobutylaluminum ($\text{H}^- \text{MgX}$), and iii) the halide from the alkoxide magnesium halide ($\text{X}^- \text{MgOR}$).

As we demonstrated that the use of a magnesium active specie combined with triisobutyl aluminum enabled the propylene oxide polymerization, but that the main initiation was coming from the halide, we decided to investigate an halide free system by using dialkylmagnesium derivatives.

6. Dialkylmagnesium-promoted deprotonation of protic precursors for the activated anionic ring-opening polymerization of epoxides

Kévin Roos^{1,2,3}, Anne-Laure Wirotius^{1,2,3}, Stéphane Carlotti*^{1,2,3}

ABSTRACT

Dialkylmagnesium (R_2Mg) compounds are investigated as deprotonating agents of various protic functions to form reactive precursors for the anionic ring-opening polymerization of epoxides, i.e. ethylene oxide, propylene oxide, butylene oxide and methyl glycidyl ether, activated by triisobutylaluminum ($i\text{-Bu}_3\text{Al}$). Experiments show a polymerizability of those monomers with the proposed system, short reaction times (hours) and a molar mass control up to 10 000 g/mol. Protic moieties such as alcohol, thiol, amine, and alkyne were first deprotonated and then shown to initiate polyether chains. A precise study of the nature of the α -end-capping of the polyether chains is presented. Monohydroxy terminated poly(ethylene oxide) and poly(dimethyl siloxane) were also used as macroinitiator after deprotonation by R_2Mg for the polymerization of propylene oxide in the presence of $i\text{-Bu}_3\text{Al}$ in order to get block copolymers.

KEYWORDS

Dialkylmagnesium, deprotonation, epoxide, anionic ring-opening polymerization, block copolymers, polyethers, monomer activation

INTRODUCTION

The anionic ring-opening polymerization (AROP) of epoxides was first described by Staudinger in 1933 and Flory in 1940. It is an important polymerization method of epoxides widely used in academia and industry due to its affordability and specific features of the corresponding polymers[2]. The initiation can be performed with basic alkali metal derivatives like hydrides, alkyls, aryls, amides, and mostly alkoxides of sodium, potassium, and cesium[1,92]. The polymerization rate constant increasing with the size of the counter ion ($\text{Na}^+ < \text{K}^+ < \text{Cs}^+$)[8]. The main approach consists in deprotonating an alcohol next able to initiate the polymerization. The formation of these alkali derivatives (i.e. $\text{KOH} + \text{ROH} \rightarrow \text{ROK} + \text{H}_2\text{O}$) involves a step of deprotonation and the rigorous drying to remove the water formed when starting from alkali metals hydroxide[93,94]. Potassium is more often used due to its good efficiency toward polymerization and its low cost despite transfer to substituted epoxides[15,95–99]. Cesium counter-ion is shown to exhibit a higher polymerization rate than potassium and a reduction of unsaturated species due to transfer to monomer, but it remains less used.

A family of extremely strong Brønsted bases called phosphazene superbases[28], were also employed as effective organic catalysts or promoters for the polymerization of various types of monomers, including epoxides[16,29,38–41,65,100,101]. Due to their high basicity, non-nucleophilic nature, good solubility in a wide range of solvents and easy handling, phosphazene bases can be readily used to turn protic moieties into nucleophilic initiating sites through deprotonation or activation of weak nucleophiles. Hydroxyl groups were the most commonly employed protic moieties due to their wide variety and high availability. Some recent reports have also demonstrated the deprotonation of other protic precursors, i.e. thiol[35–37,31], amide[44,80] and carboxylic acid[42] for effective polymerizations of cyclic monomers with mostly t-BuP₄ superbase. The obtention of hydroxy telechelic poly(propylene oxide) appears still limited by transfer to monomer reactions, giving chains initiated by an allyloxy group and limiting the molar masses. Their actual high cost may also limit their use in industry.

Besides, some studies have shown that a simple dibutylmagnesium (Bu_2Mg) enables the synthesis of polyesters by ring-opening polymerization of lactides or lactones with residual transesterification side reactions[102–106]. Alcohols with different steric bulk and acidity,

including *i*PrOH, PhCH₂OH, Ph₂CHOH, and Ph₃COH, were employed with Bu₂Mg to form magnesium alkoxides. The generated systems were shown to improve the polymerizability of cyclic esters in dilute solutions by increasing the molar masses and narrowing the dispersity values where alcohols act as control transfer agents (CTAs) [74–76,107].

We demonstrated in a previous work that propylene oxide can be polymerized with magnesium alkoxides (ROMgX) prepared from Grignard precursors in combination with triisobutylaluminum[77]. Starting from an alcohol, Grignard reagents were used as sustainable deprotonating agents for the generation of alkoxides of magnesium halide. The so-formed active species were able to initiate and polymerize propylene oxide in a controlled way. Competitive initiations were nevertheless observed. The main one was arising from the halide derivative of the Grignard. The work presented in this article concerns a halide-free system based on dialkylmagnesium compounds used as deprotonating agents of protic precursors for the anionic ring-opening polymerization of epoxides.

Experimental Section

Chemicals

Unless otherwise stated, all the products were purchased from Sigma Aldrich/Fluka. Ethylene oxide (EO, 99 %), propylene oxide (1,2-epoxypropane, PO, 99 %), butylene oxide (1,2-epoxybutane, BO, 99 %), and glycidyl methyl ether (2-(methoxymethyl)oxirane, GME, >85 %, TCI) were purified over CaH₂ and freshly distilled before use in graduated glass tubes. 2-Methyltetrahydrofuran (MeTHF, 98 %) was stored over sodium/benzophenone mixture and kept under vacuum for further distillation prior to use. Cyclohexane (99 %) was stored over polystyryllithium seeds and kept under vacuum for further distillation until use. 1,4-Dioxane (99 %) was stored over calcium hydride, degassed during 24 hours and finally kept under vacuum for further distillation until use. Triisobutylaluminum (*i*-Bu₃Al, 1 M in toluene), *n*-butyl-sec-butylmagnesium solution (*n*,*s*-Bu₂Mg, 0.7 M in hexane), ethylmagnesium bromide solution (EtMgBr 3 M in diethylether Et₂O) were used without further purification. 2,4-Dimethyl-3-pentanol (DMP, 99%), 2-allylphenol (98 %), 2-tert-butylaniline (98 %), benzyl mercaptan (99 %), 1-heptyne (98 %), N-benzylmethylaniline (97 %) were used as received.

Poly(dimethylsiloxane) monohydroxy-terminated (\overline{Mn} = 4670 g/mol), poly(ethylene glycol) methyl ether (\overline{Mn} = 1100 g/mol), poly(propylene glycol) monobutyl ether (\overline{Mn} = 1000 g/mol) were azeotropically dried 3 times with dry MeTHF prior to use.

Instrumentations

Size Exclusion Chromatography

Polymer molar masses were determined by Size Exclusion Chromatography (SEC) using THF as the eluent. Measurements in THF were performed on a PL GPC50 integrated system with RI and UV detectors and four TSK columns: HXL-L (guard column), G4000HXL (particles of 5 mm, pore size of 200A, and exclusion limit of 400 000 g/mol), G3000HXL (particles of 5 mm, pore size of 75A, and exclusion limit of 60 000 g/mol), G2000HXL (particles of 5 mm, pore size of 20 A, and exclusion limit of 10 000 g/mol) at an elution rate of 1mL/min. Polystyrene was used as the standard.

Nuclear Magnetic Resonance

^1H NMR, ^{13}C NMR, DEPT135 NMR spectra were recorded on a Bruker AC-400 spectrometer in appropriate deuterated solvents. DOSY (Diffusion Ordered Spectroscopy)[108–110] NMR measurements were performed at 298 K on a Bruker Avance III 400 spectrometer in CDCl_3 at room temperature 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, 3 mg were dissolved in 0.4 mL of CDCl_3 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 2.5 ms for the duration of the gradient pulses and 300 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 10 s between echoes was used. The data were processed using 8192 points in the F2 dimension and 64 points in the F1 dimension with the Bruker topspin software. Field gradient calibration was accomplished at 25 °C using the self-diffusion coefficient of $\text{H}_2\text{O}+\text{D}_2\text{O}$ at $19.0 \cdot 10^{-10} \text{ m}^2.\text{s}^{-1}$.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToFMS)

Analyses were performed by the CESAMO (Bordeaux, France) on a Voyager mass spectrometer (Applied Biosystems). The instrument is equipped with a pulsed N₂ laser (337 nm) and a time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron and with an accelerating voltage of 20 kV. Samples were dissolved in CH₂Cl₂ at 10 mg/mL. The DIT matrix (1,8-Anthracenetriol) solution was prepared by dissolving 10 mg in 1 mL of CH₂Cl₂. A MeOH solution of cationisation agent (NaI, 10 mg/mL) was also prepared. The solutions were combined in a 10:1:1 volume ratio of matrix to sample to cationisation agent. One to two microliters of the obtained solution was deposited onto the sample target and vacuum-dried.

Kinetic Measurements

Dilatometry measurements were performed using a glass dilatometer previously flamed under vacuum. After introduction of magnesium and aluminum compounds under argon using syringes, the solvent was evaporated under vacuum. Then cyclohexane was added to set the desired concentration and the system was thermostated at 0 °C. Propylene oxide was finally added through connected glass tubes. Monitoring of the reaction was immediately followed by recording the volume level of the solution in the capillary tube attached to the reactor.

Experimental procedure

General Procedure for epoxide polymerization

As an example, 2,4-dimethyl-3-pentanol (DMP) (5 mmol, 0.7 mL) was deprotonated by *n*-butyl-sec-butyl magnesium (*n,s*-Bu₂Mg) (2.5 mmol, 3.6 mL, corresponding to one equivalent of alkyl group per hydroxyl group) in 10 mL of dry MeTHF. All polymerizations were initiated at -30 °C under dry argon in a glass reactor equipped with a magnetic stirrer and fitted with Teflon stopcocks. The polymerization reactor was flamed under vacuum and cooled down prior to the introduction of 5.4 mL of dry MeTHF. Then 0.8 mL (0.4 mmol) of a solution (C = 0.5 M) of deprotonated DMP with *n,s*-Bu₂Mg followed by 1.5 eq of *i*-Bu₃Al (0.6 mmol, 0.6 mL, 1 M) were added via syringes under dynamic argon flow. Finally 1.2 mL of dried propylene oxide was added through a connected glass tube. The polymerization was started at -30 °C

and let to go to 20 °C for 16 h. Methanol was used to stop the reaction. The monomer conversion (100%) was determined gravimetrically after complete drying of the polymer under vacuum at 50 °C. Theoretical \overline{Mn} = 2500 g/mol and SEC \overline{Mn} = 4400 g/mol. \overline{D} = 1.15. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 2.60 ($((\text{CH}_3)_2\text{CH})_2\text{CH-O-PPO}$), 3.2–3.7 ($-\text{O}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_n-$), 1.08 ($-\text{O}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_n-$).

Procedure for the synthesis of diethylmagnesium Et_2Mg

Based on the shift of the Schlenk equilibrium[111] toward the formation of dialkylmagnesium, 4.65 mL (14 mmol) of ethylmagnesium bromide solution (3 M in diethylether Et_2O) were introduced in a glass reactor under dynamic argon flow. This reactor equipped with a magnetic stirrer and fitted with Teflon stopcocks was previously flamed under vacuum and cooled prior any reagents introduction. Then, 10 mL of dry dioxane were added. The instantaneous precipitation of MgBr_2 salts was observed. In a first time, the whole solvent was coarsely evaporated to remove the diethylether from the Grignard solution. Then 10 mL more of dry dioxane were added. The undesired white solid was filtered out through a previously flamed connected sintered glass funnel (4 to 8 μm) to give a limpid solution of Et_2Mg in dioxane. The solvent was finally removed by evaporation under vacuum over-night at 40 °C. The remaining solid was re-dissolved by addition of 10 mL of dry MeTHF and yielding a limpid solution of Et_2Mg (0.7 M).

RESULTS & DISCUSSION

Based on Kamienski report[112], a molar ratio 1/0.5 ($\text{OH}/n,s\text{-Bu}_2\text{Mg}$) was chosen to form the magnesium dialkoxide. 2,4-Dimethyl-3-pentanol was deprotonated with either *n*-butyl-sec-butylmagnesium ($n,s\text{-Bu}_2\text{Mg}$) or diethylmagnesium (Et_2Mg) and used as initiator for substituted epoxides, i.e. propylene oxide (PO) and butylene oxide (BO), polymerization in the presence of triisobutylaluminum (Table 1). All the polymers obtained present a monomodal distribution observed from size exclusion chromatography (SEC). As compared to our previous work based on Grignard reagents used as deprotonating agents[77], a trialkylaluminum is mandatory to enable the polymerization (runs 1 and 2, Table 1). Using an excess allows to decrease strongly the polymerization times (runs 3 and 4, Table 1). Regarding the polymerization completion, full monomer conversion is almost reached after 5 hours of

reaction with 1.5 eq of $i\text{-Bu}_3\text{Al}$. After termination with methanol, residual Mg and Al salts are removed by filtration.

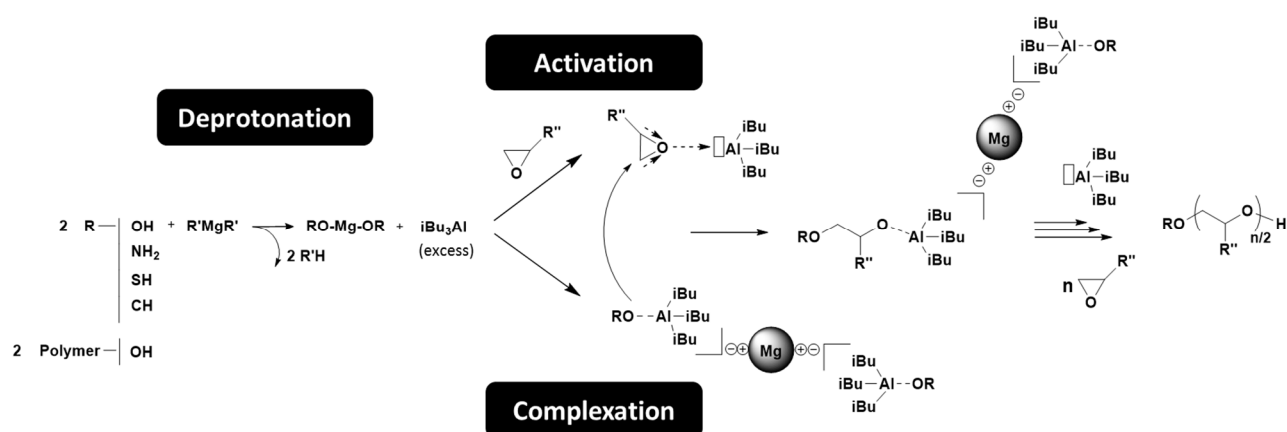
Butylene oxide (BO) was then polymerized with two different dialkylmagnesium. According to Table 1 (runs 5 and 6), alkoxides obtained from $n,s\text{-Bu}_2\text{Mg}$ and Et_2Mg have the same ability to polymerize BO. Used without alcohol, but in presence of Et_2Mg (run 7, Table 1), the polymerization still occurs with some decrease of the molar mass of the polyether chains. The nature of the initiator(s) will be discussed further. Increasing of the molar mass up to 10 000 g/mol was also successful only when the monomer concentration was increased in the reaction medium (runs 8 and 9, Table 1).

Table 1: Polymerization of propylene oxide and butylene oxide initiated by the system $\text{OH}/n,s\text{-Bu}_2\text{Mg}/i\text{-Bu}_3\text{Al}$ in 4-methyltetrahydrofuran ($\text{OH} = 2,4\text{-dimethyl-3-pentanol}$, $[\text{OH}]_0 = 0.05 \text{ mol/L}$)

Run	Monomer (M)	$[\text{M}]_0$ mol/L	Deprotonating agent (R_2Mg)	$\text{OH}/\text{R}_2\text{Mg}/$ $i\text{-Bu}_3\text{Al}$	Time (h)	Conv %	$\overline{Mn}_{\text{calcd}}^a$ (g/mol)	$\overline{Mn}_{\text{exp}}^b$ (g/mol)	\overline{D}^b
1	PO	2.15	$n,s\text{-Bu}_2\text{Mg}$	1/0.5/0	65	0	-	-	-
2	PO	2.15	$n,s\text{-Bu}_2\text{Mg}$	1/0.5/0.8	65	100	2 612	4 500	1.16
3	PO	2.15	$n,s\text{-Bu}_2\text{Mg}$	1/0.5/1.5	5	92	2 415	3 800	1.13
4	PO	2.15	$n,s\text{-Bu}_2\text{Mg}$	1/0.5/1.5	16	100	2 612	4 300	1.27
5	BO	1.74	$n,s\text{-Bu}_2\text{Mg}$	1/0.5/1.5	24	100	2 624	4 400	1.18
6	BO	1.74	Et_2Mg	1/0.5/1.5	24	100	2 624	3 740	1.27
7	BO	1.74	Et_2Mg	0/0.5/1.5	24	100	2 624	1 600	1.32
8	BO	3.47	$n,s\text{-Bu}_2\text{Mg}$	1/0.5/1.5	24	100	5 163	7 700	1.44
9	BO	6.94	$n,s\text{-Bu}_2\text{Mg}$	1/0.5/1.5	24	100	10 139	11 300	1.37

^a $\overline{Mn}_{\text{calcd}} = ([\text{M}]_0/[\text{OH}]_0 \times M_M) \times \text{conv. (\%)} + 115.2$. ^bDetermined by size exclusion chromatography in tetrahydrofuran using a calibration with polystyrene standards.

The main mechanism involved in the polymerization suggests, as a first step, the deprotonation of the starting alcohol by the dialkylmagnesium, releasing the corresponding alkane (Scheme 1). Then, part of the alkylaluminum is consumed by the resulting magnesium alkoxides. The thus-generated complex is then available to ring-open an epoxide activated by one remaining molecule of $i\text{Bu}_3\text{Al}$.



Scheme 1: General mechanism of the anionic ring-opening polymerization of epoxide initiated by the system ROH/R'₂Mg/i-Bu₃Al

¹H NMR and ¹³C DEPT135 characterizations are first proposed to identify proton and carbon atoms belonging to 2,4-dimethyl-3-pentanoxy end-group from the PBO (run 5, Table 1). Indeed (a,A), (b,B), (c,C) labels can be respectively assigned to protons (0.92; 1.79; 2.60 ppm) and carbons (20.6; 31.0; 90.7 ppm) from DMP end-group (Figure 1 and 2). (d,D), (e,E), (f,F), (g,G) are assigned to protons and carbons of butylene oxide repeating units. The proton and carbon signals (c, C) from the methine group of the initial 2,4-dimethyl-3-pentanol are shifted from 3.01 ppm and 81.8 ppm to 2.60 ppm (c) and 90.7 ppm (C) respectively. A zoom on the area of allylic protons or carbons does not reveal significant traces of unsaturated species indicating no or very limited contribution of transfer to monomer usually observed in conventional anionic ring-opening polymerization of substituted epoxides[15,16].

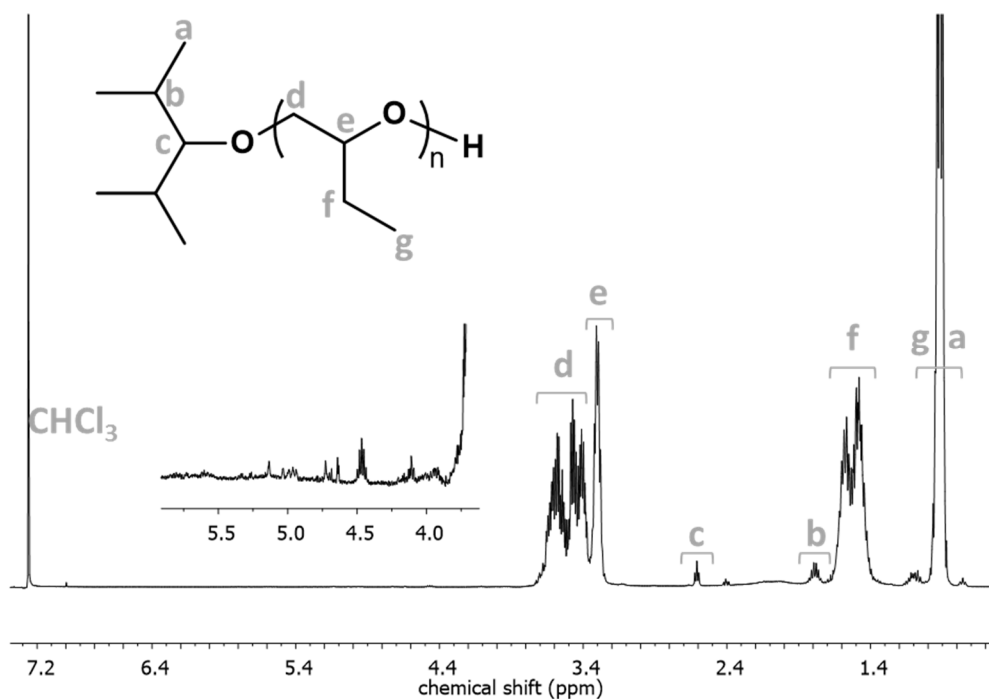


Figure 1: ^1H NMR spectrum in CDCl_3 of poly(butylene oxide) initiated by $\text{OH}/n,s\text{-Bu}_2\text{Mg}/i\text{-Bu}_3\text{Al}$ (1/0.5/1.5) (run 5, Table 1)

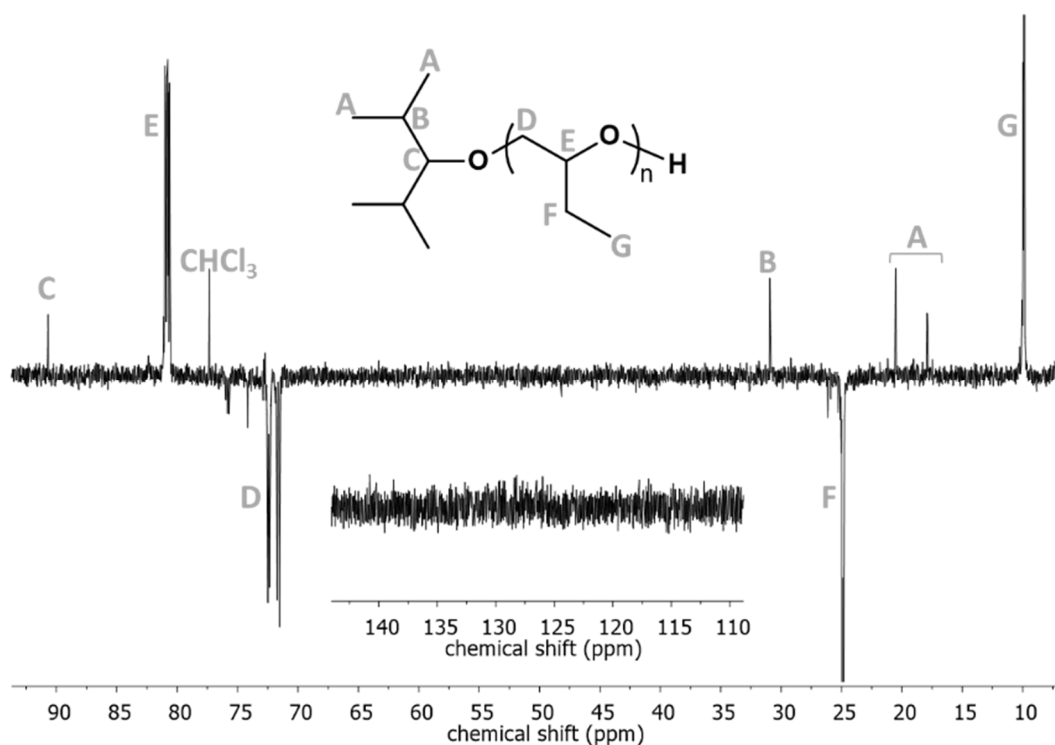


Figure 2: ^{13}C NMR DEPT 135 spectrum in CDCl_3 of poly(butylene oxide) initiated by $\text{OH}/n,s\text{-Bu}_2\text{Mg}/i\text{-Bu}_3\text{Al}$ (1/0.5/1.5) (run 5, Table 1)

The chain-end determination by MALDI-ToF-MS analysis was then performed on the same PBO sample (run 5, Table 1). The overall spectrum and a precise focus on few peak series enables to distinguish one main population and two other in lower proportions (Figure 3). The expected **F1** peak series corresponds to PBO chains with deprotonated 2,4-dimethyl-3-pentanol and hydroxide end groups, in agreement with alkoxide initiation and proton termination $\text{RO}-(\text{PBO})_n\text{-H}$. $\text{F1} = 1509.0 \text{ g/mol} = M_{\text{Na}} + M_{\text{C}_7\text{H}_{15}\text{O}} + n \times M_{\text{BO}} + M_{\text{H}}$ ($M_{\text{C}_7\text{H}_{15}\text{O}} = 115.2 \text{ g/mol}$ and $n = 19$). The second peak series is assigned to both initiation by a hydride (**H**) or transfer to monomer (**M**). The H population is representative of PBO chains with a hydrogen in the α position $\text{H}-(\text{PBO})_n\text{-H}$ coming from the transfer reaction to $i\text{-Bu}_3\text{Al}$ [58] and terminated by a proton (Scheme 2). $\text{H} = 1539.0 \text{ g/mol} = M_{\text{Na}} + n \times M_{\text{BO}} + 2 M_{\text{H}}$ ($n = 21$). On the other side the M population represents PBO chains with a butylenoxy end group with proton termination $\text{M}-(\text{PBO})_n\text{-H}$. $\text{M} = 1537.0 \text{ g/mol} = M_{\text{Na}} + M_{\text{C}_4\text{H}_8\text{O}} + n \times M_{\text{BO}} + M_{\text{H}}$ ($n = 20$). As no or very limited unsaturation signals are observed by ^1H and ^{13}C NMR spectra we believe that this population is mainly attributed to hydride initiation even though the monomer transfer is not completely excluded. With the same termination a third population (**Bu**) is assigned to butyl-initiated PBO chains, in agreement with $\text{Bu}-(\text{PBO})_n\text{-H}$ and resulting in a transfer reaction to $i\text{-Bu}_3\text{Al}$ releasing an active initiating iso-butyl (Scheme 2)[52,54]. $\text{Bu} = 1523.5 \text{ g/mol} = M_{\text{Na}} + M_{\text{C}_4\text{H}_9} + n \times M_{\text{BO}} + M_{\text{H}}$ ($n = 20$).

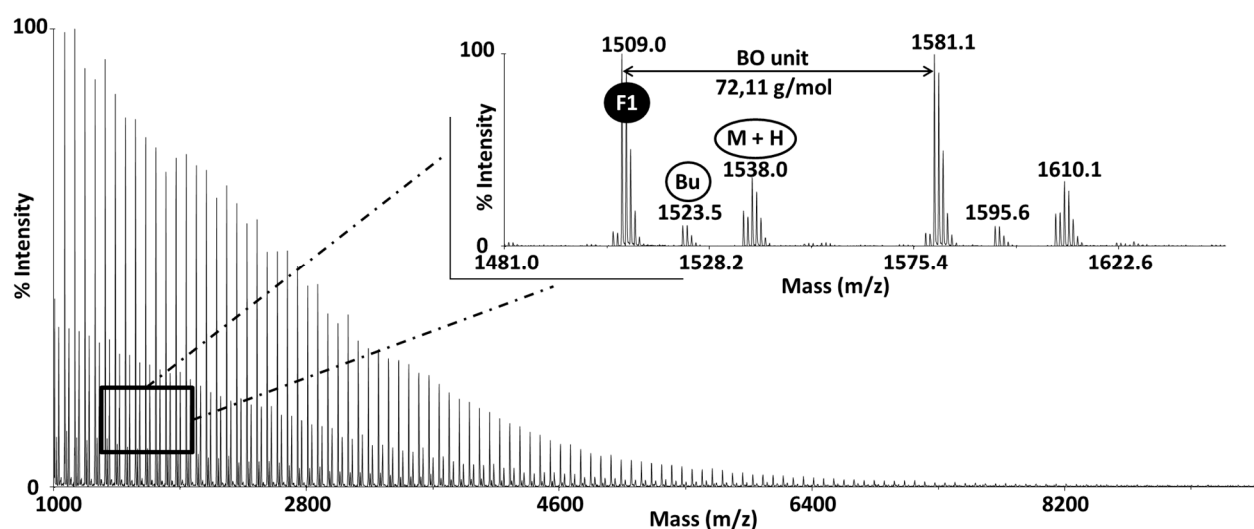


Figure 3: General and enlarged MALDI-TOF spectrum of poly(butylene oxide) ($\overline{Mn}_{\text{calcd}} = 2\,624 \text{ g/mol}$) initiated by $\text{OH}/n,s\text{-Bu}_2\text{Mg}/i\text{-Bu}_3\text{Al}$ (1/0.5/1.5) (run 5, Table 1)

A default of stoichiometry between butyl groups from n,s -Bu₂Mg and hydroxyl group from the alcohol could also be envisaged for the origin of the butyl-initiated population (Bu). This point is discriminated by the MALDI-ToF-MS analysis (Figure 4) of a PBO sample prepared with the system DMP/Et₂Mg/*i*-Bu₃Al (1/0.5/1.5) (run 6, Table 1). This polymer exhibits the same pattern than the previous one with some butyl initiation. F1, H and M are associated to the compositions previously described with “n” repeating units respectively equal to 17, 19 and 18. The Bu population is attributed to $n = 18$. No PBO chains are initiated by an ethyl group in agreement with complete consumption of Et₂Mg during the deprotonation reaction of the alcohol and no action as initiator.

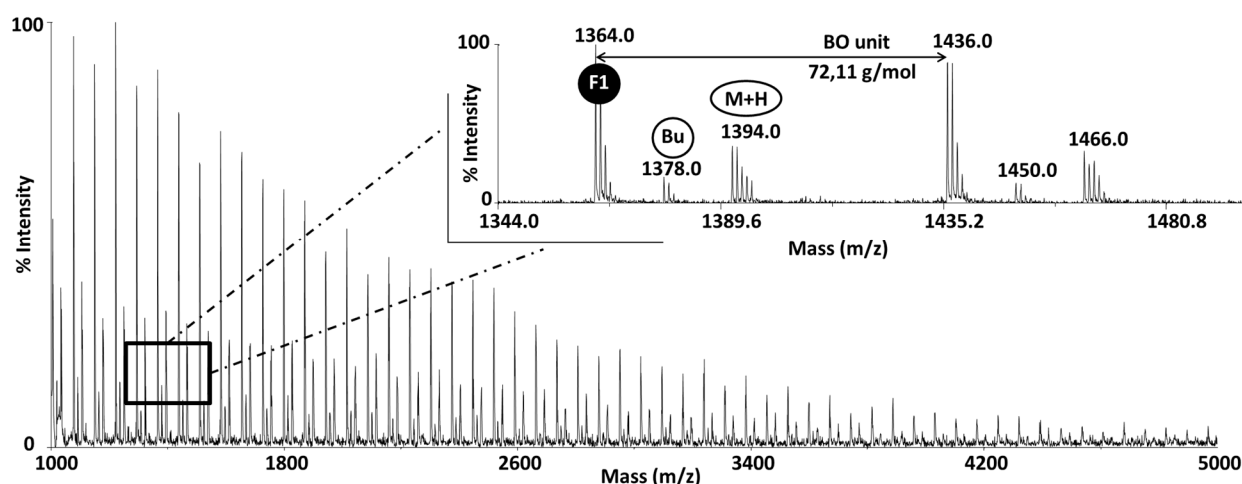


Figure 4: Enlarged MALDI-TOF spectrum of polybutylene oxide) ($\overline{M}_{n,calcd} = 2\,624$ g/mol) initiated by OH/Et₂Mg/*i*-Bu₃Al (1/0.5/1.5) (run 6, Table 1)

On the contrary, when used without alcohol (run 7, Table 1) MALDI-ToFMS analysis presents 3 main populations which can be assigned to initiation from butylenoxy (M) and/or hydride (H), ethyl (Et) and butyl (Bu) group with hydroxyl termination (Figure 5). The high proportion of M+H population can be explained by the higher basicity of the carbanion of the ethyl group leading to more transfer to monomer which is confirmed by NMR (Figure 6). Indeed, butylenoxy end-group can be identified as compared to allyloxy end-group referred for propylene oxide[95]. Ethyl group of diethylmagnesium is also acting as a nucleophile initiating poly(butylene oxide) chains. Butyl initiation coming from *i*-Bu₃Al is still observed. All initiation types are gathered on Scheme 2.

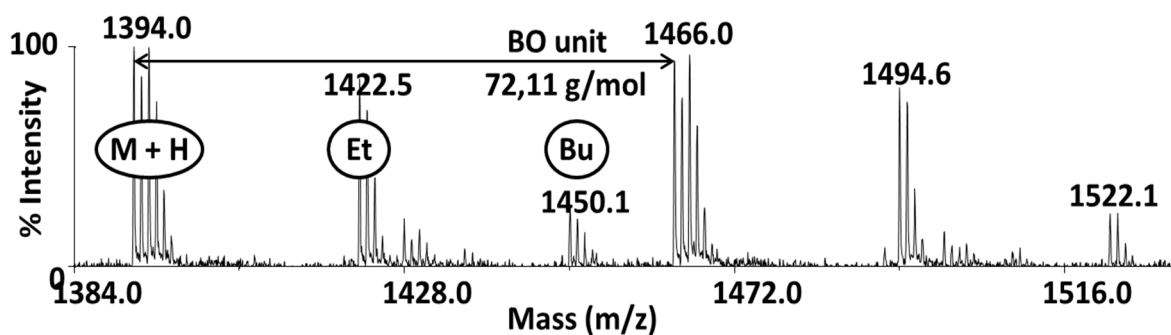


Figure 5: Enlarged MALDI-TOF spectrum of poly(butylene oxide) ($\overline{M}_{n,calcd} = 2\,624$ g/mol) initiated by $-Et_2Mg/i-Bu_3Al$ (0/0.5/1.5) (run 7, Table 1)

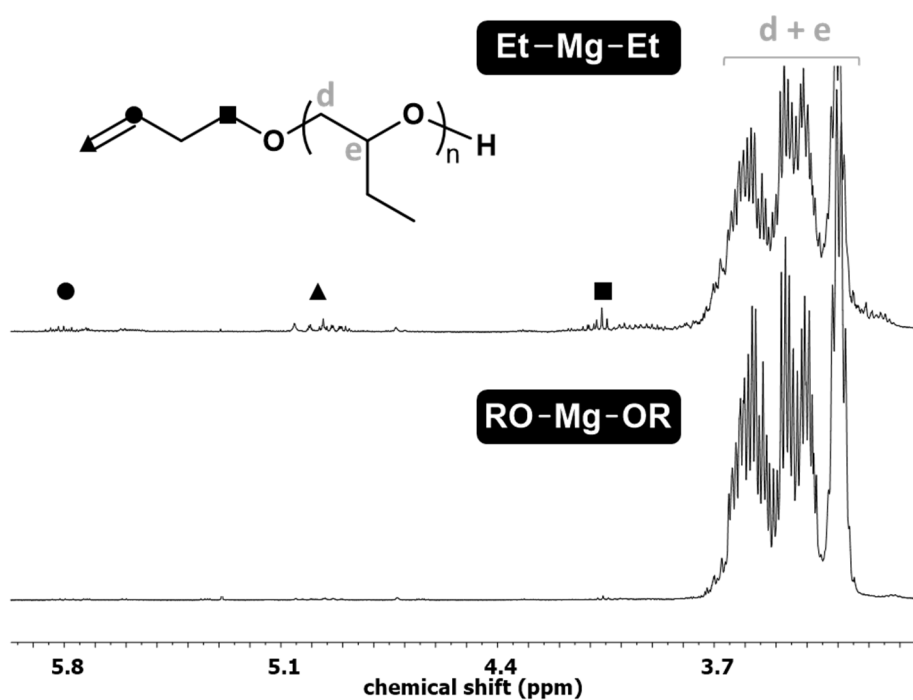
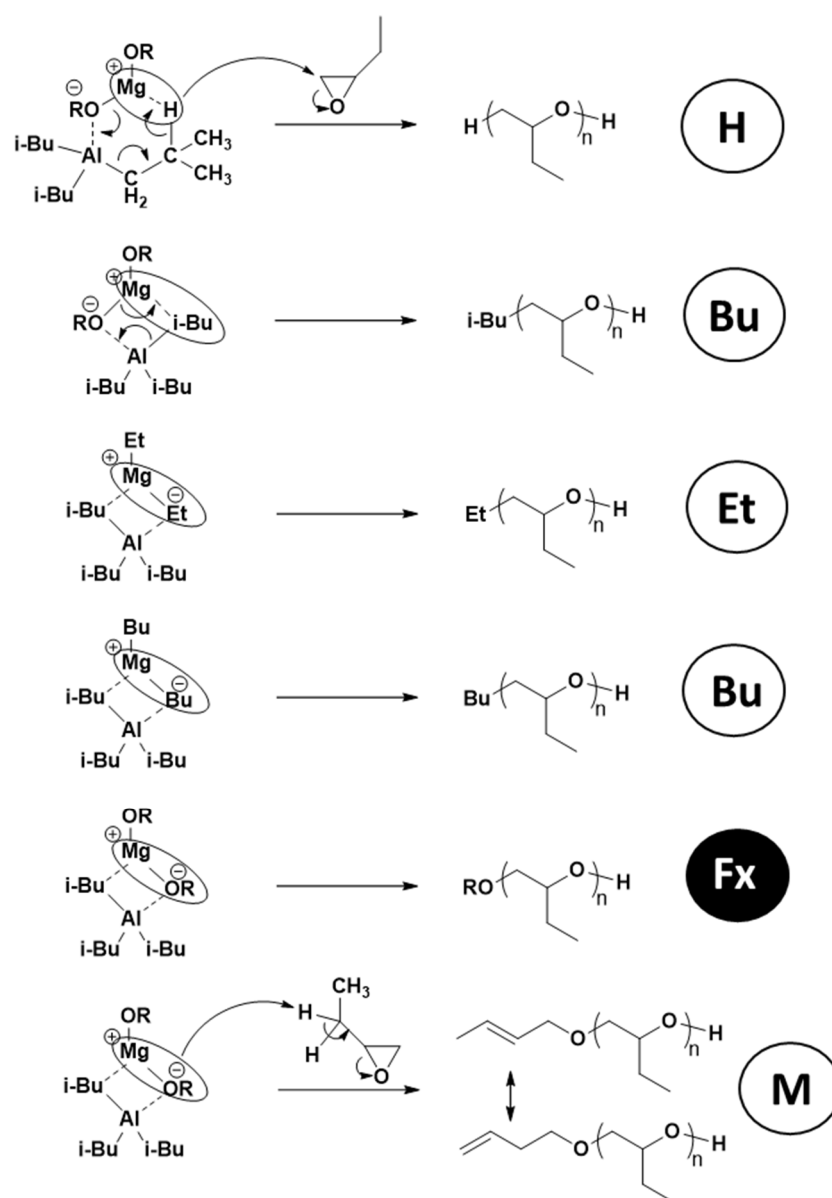


Figure 6: Enlarged view of allylic region on 1H NMR of poly(butylene oxide) initiated by (top) $-Et_2Mg/i-Bu_3Al$ (0/0.5/1.5) (run 7, Table 1) and (bottom) $ROH/Et_2Mg/i-Bu_3Al$ (1/0.5/1.5) (run 6, Table 1)



Scheme 2: Butylene oxide Initiation types observed with the system ROH/R₂Mg/i-Bu₃Al system

The molar mass control is highlighted by the dependence of molar masses with the feed ratio ([BO]₀/[OH]₀). An increase of the experimental molar mass is observed when increasing the monomer loading while keeping dispersity values in the range 1.2 - 1.4 (run 5, 8, 9, Table 1 and Figure 7) in line with transfer reactions already mentioned. One can note that the monomer concentration was increased to get polymerization and reach full monomer conversion while the dispersity values remained relatively low for 5 000 and 10 000 g/mol polymers.

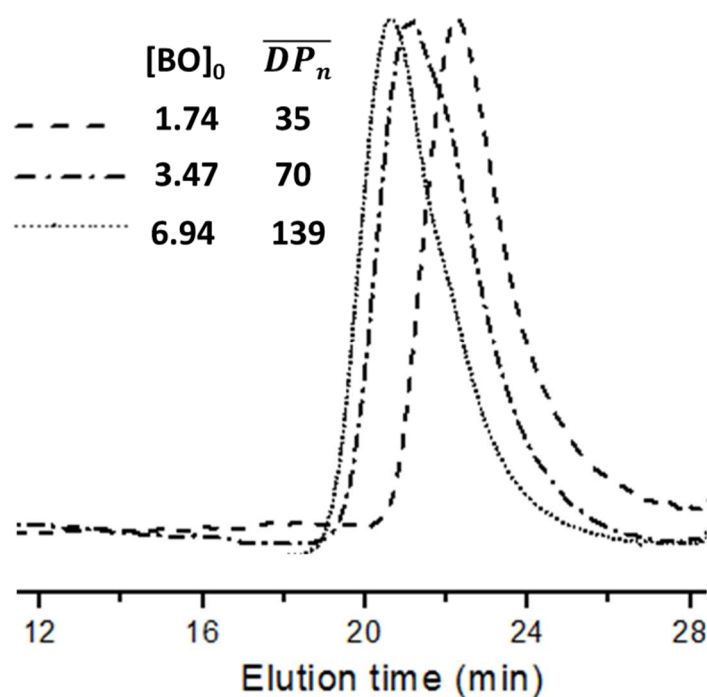
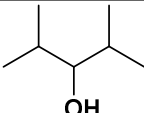
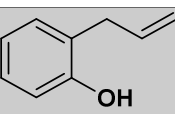
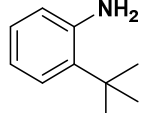
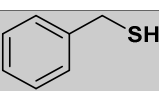
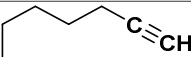


Figure 7: SEC traces (RI detector) of poly(butylene oxide) depending on the ratio $[BO]_0/[OH]_0$

Ethylene oxide (EO) and Glycidyl Methyl Ether (GME) were also shown to polymerize (SI Figure S1). The deprotonation of other functions such as a phenol derivative or even thiol, amine and alkyne was also investigated following the procedure previously described. Aromatic compounds and long or branched aliphatic compounds were used to get solubility in the reaction medium. Results summarized in Table 2 depict the initiation type and percentage calculated from MALDI-Tof-MS spectra (SI Figures S2, S3, S4 and S5). The initiation depends mainly on the formation of the difunctional magnesium species after deprotonation. The expected initiation Fx is shown generally around 70 - 80 % when alcohol (F1-H), phenol (F2-H) and primary amine (F3-H) are used. An increase of the butyl initiation is observed when the thiol is proposed as precursor for deprotonation and initiation (F4-H). Some monofunctional magnesium alkoxides are probably present yielding residual butyl group able to attack a monomer. This system shows also some partial deprotonation (35%) of a terminal alkyne (F5-H) able then to initiate butylene oxide polymerization. The numerous side initiations are explained by the carbanionic nature of the active specie in this case.

Table 2: Polymerization of butylene oxide with different protic precursors Fx-H/n,s-Bu₂Mg/i-Bu₃Al (1/0.5/1.5) in MeTHF ([BO]₀ = 1.74 mol/L, [Fx-H]₀ = 0.05 mol/L, time = 24 h)

Fx-H	Precursor	\overline{Mn}_{calcd}^a (g/mol)	\overline{Mn}_{exp}^b (g/mol)	\overline{D}^b	Conv	Initiation type (%)		
						Fx	M+H	Bu
F1-H		2 624	4 400	1.18	100	70	20	10
F2-H		2 657	5 200	1.17	100	80	20	0
F3-H		2 672	5 000	1.16	100	80	20	0
F4-H		2 647	5 700	1.20	100	55	10	35
F5-H		2 619	3 880	1.51	72	35	55	10

^a $\overline{Mn}_{calcd} = ([BO]_0/[Fx-H]_0 \times 72.11) \times \text{conv. (\%)} + (M_{Fx-H} - 1)$. ^bDetermined by size exclusion chromatography in tetrahydrofuran using a calibration with polystyrene standards.

Despite a non-quantitative alkoxide initiation, the deprotonation of monohydroxy-terminated polymer was investigated for the synthesis of block copolymers characterized by SEC and/or 2D DOSY NMR. Poly(dimethylsiloxane) monohydroxy-terminated (PDMS-OH), poly(ethylene glycol) monomethyl ether (PEO-OH) and poly(propylene glycol) monobutyl ether (PPO-OH) were the selected polymers to act as macroinitiator using a similar synthetic methodology. Results are shown Table 3.

Table 3: Polymerization of propylene oxide with deprotonated monohydroxy-terminated polymers Px-OH/Et₂Mg/i-Bu₃Al (1/0.5/1.5) in MeTHF ([PO]₀ = 4.3 mol/L, [Px-OH]₀ = 0.05 mol/L, time = 24h, conversion 100%)

Precursor Px-OH	\overline{Mn}_{exp} (1 st block) (g/mol)	\overline{Mn}_{calcd} ^a (2 nd block) (g/mol)	\overline{Mn}_{exp} ^b (g/mol)	\overline{D} ^b	Residual homoPx-OH ^c (%)
PDMS-OH	4 670	5 000	12 900	1.27	nd
PEO-OH	1 100	5 000	11 270	1.34	< 5
PPO-OH	1 000	5 000	11 700	1.29	< 5

^a $\overline{Mn}_{calcd} = ([PO]_0/[Px-OH]_0 \times 58.08 \times \text{conv.}(\%))$. ^b Determined by size exclusion chromatography in tetrahydrofuran using a calibration with polystyrene standards. ^c Determined by the ratio of the area from the SEC trace.

Starting from a polydimethylsiloxane monohydroxy-terminated, the block copolymer synthesis was confirmed by 2D DOSY NMR. The resulting DOSY map (Figure 8), showing a two-dimensional correlation, exhibits chemical shifts and diffusion coefficients on the horizontal and vertical axes, respectively. The ¹H NMR spectrum shows signals corresponding to both the PDMS block (δ =0.3 ppm) and the PPO block (δ =1.2; 3.3; 3.5 ppm). ¹H NMR signals of PDMS and PPO segments in the copolymer give rise to the same diffusion coefficient, i.e. $3.76 \cdot 10^{-11} \text{ m}^2/\text{s}$, attesting to the effective covalent linkage of the PDMS and the PPO blocks. The homoPDMS precursor ($\overline{Mn} = 4\,670 \text{ g/mol}$) was also analyzed by DOSY giving a single peak at 0.3 ppm and a diffusion coefficient of $7.95 \cdot 10^{-11} \text{ m}^2/\text{s}$. The difference between the two diffusion values agrees with the absence, or very limited amount, of residual OH-precursor. The decrease of the PDMS-b-PPO value is also in agreement with an increase of the molar mass of the diblock as compared to the PDMS-OH one. Those results are complemented by SEC measurements. The chromatogram of a PEO-b-PPO (entry 2, Table 3) reveals the presence of one main population corresponding to the block copolymer and a smaller one due to residual homoPEO precursor (Figure 9). A similar result was obtained starting from a PPO-OH precursor (SI Figure S6). The trace of the PDMS-OH residue could not be observed due to the use of RI detector and THF as solvent but the result is assumed to be identical regarding the DOSY results. Nevertheless, and as described before, homoPPOs (20-30 %) are expected by this chemistry due to transfer reactions after addition of propylene oxide to the deprotonated precursor. This residual population could not be observed by DOSY as it could overlap with the copolymer signal.

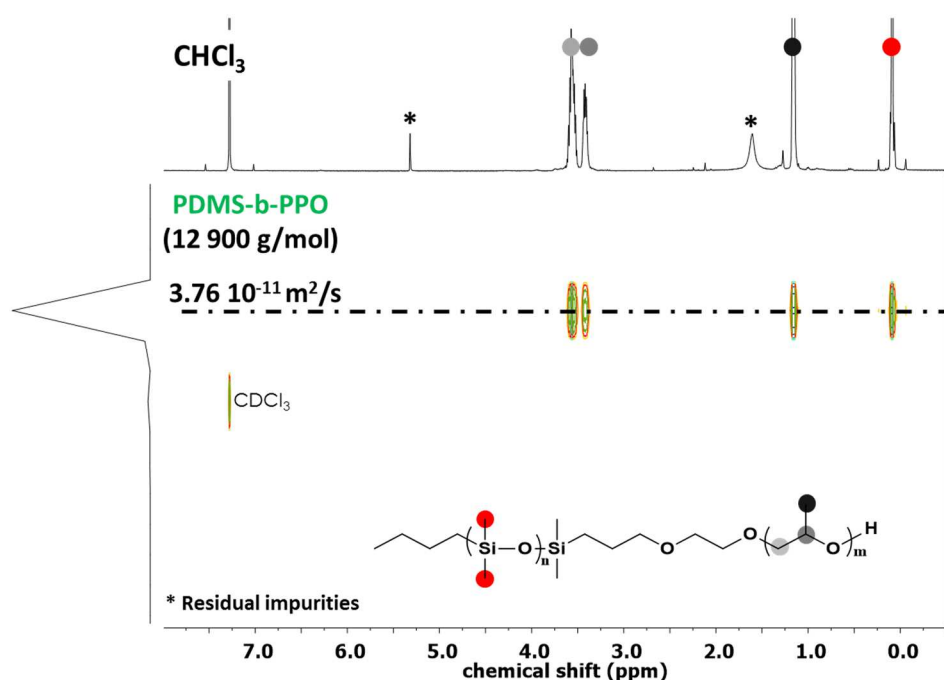


Figure 8: 400MHz 2D DOSY NMR spectrum of a PDMS-b-PPO obtained at 298 K in CDCl₃

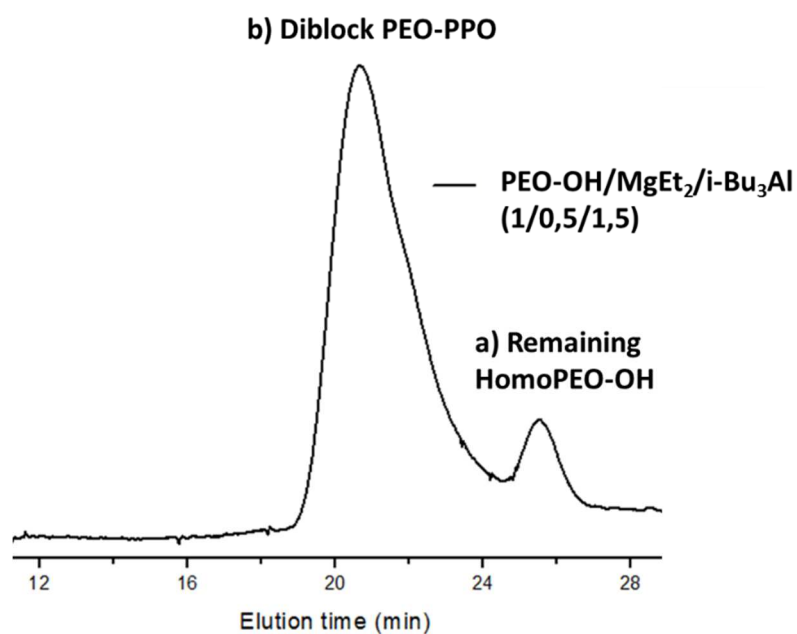


Figure 9: RI SEC trace corresponding to the synthesis of a PEO-b-PPO diblock copolymer ([Al]/[PEO-OH]= 1.5, run 2, Table 5), a) remaining PEO-OH (\overline{Mn}_{exp} = 1100 g/mol), b) diblock PEO-b-PPO (\overline{Mn}_{exp} = 11 270 g/mol).

Kinetic experiments were conducted to scale the reactivity of this Mg/Al system and to compare it with other systems from the literature. To do so, experiments were conducted in

cyclohexane, another good solvent for this chemistry. The polymerization rate R_p can be expressed by the equation $R_p = k_p[I]_0[M^*]$ where k_p is the propagation rate constant, $[I]_0$ and $[M^*]$ the initiator and activated monomer concentrations respectively. $[M^*]$ depends on the $i\text{-Bu}_3\text{Al}$ concentration available, $[M^*] = [\text{Al}]_0 - [I]_0$, since one equivalent of $i\text{-Bu}_3\text{Al}$ is trapped in the 1:1 “ate” complex formed with the initiator. As shown in Figure 10 (and SI Table S1), $k_p[M^*]$ or calculated k_p increases with the amount of $i\text{-Bu}_3\text{Al}$ added as compared to the initiator amount. Those values were calculated from the slope of the conversion versus time plot (linear part, $k_p[M^*] = \text{slope} \cdot [M]_0/[I]_0$) and were in the same range than those obtained by combination of sodium or lithium with triisobutylaluminum[54]. This magnesium system is also less active than the system using tetralkylammonium salts due the smaller size of the Mg counter-ion[58].

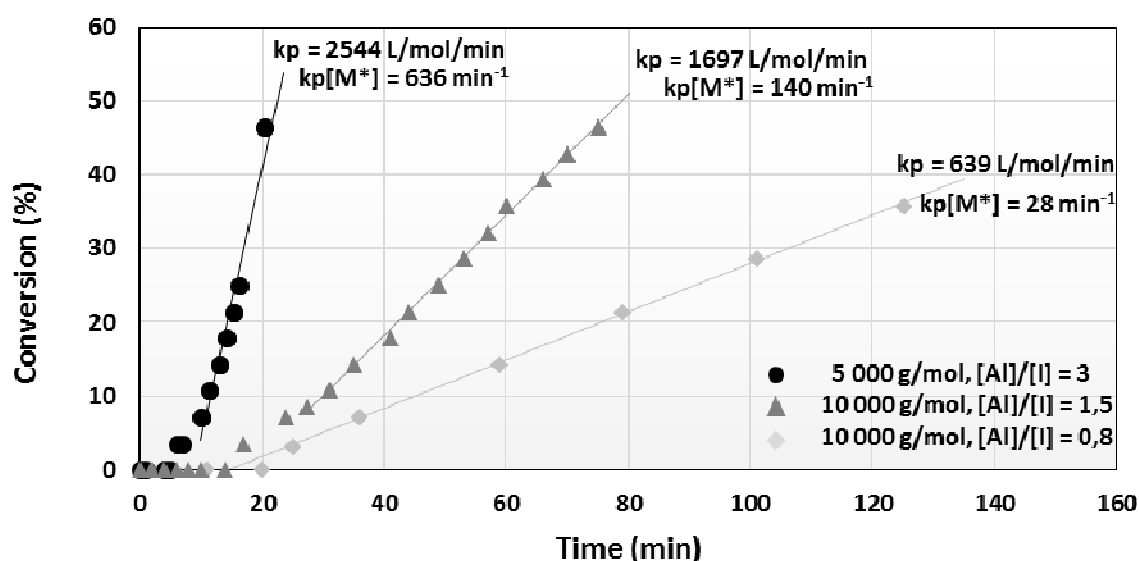


Figure 10: Conversion vs time curves of propylene oxide polymerization initiated by $\text{Mg}(\text{ODMP})_2$ in the presence of $i\text{-Bu}_3\text{Al}$ at 0°C in cyclohexane

Even if dialkylmagnesium were shown to be convenient for the deprotonation of monofunctional compounds and monohydroxy-terminated polymers, it was not possible to extend this chemistry to difunctional compounds or to α,ω -dihydroxytelechelic polymers. Indeed, after addition of the magnesium derivative, a precipitation due to insoluble organomagnesium aggregates or a gelification was respectively observed.

CONCLUSION

Dialkylmagnesium compounds are used as deprotonating agents for molecules bearing a labile proton leading to active magnesium derivatives by releasing an alkane as gaseous by-product. Using the monomer activation methodology by addition of triisobutylaluminum after deprotonation, the polymerization of propylene and butylene oxides is performed. The formation of a Mg/Al “ate” complex is believed to be formed and to act as counter-ion of the propagating chains. 70-80 % of the expected alkoxide initiation is observed. Side initiations coming from transfer reactions are also shown. Deprotonation of primary amine, thiol, and alkyne, followed by their nucleophilic attack onto epoxides are also demonstrated. Starting from OH-terminated polymers, i.e. polydimethylsiloxane and poly(ethylene oxide), block copolymers could be synthesized, the second block being poly(propylene oxide) chosen as model for substituted epoxides.

SUPPORTING INFORMATION

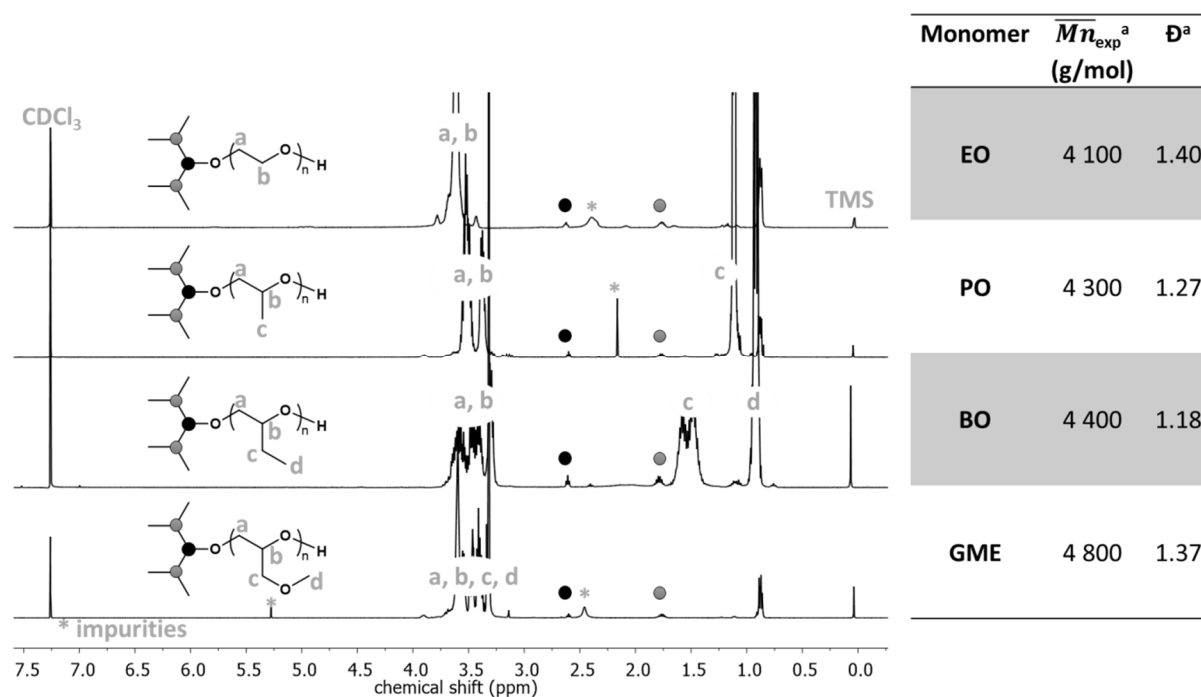


Figure S1: ^1H NMR spectra in CDCl_3 , from top to bottom, PEO, PPO, PBO, PGME, initiated by $\text{OH}/n\text{-Bu}_2\text{Mg}/i\text{-Bu}_3\text{Al}$ (1/0.5/1.5) in MeTHF

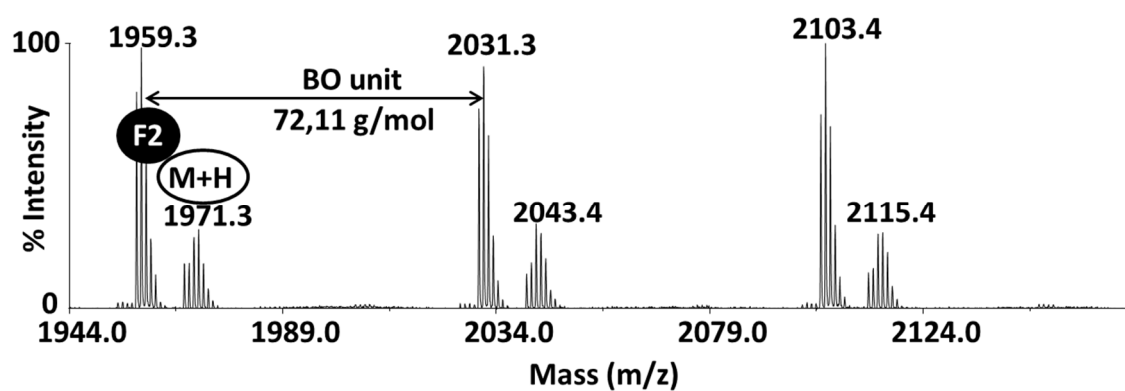


Figure S2: Enlarged MALDI-TOF spectrum of PBO ($\overline{M}_n = 2500$ g/mol) initiated by $\text{F2-H}/n\text{-Bu}_2\text{Mg}/i\text{-Bu}_3\text{Al}$ (1/0.5/1.5)

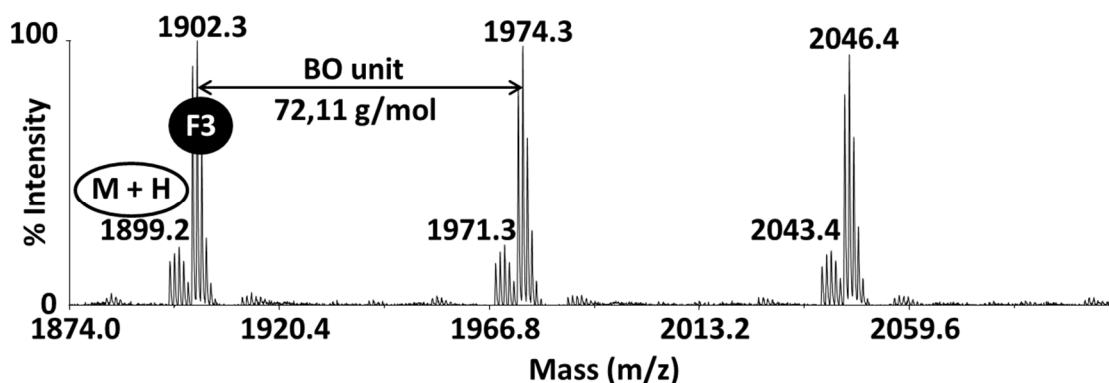


Figure S3: Enlarged MALDI-TOF spectrum of PBO ($\overline{M}_n = 2500$ g/mol) initiated by F3-H/*n,s*-Bu₂Mg/*i*-Bu₃Al (1/0.5/1.5)

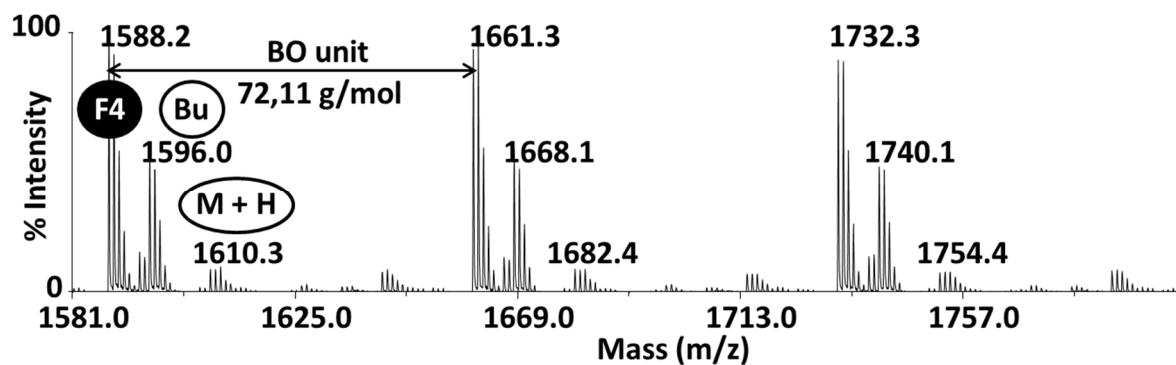


Figure S4: Enlarged MALDI-TOF spectrum of PBO ($\overline{M}_n = 2500$ g/mol) initiated by F4-H/*n,s*-Bu₂Mg/*i*-Bu₃Al (1/0.5/1.5)

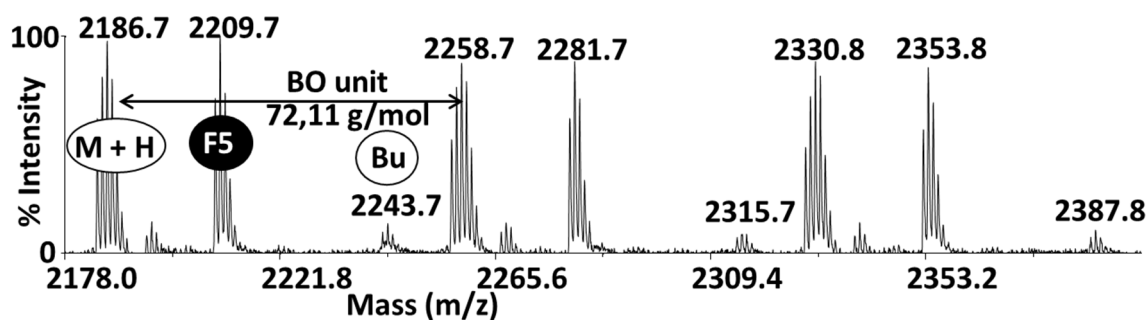


Figure S5: Enlarged MALDI-TOF spectrum of PBO ($\overline{M}_n = 2500$ g/mol) initiated by F5-H/*n,s*-Bu₂Mg/*i*-Bu₃Al (1/0.5/1.5)

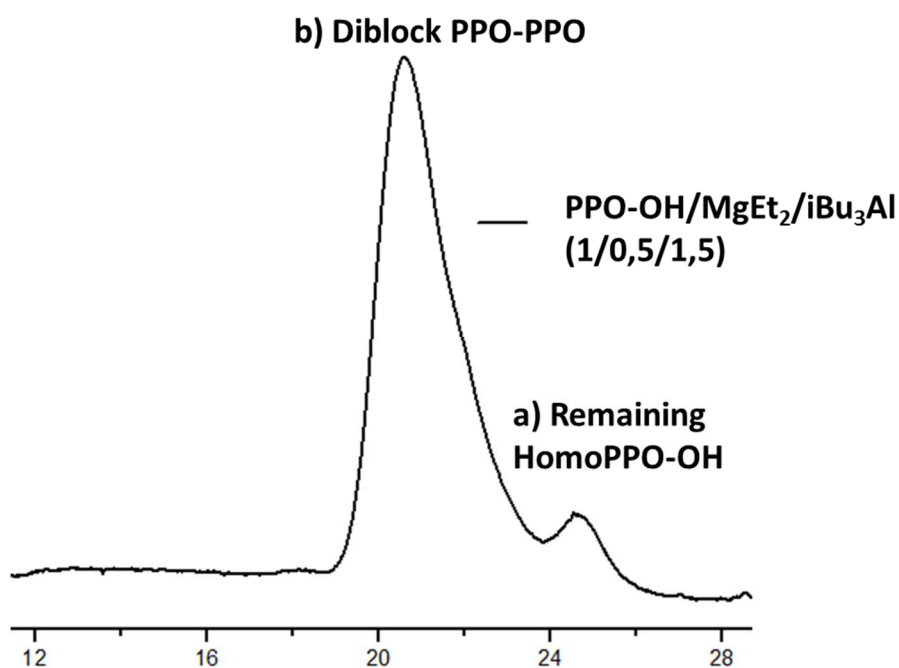


Figure S6: RI SEC trace corresponding to the synthesis of a PPO-*b*-PPO diblock copolymer ($[Al]/[PPO-OH] = 1.5$, run 2, Table 5), a) remaining PPO-OH ($\overline{Mn}_{exp} = 1000$ g/mol), b) diblock PPO-*b*-PPO (\overline{Mn}_{exp} (SEC) = 11 270 g/mol).

Table S1: Propylene oxide polymerization

Run	$[PO]_0$ (mol/L)	$[I]_0$ (mol/L)	$[Al]/[I]$	$[PO]_0/[I]_0$	$kp[M^*]^a$ (min ⁻¹)	kp^b (L/mol/min)
1	9.56	0.055	0.8	172	28	636
2	9.56	0.055	1.5	172	140	1697
3	7.16	0.083	3	86	636	2544

^aDetermined from the slope of the conversion versus time plot (linear part): $kp[M^*] = \text{slope} \cdot [PO]_0/[I]_0$.

^b $kp = kp[M^*]/[Al]_a$

$[Al] = (\text{ratio } A/I) \cdot I$

REFERENCES

1. Brocas, A.-L.; Mantzaridis, C.; Tunc, D.; Carlotti, S. Polyether synthesis: From activated or metal-free anionic ring-opening polymerization of epoxides to functionalization. *Prog. Polym. Sci.* **2013**, *38*, 845–873.
2. Klein, R.; Wurm, F. R. Aliphatic Polyethers: Classical Polymers for the 21st Century. *Macromol. Rapid Commun.* **2015**, *36*, 1147–1165.
3. Brocas, A.-L. Polymérisation anionique des epoxydes par activation du monomère: monomères renouvelables et polymères fonctionnalisés. *Thèse Univ. Bordeaux* **2011**.
4. Carlotti, S.; Peruch, F. Cyclic Monomers : Epoxides , Lactide , Lactones , Lactams , Cyclic Silicon- containing monomers , Cyclic Carbonates and others. in *Anionic Polymerization: Principles, Strength, Consequences and Applications*. Hadjichristidis, N.; Hirao, H. **2015**, Springer.
5. Childers, M. I.; Longo, J. M.; Van Zee, N. J.; LaPointe, A. M.; Coates, G. W. Stereoselective epoxide polymerization and copolymerization. *Chem. Rev.* **2014**, *114*, 8129–8152.
6. Pierre, L. E. St.; Price, C. C. The Room Temperature Polymerization of Propylene Oxide. *J. Am. Chem. Soc.* **1956**, *78*, 3432–3436.
7. Price, C. C.; Carmelite, D. D. Reactions of Epoxides in Dimethyl Sulfoxide Catalyzed by Potassium t-Butoxide. *J. Am. Chem. Soc.* **1966**, *88*, 4039–4044.
8. de Lucas, A.; Rodriguez, L.; Pirez-Collado, M.; Sanchez, P. Production of polyether polyols using caesium as catalyst. *Polym. Int.* **2002**, *51*, 1041–1046.
9. de Lucas, A.; Rodriguez, L.; Pirez-Collado, M.; Sanchez, P.; Rodriguez, J. F. Synthesis of polyols by anionic polymerization: determination of kinetic parameters of propylene oxide polymerization using caesium and potassium alcoholates. *Polym. Int.* **2002**, *51*, 1066–1071.
10. Obermeier, B.; Wurm, F.; Mangold, C.; Frey, H. Multifunctional Poly(ethylene glycol)s. *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 7988–7997.
11. Thomas, A.; Müller, S. S.; Frey, H. Beyond poly(ethylene glycol): linear polyglycerol as a multifunctional polyether for biomedical and pharmaceutical applications. *Biomacromolecules* **2014**, *15*, 1935–1954.
12. Quirk, R. P.; Ma, J.-J. Characterization of the functionalization reaction product of poly(styryl)lithium with ethylene oxide. *J. Polym. Sci. Part A Polym. Chem.* **1988**, *26*, 2031–2037.
13. Allgaier, J.; Willbold, S.; Chang, T. Synthesis of Hydrophobic Poly(alkylene oxide)s and

Amphiphilic Poly(alkylene oxide) Block Copolymers. *Macromolecules* **2007**, *40*, 518–525.

14. Flory, P. J. Molecular Size Distribution in Ethylene Oxide Polymers. *J. Am. Chem. Soc.* **1940**, *62*, 1561–1565.

15. Hans, M.; Keul, H.; Möller, M. Chain transfer reactions limit the molecular weight of polyglycidol prepared via alkali metal based initiating systems. *Polymer (Guildf)*. **2009**, *50*, 1103–1108.

16. Keul, H.; Möller, M. Synthesis and degradation of biomedical materials based on linear and star shaped polyglycidols. *J. Polym. Sci. Part A Polym. Chem.* **2009**, *47*, 3209–3231.

17. Stolarzewicz, A. A new chain transfer reaction in the anionic polymerization of 2,3-epoxypropyl phenyl ether and other oxiranes. *Die Makromol. Chemie* **1986**, *187*, 745–752.

18. Price, C. C.; Akkapeddi, M. K. Kinetics of base-catalyzed polymerization of epoxides in dimethyl sulfoxide and hexamethylphosphoric triamide. *J. Am. Chem. Soc.* **1972**, *94*, 3972–3975.

19. Stolarzewicz, A.; Neugebauer, D. Influence of substituent on the polymerization of oxiranes by potassium hydride. *Macromol. Chem. Phys.* **1999**, *200*, 2467–2470.

20. Deffieux, A.; Boileau, S. Anionic polymerization of ethylene oxide with cryptates as counterions: 1. *Polymer (Guildf)*. **1977**, *18*, 1047–1050.

21. Deng, Y.; Ding, J.; Yu, G.; Mobbs, R. H.; Heatley, F.; Price, C.; Booth, C. Preparation and properties of stat-copoly-(oxyethylene-oxypropylene)-block-poly (oxyethylene): 1. Use of crown ether in the anionic copolymerization of propylene oxide and ethylene oxide. *Polymer (Guildf)*. **1992**, *33*, 1959–1962.

22. Ding, J.; Heatley, F.; Price, C.; Booth, C. Use of crown ether in the anionic polymerization of propylene oxide—2. Molecular weight and molecular weight distribution. *Eur. Polym. J.* **1991**, *27*, 895–899.

23. Stolarzewicz, A.; Neugebauer, D.; Grobelny, Z. Influence of the crown ether concentration and the addition of tert-butyl alcohol on anionic polymerization of (butoxymethyl)oxirane initiated by potassium tert-butoxide. *Macromol. Chem. Phys.* **1995**, *196*, 1295–1300.

24. Ding, J.; Attwood, D.; Price, C.; Booth, C. Use of crown ether in the anionic polymerization of propylene oxide—3. Preparation and micellization of diblock-copoly(oxypropylene/oxyethylene). *Eur. Polym. J.* **1991**, *27*, 901–905.

25. Stolarzewicz, A.; Neugebauer, D.; Grobelny, Z. Influence of the kind of crown ether on the anionic polymerization of (phenoxymethyl)oxirane initiated by potassium tert-butoxide. *Macromol. Chem. Phys.* **1995**, *196*, 1301–1306.

26. Ding, J.; Price, C.; Booth, C. Use of crown ether in the anionic polymerization of propylene oxide—1. Rate of polymerization. *Eur. Polym. J.* **1991**, *27*, 891–894.
27. Grobelny, Z.; Matlengiewicz, M.; Jurek, J.; Michalak, M.; Kwapulińska, D.; Swinarew, A.; Schab-Balcerzak, E. The influence of macrocyclic ligands and water on propylene oxide polymerization initiated with anhydrous potassium hydroxide in tetrahydrofuran. *Eur. Polym. J.* **2013**, *49*, 3277–3288.
28. Schwesinger, R.; Schlemper, H. Peralkylierte Polyaminophosphazene -extrem starke neutrale Stickstoffbasen. *Angew. Chemie* **1987**, *99*, 1212–1214.
29. Esswein, B.; Möller, M. Polymerization of Ethylene Oxide with Alkylolithium Compounds and the Phosphazene Base “t-BuP4.” *Angew. Chemie Int. Ed. English* **1996**, *35*, 623–625.
30. Schmalz, H.; Lanzendörfer, M. G.; Abetz, V.; Müller, A. H. E. Anionic Polymerization of Ethylene Oxide in the Presence of the Phosphazene Base ButP4 – Kinetic Investigations Using In-Situ FT-NIR Spectroscopy and MALDI-ToF MS. *Macromol. Chem. Phys.* **2003**, *204*, 1056–1071.
31. Boileau, S.; Illy, N. Activation in anionic polymerization: Why phosphazene bases are very exciting promoters. *Prog. Polym. Sci.* **2011**, *36*, 1132–1151.
32. Zhao, J.; Hadjichristidis, N. Polymerization of 5-alkyl δ -lactones catalyzed by diphenyl phosphate and their sequential organocatalytic polymerization with monosubstituted epoxides. *Polym. Chem.* **2015**, *6*, 2659–2668.
33. Alamri, H.; Zhao, J.; Pahovnik, D.; Hadjichristidis, N. Phosphazene-catalyzed ring-opening polymerization of ϵ -caprolactone: influence of solvents and initiators. *Polym. Chem.* **2014**, *5*, 5471–5478.
34. Yang, H.; Zhao, J.; Yan, M.; Pispas, S.; Zhang, G. Nylon 3 synthesized by ring opening polymerization with a metal-free catalyst. *Polym. Chem.* **2011**, *2*, 2888–2892.
35. Illy, N.; Boileau, S.; Penelle, J.; Barbier, V. Metal-free activation in the anionic ring-opening polymerization of cyclopropane derivatives. *Macromol. Rapid Commun.* **2009**, *30*, 1731–1735.
36. Illy, N.; Boileau, S.; Winnik, M. A.; Penelle, J.; Barbier, V. Thiol-ene “clickable” carbon-chain polymers based on diallyl cyclopropane-1,1-dicarboxylate. *Polymer (Guildf)*. **2012**, *53*, 903–912.
37. Illy, N.; Boileau, S.; Buchmann, W.; Penelle, J.; Barbier, V. Control of End Groups in Anionic Polymerizations Using Phosphazene Bases and Protic Precursors As Initiating System (XH-tBuP4 Approach): Application to the Ring-Opening Polymerization of Cyclopropane-1,1-Dicarboxylates. *Macromolecules* **2010**, *43*, 8782–8789.

38. Misaka, H.; Tamura, E.; Makiguchi, K.; Kamoshida, K.; Sakai, R.; Satoh, T.; Kakuchi, T. Synthesis of end-functionalized polyethers by phosphazene base-catalyzed ring-opening polymerization of 1,2-butylene oxide and glycidyl ether. *J. Polym. Sci. Part A Polym. Chem.* **2012**, *50*, 1941–1952.
39. Isono, T.; Kamoshida, K.; Satoh, Y.; Takaoka, T.; Sato, S.; Satoh, T.; Kakuchi, T. Synthesis of Star- and Figure-Eight-Shaped Polyethers by t-BuP4 -Catalyzed Ring-Opening Polymerization of Butylene Oxide. *Macromolecules* **2013**, *46*, 3841–3849.
40. Isono, T.; Asai, S.; Satoh, Y.; Takaoka, T.; Tajima, K.; Kakuchi, T.; Satoh, T. Controlled/Living Ring-Opening Polymerization of Glycidylamine Derivatives Using t -Bu-P 4 /Alcohol Initiating System Leading to Polyethers with Pendant Primary, Secondary, and Tertiary Amino Groups. *Macromolecules* **2015**, *48*, 3217–3229.
41. Zhao, J.; Pahovnik, D.; Gnanou, Y.; Hadjichristidis, N. One-pot synthesis of linear- and three-arm star-tetrablock quarterpolymers via sequential metal-free ring-opening polymerization using a “catalyst switch” strategy. *J. Polym. Sci. Part A Polym. Chem.* **2015**, *53*, 304–312.
42. Zhao, J.; Pahovnik, D.; Gnanou, Y.; Hadjichristidis, N. Phosphazene-Promoted Metal-Free Ring-Opening Polymerization of Ethylene Oxide Initiated by Carboxylic Acid. *Macromolecules* **2014**, *47*, 1693–1698.
43. Zhao, J.; Schlaad, H.; Weidner, S.; Antonietti, M. Synthesis of terpene–poly(ethylene oxide)s by t-BuP4-promoted anionic ring-opening polymerization. *Polym. Chem.* **2012**, *3*, 1763–1768.
44. Zhao, J.; Schlaad, H. Controlled Anionic Graft Polymerization of Ethylene Oxide Directly from Poly(N -isopropylacrylamide). *Macromolecules* **2011**, *44*, 5861–5864.
45. Inoue, S.; Sugimoto, H.; Aida, T. Metalloporphyrin catalysts for living and immortal polymerizations. *Macromol. Symp.* **1996**, *101*, 11–18.
46. Kuroki, M.; Watanabe, T.; Aida, T.; Inoue, S. Steric separation of nucleophile and Lewis acid providing dramatically accelerated reaction. High-speed polymerization of methyl methacrylate with enolate-aluminum porphyrin/sterically crowded organoaluminum systems. *J. Am. Chem. Soc.* **1991**, *113*, 5903–5904.
47. Endo, M.; Aida, T.; Inoue, S. Immortal polymerization of .epsilon.-caprolactone initiated by aluminum porphyrin in the presence of alcohol. *Macromolecules* **1987**, *20*, 2982–2988.
48. Aida, T.; Inoue, S. Living polymerization of epoxides with metalloporphyrin and synthesis of block copolymers with controlled chain lengths. *Macromolecules* **1981**, *14*, 1162–1166.
49. Aida, T.; Mizuta, R.; Yoshida, Y.; Inoue, S. Polymerization of epoxides catalysed by metalloporphine. *Die Makromol. Chemie* **1981**, *182*, 1073–1079.

50. Aida, T.; Wada, K.; Inoue, S. Copolymerization of epoxides by aluminum porphyrin - reactivity of (porphinato)aluminum alkoxide as growing species. *Macromolecules* **1987**, *20*, 237–241.
51. Braune, W.; Okuda, J. An Efficient Method for Controlled Propylene Oxide Polymerization: The Significance of Bimetallic Activation in Aluminum Lewis Acids. *Angew. Chemie Int. Ed.* **2003**, *42*, 64–68.
52. Billouard, C.; Carlotti, S.; Desbois, P.; Deffieux, A. “Controlled” High-Speed Anionic Polymerization of Propylene Oxide Initiated by Alkali Metal Alkoxide/Trialkylaluminum Systems. *Macromolecules* **2004**, *37*, 4038–4043.
53. Carlotti, S.; Desbois, P.; Billouard, C.; Deffieux, A. Reactivity control in anionic polymerization of ethylenic and heterocyclic monomers through formation of “ate” complexes. *Polym. Int.* **2006**, *55*, 1126–1131.
54. Rejsek, V.; Desbois, P.; Deffieux, A.; Carlotti, S. Polymerization of ethylene oxide initiated by lithium derivatives via the monomer-activated approach: Application to the direct synthesis of PS-*b*-PEO and PI-*b*-PEO diblock copolymers. *Polymer (Guildf)*. **2010**, *51*, 5674–5679.
55. Labbé, A.; Brocas, A. L.; Ibarboure, E.; Ishizone, T.; Hirao, A.; Deffieux, A.; Carlotti, S. Selective ring-opening polymerization of glycidyl methacrylate: Toward the synthesis of cross-linked (co)polyethers with thermoresponsive properties. *Macromolecules* **2011**, *44*, 6356–6364.
56. Brocas, A.-L.; Cendejas, G.; Caillol, S.; Deffieux, A.; Carlotti, S. Controlled synthesis of polyepichlorohydrin with pendant cyclic carbonate functions for isocyanate-free polyurethane networks. *J. Polym. Sci. Part A Polym. Chem.* **2011**, *49*, 2677–2684.
57. Gervais, M.; Brocas, A.-L.; Cendejas, G.; Deffieux, A.; Carlotti, S. Synthesis of Linear High Molar Mass Glycidol-Based Polymers by Monomer-Activated Anionic Polymerization. *Macromolecules* **2010**, *43*, 1778–1784.
58. Labbé, A.; Carlotti, S.; Billouard, C.; Desbois, P.; Deffieux, A. Controlled High-Speed Anionic Polymerization of Propylene Oxide Initiated by Onium Salts in the Presence of Triisobutylaluminum. *Macromolecules* **2007**, *40*, 7842–7847.
59. Carlotti, S.; Labbé, A.; Rejsek, V.; Doutaz, S.; Gervais, M.; Deffieux, A. Living/Controlled Anionic Polymerization and Copolymerization of Epichlorohydrin with Tetraoctylammonium Bromide–Triisobutylaluminum Initiating Systems. *Macromolecules* **2008**, *41*, 7058–7062.
60. Labbé, A.; Carlotti, S.; Deffieux, A.; Hirao, A. Controlled Polymerization of Glycidyl Methyl Ether Initiated by Onium Salt/Triisobutylaluminum and Investigation of the Polymer LCST. *Macromol. Symp.* **2007**, *249-250*, 392–397.

61. Gervais, M.; Brocas, A.-L.; Deffieux, A.; Ibarboure, E.; Carlotti, S. Rapid and controlled synthesis of hydrophobic polyethers by monomer activation. *Pure Appl. Chem.* **2012**, *84*, 2103–2111.
62. Labbé, A.; Brocas, A.-L.; Ibarboure, E.; Ishizone, T.; Hirao, A.; Deffieux, A.; Carlotti, S. Selective Ring-Opening Polymerization of Glycidyl Methacrylate: Toward the Synthesis of Cross-Linked (Co)polyethers with Thermoresponsive Properties. *Macromolecules* **2011**, *44*, 6356–6364.
63. Müller, S. S.; Moers, C.; Frey, H. A Challenging Comonomer Pair: Copolymerization of Ethylene Oxide and Glycidyl Methyl Ether to Thermoresponsive Polyethers. *Macromolecules* **2014**, *47*, 5492–5500.
64. Brocas, A.-L.; Cendejas, G.; Caillol, S.; Deffieux, A.; Carlotti, S. Controlled synthesis of polyepichlorohydrin with pendant cyclic carbonate functions for isocyanate-free polyurethane networks. *J. Polym. Sci. Part A Polym. Chem.* **2011**, *49*, 2677–2684.
65. Brocas, A.-L.; Deffieux, A.; Le Malicot, N.; Carlotti, S. Combination of phosphazene base and triisobutylaluminum for the rapid synthesis of polyhydroxy telechelic poly(propylene oxide). *Polym. Chem.* **2012**, *3*, 1189–1195.
66. Silverman S, G.; Rakita E, P. Grignard Reactions. *Kirk-Othmer Encycl. Chem. Technol.* **2000**, DOI: 10.1002/0471238961.0718090719091222.a01.pub2.
67. Piskun, Y.; Vasilenko, I.; Gaponik, L.; Kostjuk, S. Activated anionic ring-opening polymerization of ϵ -caprolactam with magnesium di(ϵ -caprolactamate) as initiator: effect of magnesium halides. *Polym. Bull.* **2012**, *68*, 1501–1513.
68. Nováková, V.; Šáchová, M.; Brožek, J.; Bernat, P.; Roda, J. Polymerization of lactams, 89 magnesium caprolactamates as initiators of ϵ -caprolactam polymerization. *Macromol. Symp.* **1996**, *102*, 115–122.
69. Bernášková, A.; Chromcová, D.; Brožek, J.; Roda, J. Polymerization of lactams, 95 Preparation of polyesteramides by the anionic polymerization of ϵ -caprolactam in the presence of poly(ϵ -caprolactone). *Polymer (Guildf)*. **2004**, *45*, 2141–2148.
70. Malinová, L.; Brožek, J. Ethyl magnesium bromide as an efficient anionic initiator for controlled polymerization of ϵ -caprolactone. *Polym. Bull.* **2014**, *71*, 111–123.
71. Guillaume, C.; Carpentier, J.-F.; Guillaume, S. M. Immortal ring-opening polymerization of β -butyrolactone with zinc catalysts: Catalytic approach to poly(3-hydroxyalkanoate). *Polymer (Guildf)*. **2009**, *50*, 5909–5917.
72. Helou, M.; Miserque, O.; Brusson, J.-M.; Carpentier, J.-F.; Guillaume, S. M. Poly(trimethylene carbonate) from Biometals-Based Initiators/Catalysts: Highly Efficient

Immortal Ring-Opening Polymerization Processes. *Adv. Synth. Catal.* **2009**, *351*, 1312–1324.

73. Wang, Y.; Zhao, W.; Liu, X.; Cui, D.; Chen, E. Y.-X. Ligand-Free Magnesium Catalyst System: Immortal Polymerization of L-Lactide with High Catalyst Efficiency and Structure of Active Intermediates. *Macromolecules* **2012**, *45*, 6957–6965.

74. Wang, Y.; Liu, B.; Wang, X.; Zhao, W.; Liu, D.; Liu, X.; Cui, D. Immortal ring-opening polymerization of ϵ -caprolactone by a neat magnesium catalyst system: an approach to obtain block and amphiphilic star polymers in situ. *Polym. Chem.* **2014**, 4580–4588.

75. Wilson, J. A.; Hopkins, S. A.; Wright, P. M.; Dove, A. P. “Immortal” ring-opening polymerization of ω -pentadecalactone by $\text{Mg}(\text{BHT})_2(\text{THF})_2$. *Polym. Chem.* **2014**, *5*, 2691–2694.

76. Wilson, J. A.; Hopkins, S. A.; Wright, P. M.; Dove, A. P. Synthesis of ω -Pentadecalactone Copolymers with Independently Tunable Thermal and Degradation Behavior. *Macromolecules* **2015**, *48*, 950–958.

77. Roos, K.; Carlotti, S. Grignard-based anionic ring-opening polymerization of propylene oxide activated by triisobutylaluminum. *Eur. Polym. J.* **2015**, *70*, 240–246.

78. Tasdelen, M. A.; Kahveci, M. U.; Yagci, Y. Telechelic polymers by living and controlled/living polymerization methods. *Prog. Polym. Sci.* **2011**, *36*, 455–567.

79. Esswein, B.; Steidl, N. M.; Möller, M. Anionic polymerization of oxirane in the presence of the polyiminophosphazene base t-BuP4. *Macromol. Rapid Commun.* **1996**, *17*, 143–148.

80. Zhao, J.; Alamri, H.; Hadjichristidis, N. A facile metal-free “grafting-from” route from acrylamide-based substrate toward complex macromolecular combs. *Chem. Commun. (Camb)*. **2013**, *49*, 7079–7081.

81. Sugimoto, H.; Kawamura, C.; Kuroki, M.; Aida, T.; Inoue, S. Lewis Acid-Assisted Anionic Ring-Opening Polymerization of Epoxide by the Aluminum Complexes of Porphyrin, Phthalocyanine, Tetraazaannulene, and Schiff Base as Initiators. *Macromolecules* **1994**, *27*, 2013–2018.

82. Ashby, E. C. A detailed description of the mechanism of reaction of Grignard reagents with ketones. *Pure Appl. Chem.* **1980**, *52*, 545–569.

83. Sato, F.; Oguro, K.; Watanabe, H.; Sato, M. Reinvestigation of the grignard reactions with formic acid. A convenient method for preparation of aldehydes. *Tetrahedron Lett.* **1980**, *21*, 2869–2872.

84. Sada, M.; Matsubara, S. Transition-metal chloride mediated addition reaction of diorganomagnesium to easily enolizable ketones. *Tetrahedron* **2011**, *67*, 2612–2616.

85. Brunner, G.; Eberhard, L.; Oetiker, J.; Schröder, F. Cyclopropanation with Dibromomethane under Grignard and Barbier Conditions. *Synthesis (Stuttg)*. **2009**, 2009, 3708–3718.
86. Pace, V.; Hoyos, P.; Castoldi, L.; Domínguez de María, P.; Alcántara, A. R. 2-Methyltetrahydrofuran (2-MeTHF): a biomass-derived solvent with broad application in organic chemistry. *ChemSusChem* **2012**, 5, 1369–1379.
87. Boileau, S. Anionic Ring-opening Polymerization: Epoxides and Episulfides. *Compr. Polym. Sci. Suppl.* **1989**, 3, 467–487.
88. Gaylord, N. G.; Becker, E. I. The Reaction between Grignard Reagents and the Oxirane Ring. *Chem. Rev.* **1951**, 49, 413–533.
89. Ashby, E. C.; Nackashi, J.; Parris, G. E. Composition of Grignard compounds. X. NMR, ir, and molecular association studies of some methylmagnesium alkoxides in diethyl ether, tetrahydrofuran, and benzene. *J. Am. Chem. Soc.* **1975**, 97, 3162–3171.
90. Gao, Y.; Dai, Z.; Zhang, J.; Ma, X.; Tang, N.; Wu, J. Trinuclear and Tetranuclear Magnesium Alkoxide Clusters as Highly Active Initiators for Ring-Opening Polymerization of L-Lactide. *Inorg. Chem.* **2013**, 53, 716–726.
91. Liao, C.; Guo, B.; Jiang, D.; Custelcean, R.; Mahurin, S. M.; Sun, X.-G.; Dai, S. Highly soluble alkoxide magnesium salts for rechargeable magnesium batteries. *J. Mater. Chem. A* **2014**, 2, 581–584.
92. Penczek, S.; Cypriak, M.; Duda, A.; Kubisa, P.; Słomkowski, S. Living ring-opening polymerizations of heterocyclic monomers. *Prog. Polym. Sci.* **2007**, 32, 247–282.
93. Francis, R.; Taton, D.; Logan, J. L.; Masse, P.; Gnanou, Y.; Duran, R. S. Synthesis and Surface Properties of Amphiphilic Star-Shaped and Dendrimer-like Copolymers Based on Polystyrene Core and Poly(ethylene oxide) Corona. *Macromolecules* **2003**, 36, 8253–8259.
94. Mangold, C.; Dingels, C.; Obermeier, B.; Frey, H.; Wurm, F. PEG-based Multifunctional Polyethers with Highly Reactive Vinyl-Ether Side Chains for Click-Type Functionalization. *Macromolecules* **2011**, 44, 6326–6334.
95. Yu, G.-E.; Heatley, F.; Booth, C.; Blease, T. G. Anionic polymerization of propylene oxide: Isomerization of allyl ether to propenyl ether end groups. *J. Polym. Sci. Part A Polym. Chem.* **1994**, 32, 1131–1135.
96. Dworak, A.; Panchev, I.; Trzebicka, B.; Walach, W. Hydrophilic and amphiphilic copolymers of 2,3-epoxypropanol-1. *Macromol. Symp.* **2000**, 153, 233–242.
97. Mangold, C.; Wurm, F.; Frey, H. Functional PEG-based polymers with reactive groups via anionic ROP of tailor-made epoxides. *Polym. Chem.* **2012**, 3, 1714–1721.

98. Lee, B. F.; Kade, M. J.; Chute, J. A.; Gupta, N.; Campos, L. M.; Fredrickson, G. H.; Kramer, E. J.; Lynd, N. A.; Hawker, C. J. Poly(allyl glycidyl ether)-A versatile and functional polyether platform. *J. Polym. Sci. A. Polym. Chem.* **2011**, *49*, 4498–4504.
99. Herzberger, J.; Kurzbach, D.; Werre, M.; Fischer, K.; Hinderberger, D.; Frey, H. Stimuli-Responsive Tertiary Amine Functional PEGs Based on N , N -Dialkylglycidylamines. *Macromolecules* **2014**, *47*, 7679–7690.
100. Schlaad, H.; Kukula, H.; Rudloff, J.; Below, I. Synthesis of α,ω -Heterobifunctional Poly(ethylene glycol)s by Metal-Free Anionic Ring-Opening Polymerization. *Macromolecules* **2001**, *34*, 4302–4304.
101. Rexin, O.; Mülhaupt, R. Anionic ring-opening polymerization of propylene oxide in the presence of phosphonium catalysts. *J. Polym. Sci. Part A Polym. Chem.* **2002**, *40*, 864–873.
102. Kasperczyk, J.; Bero, M. Stereoselective polymerization of racemic dl-lactide in the presence of butyllithium and butylmagnesium. Structural investigations of the polymers. *Polymer (Guildf)*. **2000**, *41*, 391–395.
103. Liu, L.; Wei, Z. Y.; Qi, M. Synthesis and characterization of biodegradable aliphatic polyesters using dibutylmagnesium as initiator. *Chinese Chem. Lett.* **2007**, *18*, 744–746.
104. Kricheldorf, H. R.; Lee, S.-R. Polylactones: 32. High-molecular-weight polylactides by ring-opening polymerization with dibutylmagnesium or butylmagnesium chloride. *Polymer (Guildf)*. **1995**, *36*, 2995–3003.
105. Kricheldorf, H. R.; Berl, M.; Scharnagl, N. Poly(lactones). 9. Polymerization mechanism of metal alkoxide initiated polymerizations of lactide and various lactones. *Macromolecules* **1988**, *21*, 286–293.
106. Wurm, B.; Keul, H.; Höcker, H.; Sylvester, G.; Leitz, E.; Ott, K. Dibutylmagnesium—an initiator for the ring-opening polymerization of 2,2-dimethyltrimethylene carbonate and ϵ -caprolactone. *Die Makromol. Chemie, Rapid Commun.* **1992**, *13*, 9–14.
107. Wang, Y.; Zhao, W.; Liu, X.; Cui, D.; Chen, E. Y. X. Ligand-Free Magnesium Catalyst System: Immortal Polymerization of l-Lactide with High Catalyst Efficiency and Structure of Active Intermediates. *Macromolecules* **2012**, *45*, 6957–6965.
108. Johnson, C. S. Diffusion ordered nuclear magnetic resonance spectroscopy: principles and applications. *Prog. Nucl. Magn. Reson. Spectrosc.* **1999**, *34*, 203–256.
109. Stilbs, P. Molecular self-diffusion coefficients in Fourier transform nuclear magnetic resonance spectrometric analysis of complex mixtures. *Anal. Chem.* **1981**, *53*, 2135–2137.
110. Viel, S.; Mazarin, M.; Giordanengo, R.; Phan, T. N. T.; Charles, L.; Caldarelli, S.; Bertin, D.

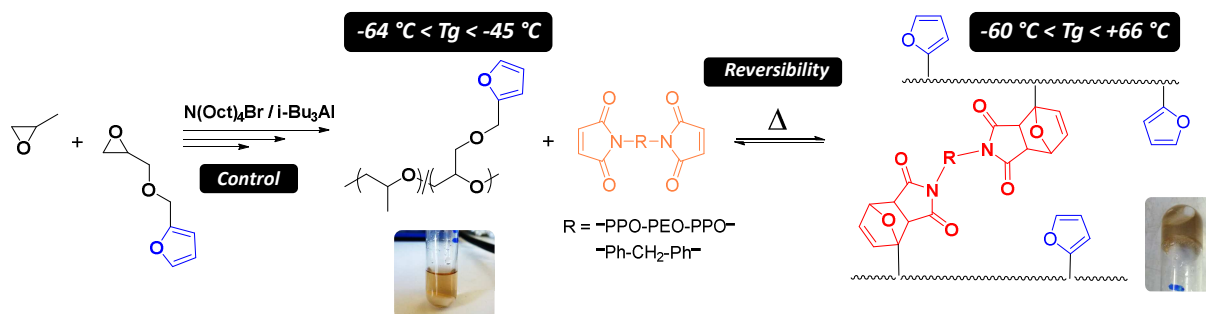
Improved compositional analysis of block copolymers using diffusion ordered NMR spectroscopy. *Anal. Chim. Acta* **2009**, 654, 45–48.

111. Schlenk, W.; Schlenk, W. Über die Konstitution der Grignardschen Magnesiumverbindungen. *Berichte der Dtsch. Chem. Gesellschaft (A B Ser.* **1929**, 62, 920–924.

112. Kamienski, W. Hydrocarbon and chlorinated hydrocarbon-soluble magnesium dialkoxides **1988**, US patent 4,748,283.

CHAPTER II.

Synthesis of cross-linkable polyethers by anionic polymerization



CHAPTER II. Synthesis of cross-linkable polyethers by anionic polymerization

1. Introduction	83
2. Cross-linking via Diels-Alder chemistry: furan/maleimide	84
2.1. In-chain approach	85
2.1.1. Polymerization by DA reactions	85
2.1.2. Polymerization of the DA adducts.....	86
2.2. Side-chain approach	87
2.2.1. Post-functionalization	88
2.2.2. Copolymerization	88
3. Ring-opening polymerization of Maleic Anhydride	91
3.1. Coordinative approach	92
3.2. Anionic approach.....	94
3.3. Radical polymerization	96
4. Examples of cross-linked polyether-based materials.....	96
4.1. Polycondensation approach	96
4.1.1. For proton exchange membrane fuel cells	97
4.1.2. For gas separation membranes.....	98
4.1.3. Epoxy resins.....	99
4.1.4. Polymers for blood-interfacing applications.....	100
4.2. Cationic approach.....	101
4.3. Radical approach	103
4.4. Anionic polymerization approach of epoxide monomers.....	103

5. Activated anionic ring-opening polymerization for the synthesis of reversibly cross-linkable poly(propylene oxide) based on furan/maleimide chemistry	109
6. Activated copolymerization of propylene oxide with maleic anhydride for the synthesis of cross-linkable poly(propylene oxide)	127
REFERENCES	130

1. Introduction

Due to a wide range of epoxides available and using an appropriate polymerization method, it is possible to tune the properties of the final materials or to bring various kind of functionality along the polyether chains which render them very attractive. Various polyether structures can be obtained such as functionalized or hyperbranched polyethers (anionic approach), high molar mass polyethers with controlled stereochemistry (coordination approach), or aromatic polyethers (polycondensation approach). The cross-linking of such materials is believed to further enlarge their application fields potentially as curing resin, for coating of organic and inorganic surfaces, as adhesives, as well as precursors for the formation of hydrophilic, hydrophobic, or thermosensitive gels depending on the nature of the polyether. However, the chemistry used mainly governs the properties of the polyethers obtained. Despite their incontestable interest, polyethers are poorly investigated under the form of cross-linked materials.

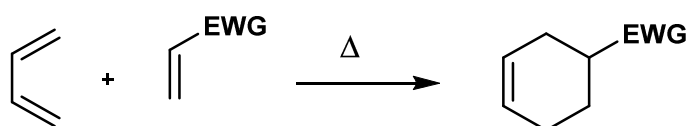
In this chapter, the literature review will describe two chemistries in line with the synthesis we proposed for cross-linkable polyethers. The first one is a reversible approach based on Diels-Alder chemistry which enables the formation of thermally reversible adduct between furan and maleimide. The second one is the ring-opening of maleic anhydride which is widely investigated by copolymerization with substituted epoxides for the synthesis of polyesters. Finally, we will end this literature review by presenting the few examples of materials involving polyethers or epoxides in cross-linked networks.

The synthesis of reversibly or permanently cross-linkable polyethers by anionic ring-opening polymerization of substituted epoxides or maleic anhydride is then presented and discussed. Involving either the incorporation of pendant furan groups able to react with maleimides via Diels-Alder chemistry or the incorporation of double bonds inside the polyether backbone able to form covalent linkages with sulphur bonding by vulcanization.

2. Cross-linking via Diels-Alder chemistry: furan/maleimide

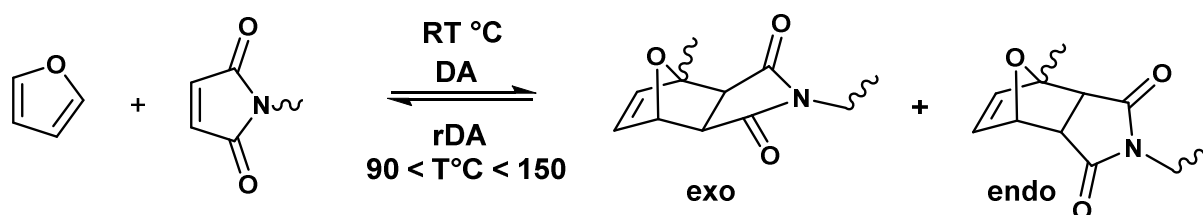
The Diels-Alder reaction is a powerful click chemistry that was discovered in the 1920s[1] and widely used in organic chemistry[2,3]. It consists in a [4+2]-cycloaddition of a conjugated diene and a dienophile usually activated by an electron withdrawing group (Scheme II-1). This electrocyclic reaction involves the 4 π -electrons of the diene and 2 π -electrons of the dienophile. The driving force of this reaction is the formation of new σ -bonds, which are energetically more stable than the π -bonds.

EWG = electron withdrawing group



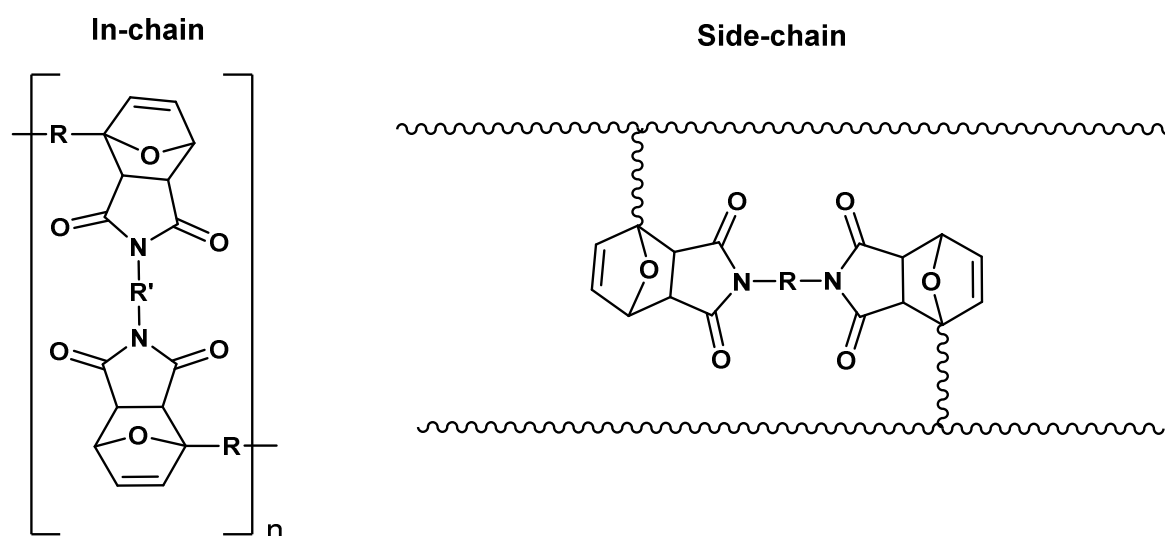
Scheme II-1: General Diels-Alder reaction

Since then, it has been used in the synthesis and functionalization of many novel macromolecules.[4–10] Most of all some forms of the Diels–Alder (DA) reactions are thermally reversible enabling retro-Diels-Alder reactions (rDA) such as the reaction between furan and maleimide. This couple is commonly chosen because of its good reactivity. Indeed maleimides are good dienophiles due to their conjugated double bond[11] allowing high reaction yields, few side reactions, and mild reactions conditions[4,9,11,12]. Thus, at ambient temperature, the two compounds react to form an adduct (exo and endo form). At higher temperatures, this adduct breaks to reform the reactants. The following thermal equilibrium is proposed (Scheme II-2)[9].



Scheme II-2: Diels-Alder reaction between furan and maleimide under thermal stimulus

In polymer science there are two main approaches to integrate this couple within polymer materials. The first one is an in-chain (or multiblock) approach where DA adducts are involved directly in the polymer backbone[7,13–20]. The second one is a side-chain (or cross-linked) approach aiming to introduce either the maleimide or the furan as pendant groups aside the polymer backbone and to achieve to a cross-linked material (Scheme II-3). In the following, those two approaches are briefly exemplified.

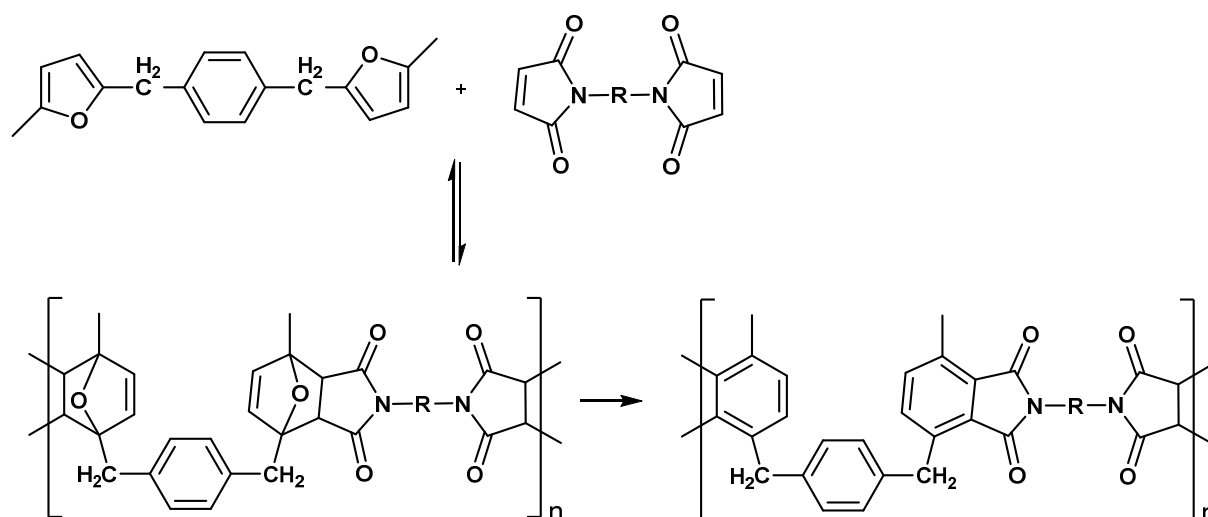


Scheme II-3: In-chain and side-chain approach for the synthesis of furan/maleimide based materials

2.1. In-chain approach

2.1.1. Polymerization by DA reactions

The DA reaction can be used as step-growth polymerization by performing DA polycondensation between AA and BB-type monomers such as bisfuran and bismaleimide (Scheme II-4)[16,20]. However, DA poly-addition is rather slow and similarly to polycondensation reactions, the molar masses are highly depending on the difunctional monomer stoichiometry. Aromatization of the polymer was also observed during the polymerization leading to an irreversible chemical modification. Despite getting thermally more stable macromolecules the retro-Diels-Alder reaction could not longer be performed.

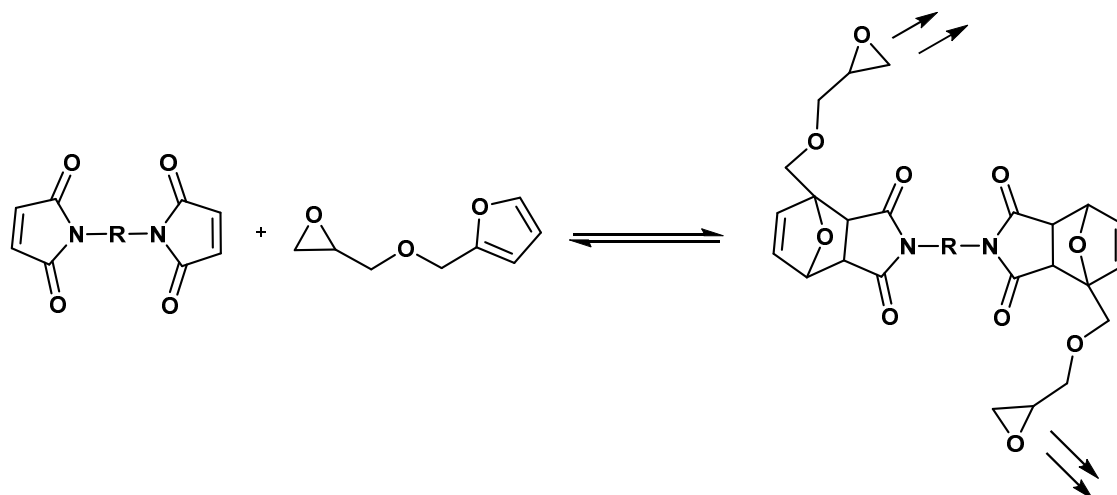


Scheme II-4: DA polycondensation of a bisfuran and a bismaleimide followed by the aromatization of the so-formed polyadduct.

Some other studies were performed with AB-type monomers bearing both a furan and a maleimide group in order to face the molar masses limitations inherent to the stoichiometry between AA and BB-type monomer. But, in all instances the polymer adducts were finally converted into their aromatic counterparts [7,14]. This study was also extended to trifunctional compounds in order to get reversible thermosets[9,20] but it can be reasonably assumed that the same drawbacks can occur. In general DA poly-addition is rather slow, which constitutes an issue for its development in industry. As a consequence the functionalized DA adduct polymerization is often favoured.

2.1.2. Polymerization of the DA adducts

This method consists to introduce the DA adduct directly in the reaction medium and to use it as a precursor for a subsequent synthesis. As an example, a bisepoxy compound was synthesized by DA reaction between a bismaleimide and furfuryl glycidyl ether (Scheme II-5)[21–23]. This method of interest was mainly reported to prepare thermo-reversible epoxy or polyurethane resins [11,24] as the working temperature must be lower than the retro-Diels-Alder temperature to get higher degree of polymerization and preserve the DA adduct integrity.



Scheme II-5: Synthesis of a bisepoxy compound from a bismaleimide and furfuryl glycidyl ether

It must be noticed that with both in-chain methods the polymer is fragmented after each rDA reactions meaning that the macromolecular dimensions are never conserved.

2.2. Side-chain approach

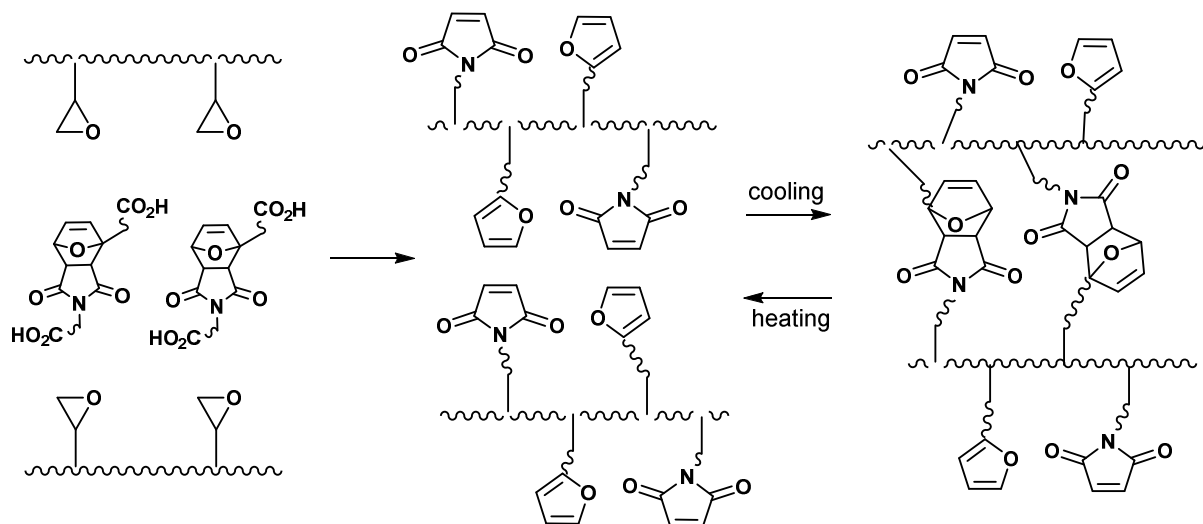
On the contrary, this second approach enables to preserve the macromolecular dimensions and the polymer characteristics such as viscosity or glass transition temperature of the starting materials. Indeed, here, the introduction of DA adducts is performed via pendant reactive groups, such as furans or maleimides, along the polymer chains. As a consequence, the polymer precursors remain unchanged after de-cross-linking.

Based on this approach still with furan/maleimide systems, the development of self-healing cross-linked materials was highly investigated on numerous polymer derivatives such as polyurethanes[25–32] or non-isocyanate polyurethanes[33], but also lignin[34], polystyrene[35,36], polyketones[37], poly(methyl)methacrylates[5,38,39], polysiloxanes[5], polyoxazolines[8], polyamides[40], polyethylene[41], and some polyethers[42,43].

Similarly to the in-chain approach, the side-chain approach can be separated in two main methods depicted below:

2.2.1. Post-functionalization

By a post-functionalization method the polymer constituting the final cross-linked materials can be independently obtained. As an example, an interesting study proposed by Zerroukhi and col. presented a polyethylene-based material reversibly cross-linked by furan/maleimide adducts[41]. Starting from commercial Lotader® (Arkema, polyethylene-co-glycidymethacrylate, $\overline{Mn} = 135\,000$ g/mol), this copolymer was epoxidized in order to react with acid-functionalized furan/maleimide adducts. The grafting step was performed by epoxy-acid reaction in the molten state. The resulting grafted Lotader® was then able to reversibly cross-link under thermal treatments (Scheme II-6).



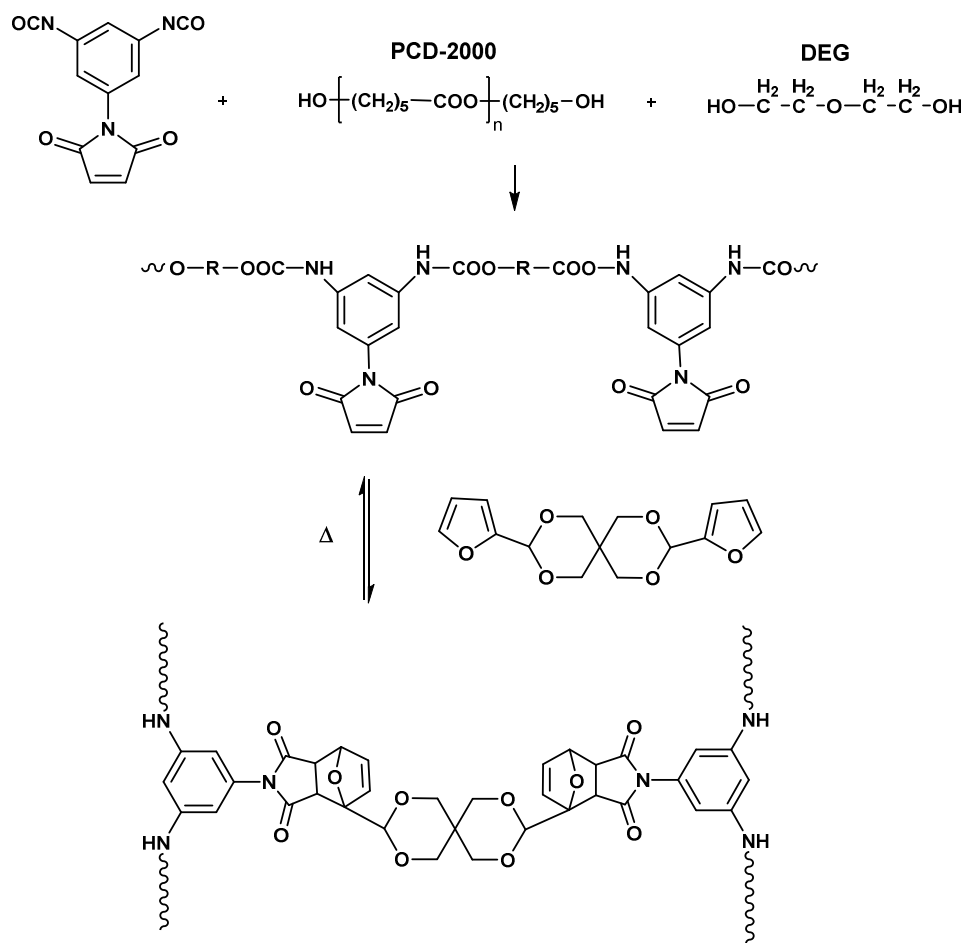
Scheme II-6: Reaction between epoxidized Lotader® (polyethylene-co-glycidymethacrylate) and furan/maleimide adducts

This so called one-step procedure is of interest because it enables a quite direct access to cross-linked materials. Nevertheless, an epoxidation step was still required to make the polymer precursor reactive toward furan/maleimide adducts.

2.2.2. Copolymerization

The copolymerization of monomers bearing maleimide or furan functions is also a mean to distribute reactive moieties along the polymer chain. Thus, maleimide-functionalized diisocyanate derivatives can be copolymerized with polyols (polycaprolactone

diol PCD-2000 + diethylene glycol DEG) to obtain thermo-reversible polyurethane resins where a bisfuran compound is used as cross-linker(Scheme II-7)[32].

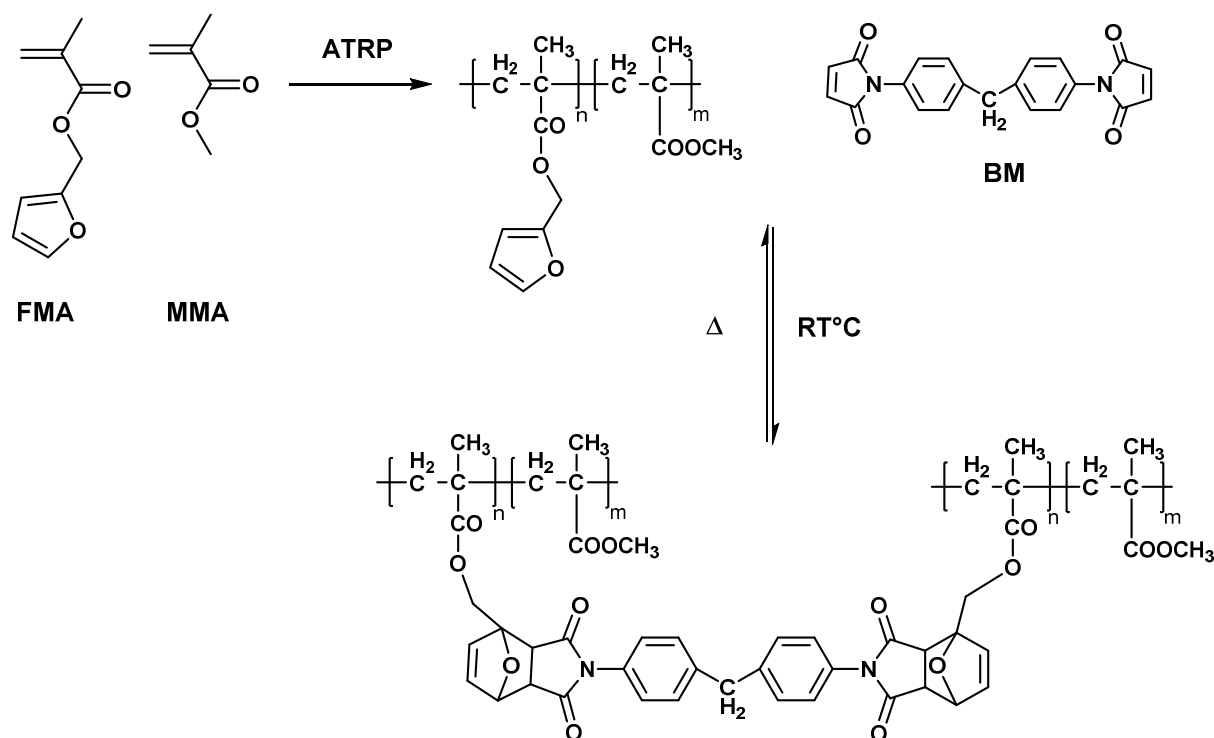


Scheme II-7: Synthesis of polyurethane network in presence of a bisfuran compound starting from a maleimide-functionnalized poly(ester-urethane)

Despite no further indications were given regarding the polymer molar masses, this chemistry is still based on a step-growth approach involving the common features of such a polymerization.

A copolymerization method based on a chain-growth polymerization was used by Singha and col. for the preparation of reversibly cross-linkable polymers consisting of furan-bearing polymer chains reacted with an aromatic bismaleimide (BM) used as a cross-linker in that case.(Scheme II-8)[39]. By atom transfer radical polymerization (ATRP) they performed the

controlled copolymerization of furfuryl methacrylate (FMA) with methyl methacrylate (MMA) and obtained copolymers with molar masses up to 10 000g/mol.



Scheme II-8: Copolymerization of FMA with MMA by ATRP, the so-formed polymers are then cross-linked in presence of bismaleimide

To conclude with the side-chain approach, it is easier to introduce pendant furan groups since they are less reactive than maleimides. A maleimide-based monomer can undergo several side-reactions (such as radical homopolymerization via the maleimide moiety[44]), making them inert toward furans for subsequent cross-linking reactions. Moreover and most of the time, aromatic bismaleimide are preferred. Indeed, it has been shown in a complementary study that aliphatic maleimides are less effective due to the flexibility of their hydrocarbon units, which increases their diffusion in the polymer, thereby reducing the amount of maleimide at a cracked area when self-healing is desired[45].

In general, DA reactions offer convenient and catalyst-free methods leading to thermos-responsive products (in fairly high yields) that enable a large variety of interesting systems. The maleimide/furan couple is the most used DA system in material chemistry due to its

excellent reactivity. Based on these features and its reversible character, DA reaction has been chosen to be involved as a model system in our work aiming at synthesizing cross-linkable polyethers. In this field of research some previous works have already been reported and are referenced in the following part concerning the existing examples of cross-linked polyethers. (see paragraph 4)

3. Ring-opening polymerization of Maleic Anhydride

In the previous part we have seen that the most interesting approach regarding the incorporation of reactive moieties for cross-linking reactions was to introduce them as a side group. Indeed, introduced in-chain, the de-cross-linking leads to the fragmentation of the polymers. Therefore it appears rather complicated to pursue with an in-chain approach with such functionalities.

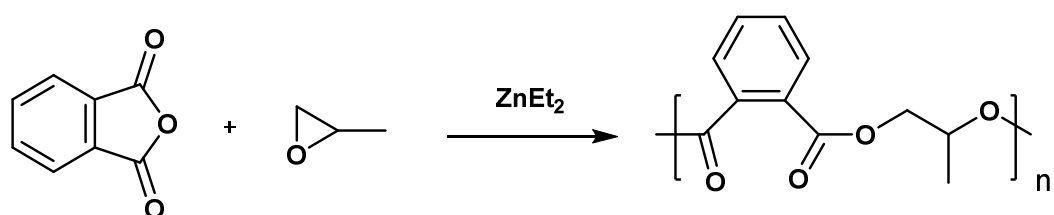
Despite a loss of reversibility, we decided to focus our attention on the ring-opening copolymerization of epoxides with cyclic anhydrides such as maleic anhydride to introduce a C=C double bonds inside a polyether backbone. Indeed double bond is a versatile reactive moiety able to undergo a wide range of post-reactions like oxidation, addition, ..., but also cross-linking reactions.

The ring-opening polymerization of maleic anhydride is mainly involved in the preparation of unsaturated polyesters resins (UPR) usually obtained by polycondensation of maleic anhydride (MA) with phthalic anhydride (PA) and propylene glycol (PG) at 220°C. A reactive diluent (such as styrene or methyl methacrylate) is added to reduce the viscosity of the polyesters during the processing, and is finally copolymerized by free-radical reactions to cure the material and form the resin.[46]

The copolymerization of cyclic anhydrides was also intensively studied with epoxides for the synthesis of new linear polyesters. A few features of this copolymerization are briefly presented hereafter as we are more interested in polyethers. The range of polyesters accessible through this method is nevertheless evoked and the link is mentioned for the synthesis of cross-linkable polyethers.

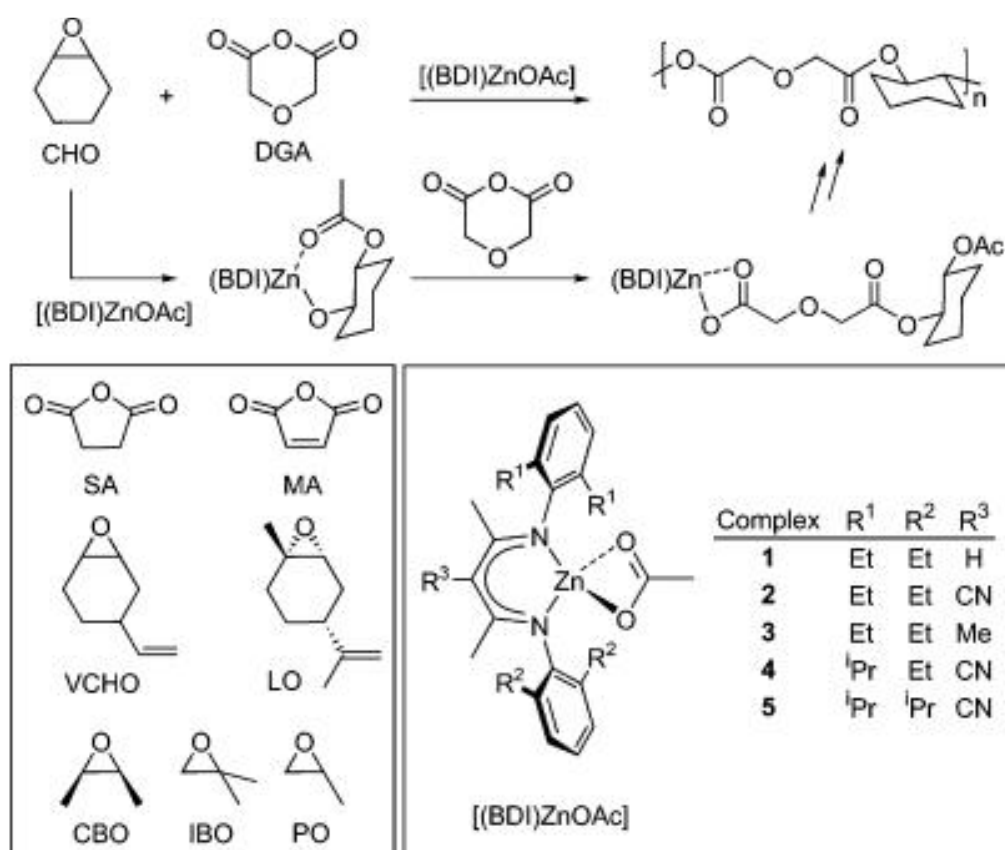
3.1. Coordinative approach

The copolymerization between cyclic anhydrides and cyclic ethers was firstly reported by Fischer et al. in 1960 in the presence of anionic and cationic catalysts at high temperatures[47]. In the presence of organometallic catalyst such as diethylzinc, Inoue et al. postulated that copolymerization of phthalic anhydride and propylene oxide proceeded via an anionic-coordination mechanism in 1969 (Scheme II-9)[48].



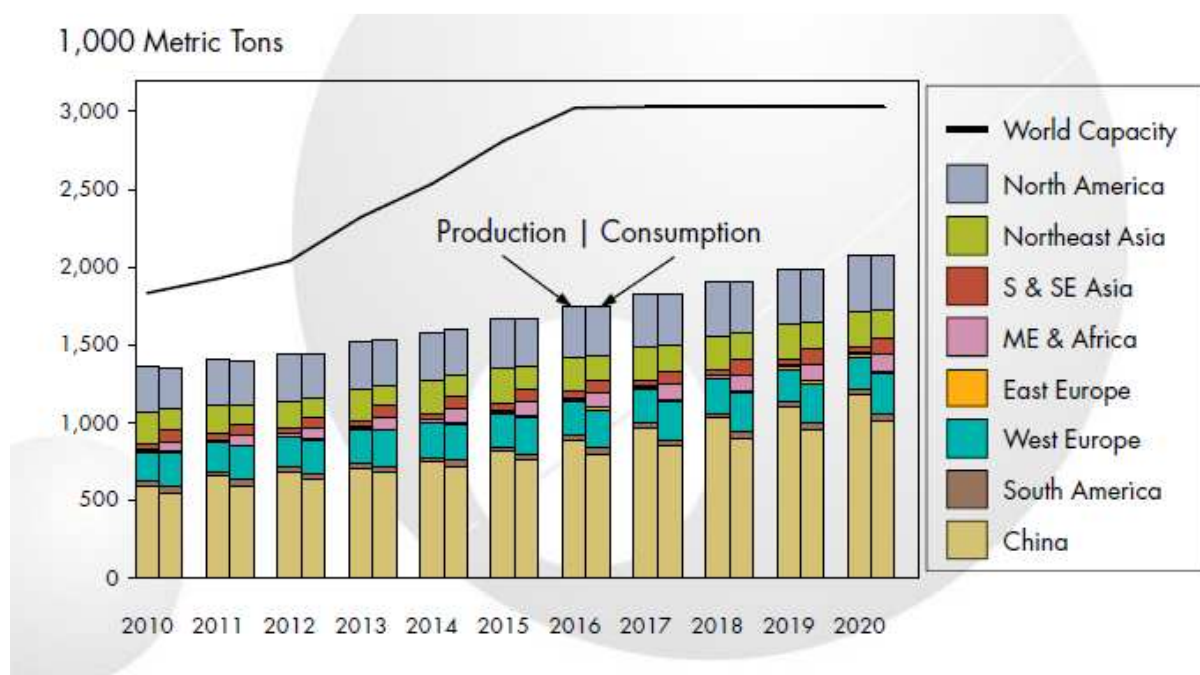
Scheme II-9: Copolymerization of phthalic anhydride and propylene oxide in presence of diethylzinc

This kind of copolymerization was further investigated to form polyesters because of the high tendency to polymerize alternatively such O-heterocycles. Nowadays, it is commonly called ROCOP for ring-opening copolymerization and presented as a more efficient method to get aliphatic polyesters than polycondensation which requires intensive energy, high temperature, and the removal of the by-product (alcohol or water) to favour the esterification reaction to achieve high molar mass polymers. The design of various catalyst with abundance of ligands was for a long time a challenging field of research. The systems reported for the ROCOP generally exhibited low activities, low molar mass values[48–54] and undesired ether formation[55,56]. But, a noticeable breakthrough was pioneered by Coates and co-workers in 2007[57]. They prepared perfectly alternating polyesters with high molar masses (up to 55 000 g/mol) and narrow dispersity (\bar{D} =1.1) by using (BDI)ZnOAc (BDI = β -diiminate) complexes with withdrawing substituents on the ligands as catalysts for the ROCOP of alicyclic epoxides and anhydrides (Scheme II-10).



Scheme II-10: Synthesis of various aliphatic polyesters by ROCOP in presence of (BDI)ZnOAc complexes.

For a long time, attention was paid on decreasing the ether bond amounts. However, in our case, that is exactly the reverse that we want. Here, this coordinative ROCOP was only presented to highlight the interest given by the scientific community toward this pathway. The sustainability of such a copolymerization is also supported by the fact that epoxides and cyclic anhydrides are easily accessible and relatively cheap feed-stocks produced on a large scale. As a convincing example the evolution of the world maleic anhydride supply and demand is given by the following graph(Figure II-1)[58]. Maleic anhydride is produced around 1700 kilotons per year and its price is dependent on the one of benzene or butane which are the two common precursors largely available from the petroleum industry.



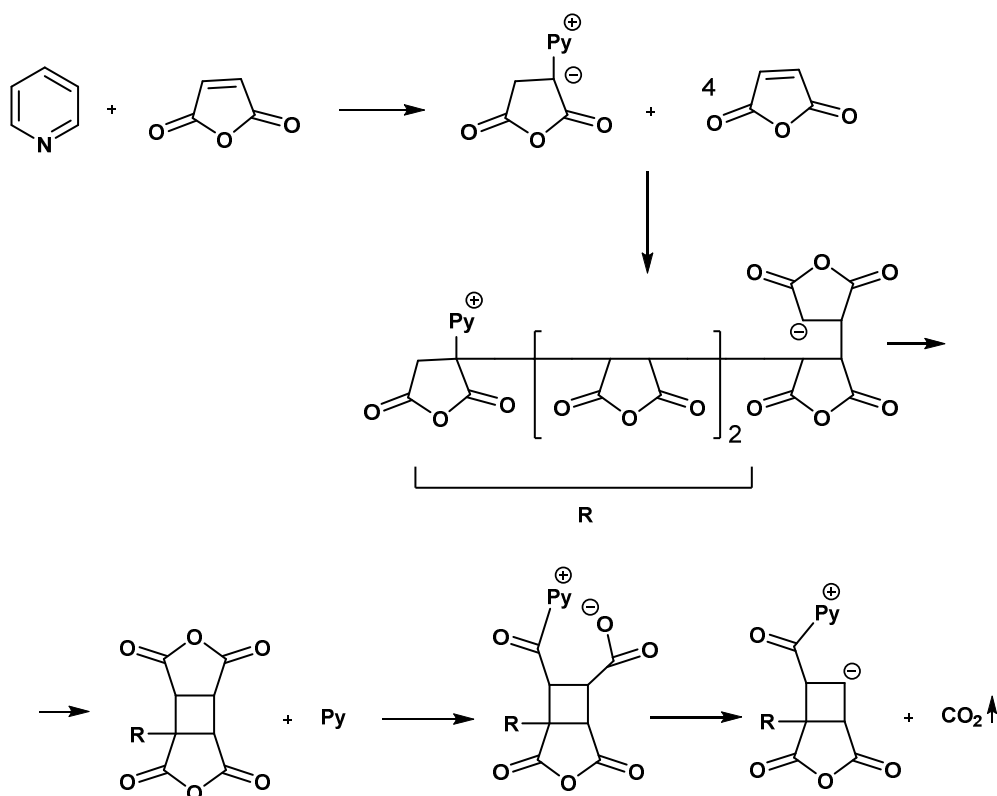
Source: Tecnon OrbiChem

Figure II-1: World maleic anhydride world supply & demand by region.

3.2. Anionic approach

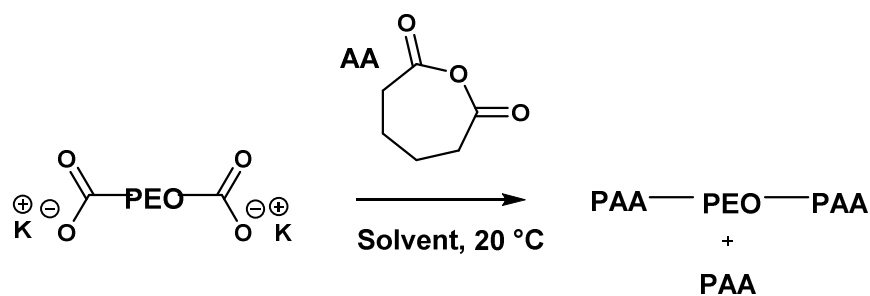
Based on an anionic approach, the example of copolymerization between maleic anhydride and epoxides are much less numerous as the coordinative one rapidly gave better results in terms of well-defined polyesters. The polymerization of such monomers appears to be rather limited as oligomerization is mainly observed and can also (rarely) occur through the double bond only.

As an example, Severini and coll. showed the oligomerization of maleic anhydride initiated by pyridine. A zwitterionic mechanism suffering from decarboxylation reactions is proposed (Scheme II-11) and poly(maleic anhydride) are obtained from 400 to 700 g/mol[59].



Scheme II-11: Maleic anhydride polymerization initiated by pyridine, decarboxylation mechanism proposed.

Another example based on a more conventional anionic mechanism is using a α,ω -carboxyl-terminated poly(ethylene oxide) (PEO) and deprotonated by solid potassium[60]. The so-formed potassium carboxylate was used to initiate the adipic anhydride (AA) ring-opening polymerization in toluene, THF and CHCl_3 (Scheme II-12). The polymerization product was a mixture of poly(adipic anhydride) (PAA) and PAA-PEO-PAA. The length of the PAA block was barely estimated at 1500 g/mol (around 12 AA units) and shown to be independent from the initiator amount. Partial conversion were observed and even very low in toluene. This was attributed by the authors to a lower livingness of the initiator in apolar solvent.

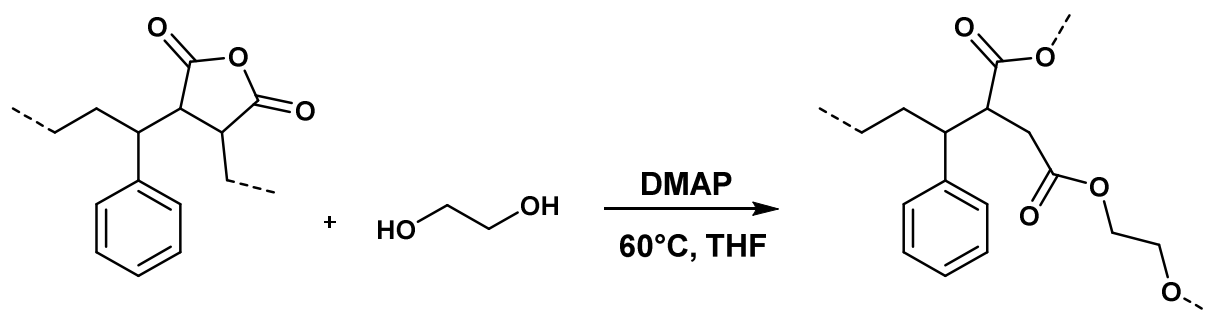


Scheme II-12: AROP of adipic anhydride initiated by potassium dicarboxylate precursor

As can be seen, the anionic approach regarding the ring-opening polymerization of anhydride is poorly referenced due to a weak nucleophilicity of the growing carboxylate. Such an approach was not investigated for the synthesis of cross-linkable polyether-based materials.

3.3. Radical polymerization

Despite its used in polycondensation reactions or ROCOP, it has to be mentioned that maleic anhydride can also be copolymerized with a number of alkene such as styrene, ethylene, isobutylene, etc. via the double bonds to get copolymers which can also be cured by subsequent ring-opening of the maleic ring in presence of ethylene glycol (Scheme II-13). [61,62]



Scheme II-13: General scheme for the cross-linking reaction of poly(styrene-co-maleic anhydride) with ethylene glycol

4. Examples of cross-linked polyether-based materials

Some examples involving the use of polyethers in cross-linked materials can be found. Four approaches can be distinguished and are depicted below.

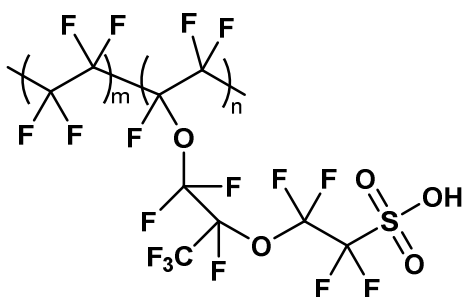
4.1. Polycondensation approach

The main application for cross-linked polyethers-like is the field of membranes. Usually obtained by polycondensation reactions the so-formed polyether-based materials are often used due to their high-ionic conductivity and good thermal stability for the preparation of

proton exchange membrane fuel cells (PEMFC)[63–65]. They are also used for gas separation membranes due to the flexible properties they can provide[66].

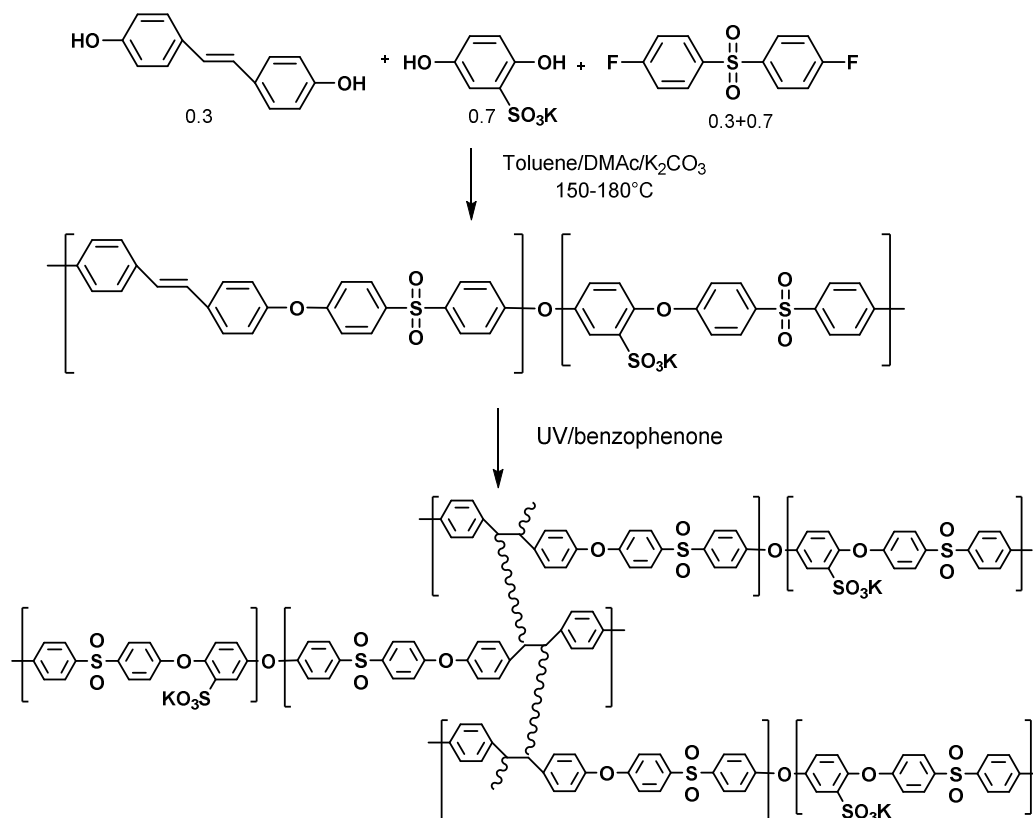
4.1.1. For proton exchange membrane fuel cells

Cross-linked poly(ether sulfone) (PES) membranes are developed intending to compete with perfluorosulfonated polymers such as Nafion®(DUPONT) which is the most commonly used polymer electrolyte membrane for PEMFC (obtained by the copolymerization of tetrafluoroethylene, a derivative of a perfluoroalkyl vinyl ether with sulfonyl acid fluoride (Scheme II-14)[67].



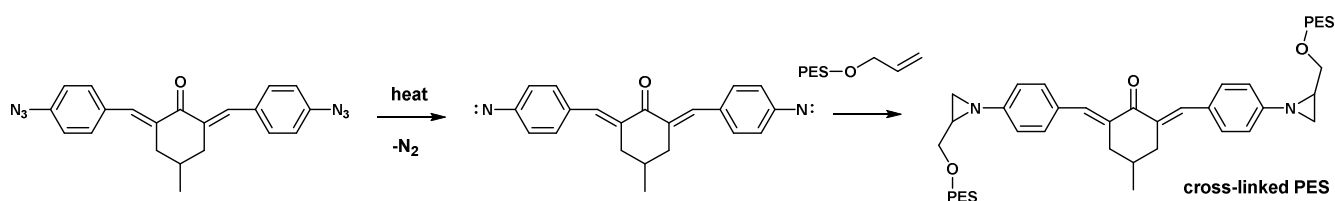
Scheme II-14: Chemical structure of Nafion®

The cross-linking of PES has been used as an efficient means to limit methanol crossover (which is the migration of methanol through the membrane and results in a decreased efficiency of the fuel cell by the presence of mixed potential at the cathode) and also to enhance physical properties of the highly sulfonated polymers[68]. Cross-linked sulfonated poly(ether sulfone) (PES) membranes containing double bonds can derive from the cross-linking with benzophenone under UV irradiation. The polymer is obtained by polycondensation of 4,4-dihydroxystilbene with 4-fluorophenyl sulfone and hydroquinone 2-potassium sulfonate (Scheme II-15)[63]. The cross-linking of sulfonated poly(ether ether ketone) (PEEK) was also reported by UV irradiations for PEMFC applications.[69,70]



Scheme II-15: Synthesis of cross-linked poly(ether sulfone) under UV irradiations

Some sulfonated PES membranes derivatives were also cross-linked by reacting allyl-terminated PES with a thermally treated bisazide as crosslinker (Scheme II-16)[64].



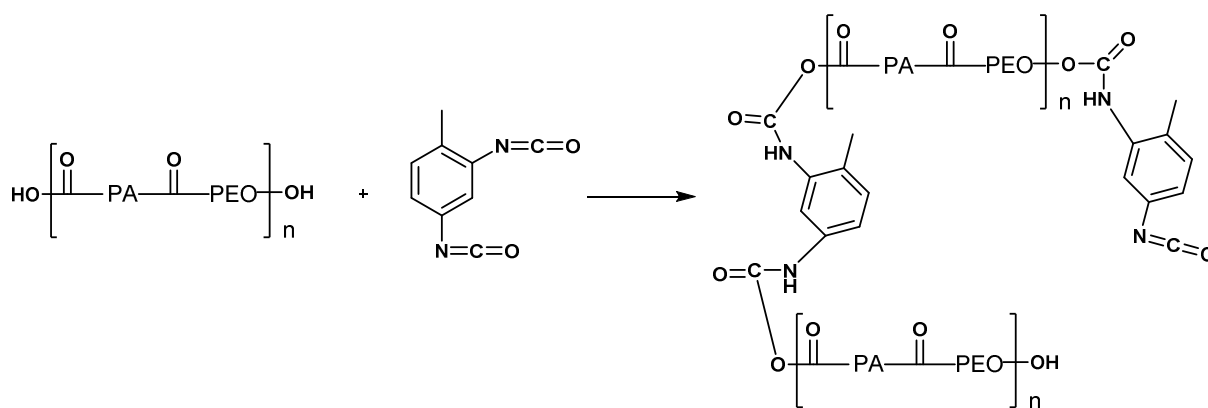
Scheme II-16: Cross-linking reaction of sulfonated PES using bisazide as cross-linker

4.1.2. For gas separation membranes

The development of inexpensive but up-scalable polymeric membranes capable of giving high gas separation factors and permeability, is also a challenging task. Numerous attempts have been made to develop efficient membranes for CO₂/CH₄ separation [71–73]. Poly(ether-block-amide) (PEBA) resin best known under the trademark PEBAX® (ARKEMA), is a thermoplastic

elastomer combining linear chains of rigid polyamide segments interspaced with flexible polyether segments. This crystalline/amorphous structure creates a blend with properties of thermoplastics and rubbers. It was believed that the hard amide block provides the mechanical strength, whereas gas transport occurs primarily through the soft ether block[74].

This block copolymer is obtained by polycondensation of a carboxylic acid-terminated polyamide (PA6, PA11, PA12) with an hydroxyl-terminated polyether. The cross-linking of poly(ether-b-amide) was so investigated to study the final properties of such a polymer[66]. This was performed by formation of a urethane function by reaction between hydroxyl-terminated PEBAX in presence of toluene diisocyanate (TDI) (Scheme II-17).

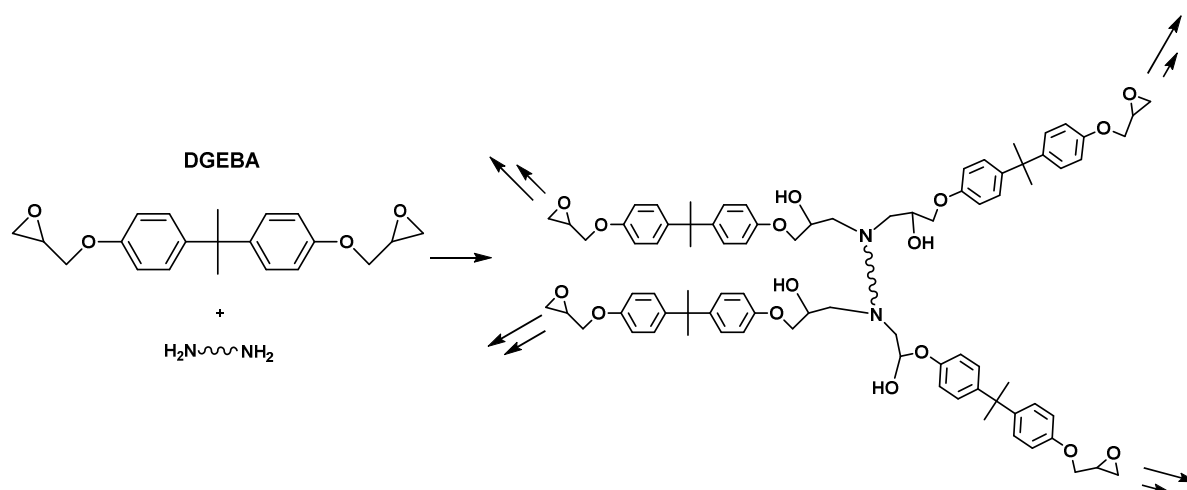


Scheme II-17: Cross-linking reaction of poly(ether-b-amide) in presence of toluene diisocyanate

4.1.3. Epoxy resins

As a part of the cross-linked materials using epoxides we can briefly talk about epoxy resins. They are not literally polyethers materials but possess the epoxide units to enable the formation of a 3D network usually composed of aromatic units. Epoxy resins constitute widely used materials, employed in many fields such as aeronautic, automotive, constructions (paints, adhesives...), electronics (encapsulation) and sports (bikes, racquets...)[75]. Polyaddition is the most commonly used reaction for the cure of epoxy resins. The common curing agents based on active-hydrogen compounds such as polyphenols, polyamines, polyamides, polyacids, polymercaptans, undergo the additions via the active hydrogen and the less steric hindered oxirane carbon with the subsequent ring-opening and formation of an

hydroxyl group (Scheme II-18). Today, 95% of epoxy resins are produced from diglycidylether of bisphenol-A (DGEBA) which is easily prepared by nucleophilic substitution reaction between bisphenol-A and epichlorohydrin under basic conditions. Note that oligomers of DGEBA could also be used in order to space the cross-linking nodes and therefore to tune the mechanical properties of the final epoxy resins.

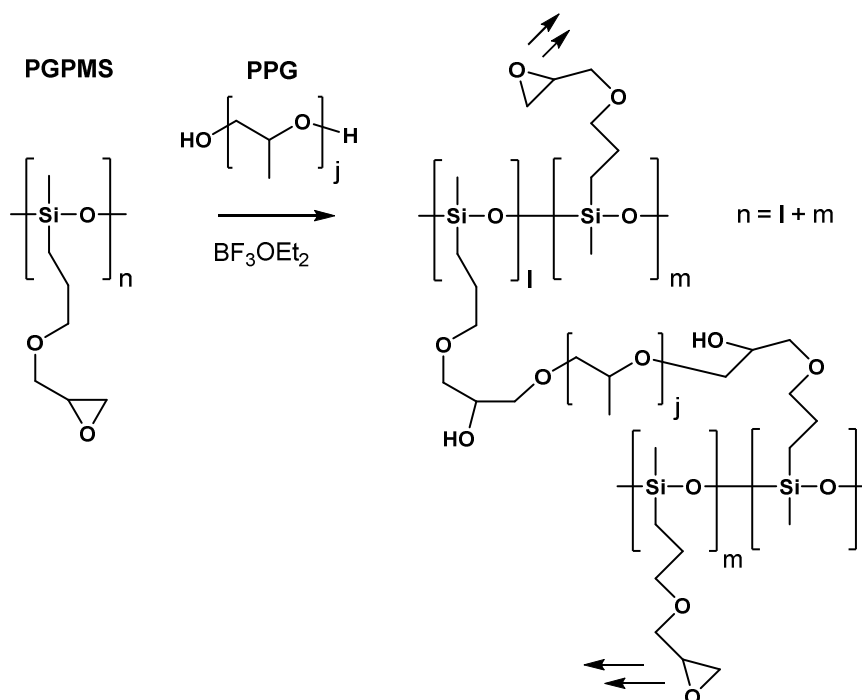


Scheme II-18: Curing reaction between DGEBA and a diamine for the preparation of epoxy resin

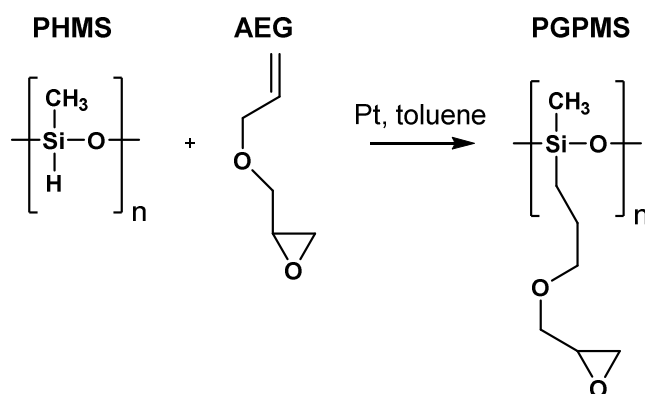
4.1.4. Polymers for blood-interfacing applications

One other example for the preparation of cross-linked polyether-based materials is the synthesis of polyether/polysiloxane networks aiming blood-interfacing applications[76]. Indeed, the interaction of blood with artificial surfaces is an area of continual medical interest[77–79]. The presented materials were produced by reacting the epoxy groups of poly glycidoxypropyl methyl siloxane (PGPMS) with the hydroxyl end groups of polypropylene glycol (PPG) (Scheme II-19). Various amounts of PPG were used. The PGPMS is basically produced via the platinum-catalysed addition of allylglycidylether (AGE) to polymethylhydrosiloxane (PMHS) (Scheme II-20). With such a polymer, the authors were intending to compete with some polyurethane materials. Indeed the blood platelet reactivity was found to vary with the contact to polyurethanes of various compositions[80]. The mix between PGPMS and PPG was so investigated because the long side chain along the PGPMS inhibits access to the Si-CH group which can undergo hydrophobic interactions with proteins and the polyether part provides to the polymer some polar character. Moreover, the presence

of trace amounts of water during network formation are not as critical as in the case of polyurethanes[81].



Scheme II-19: Cross-linking reaction between poly(glycidoxypropyl methyl siloxane) (PGPMS) and poly(propylene glycol) (PPG)

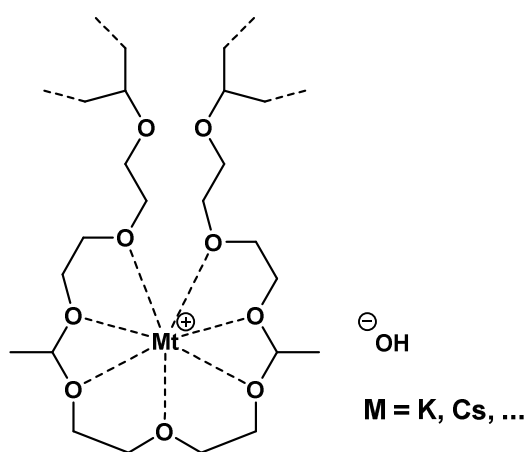


Scheme II-20: Synthesis of PGPMS via platinum-catalysed addition of allyglycidylether (AGE) to polymethylhydrosiloxane (PMHS)

4.2. Cationic approach

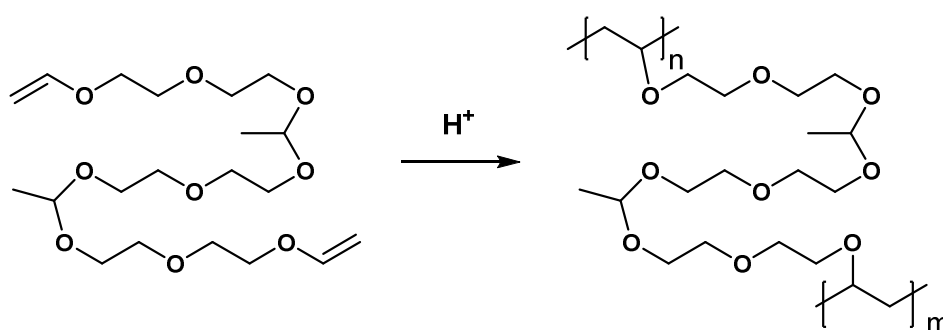
Cross-linked polyether-based materials were also found to be employed for the conception of solid superbase catalysts. Solid superbase catalysts are mostly inorganic and cover a rather limited range of components combination, e.g., alkali metals or their hydroxides, alkoxides or

amides deposited on $\text{c-Al}_2\text{O}_3$, SiO_2 , or Si_3N_4 , that, in turns, restricts their tunability and hence applications.[82] Meanwhile, organic ligands having a good affinity toward alkali metal cations can extend the scope of application of superbase catalysts. The superbase is commonly defined as a strong base complexed with an appropriate ligand which separates the alkali metal cation from the accompanying basic anion that enhances activity of the latter, for example: the complex of KOH with a crown ether. However, such complexes are soluble and quite unstable stoichiometrically.[83] The development of solid superbases by reactive cross-linked polymers was so studied by Trofimov and coll. under the form of polyetheracetal macrocyclic matrix able to incorporate alkali metal hydroxides (Scheme II-21). With this kind of polymer, the heterogenous base-catalyzed alkynyl synthesis and acetylene-allene isomerization of methyl propargyl ether were investigated[84].



Scheme II-21: Complexed metal cation in a cross-linked polyether-based matrix

The synthesis of this cross-linked polyether based material mainly derived from the cationic polymerization of vinyl ether. Under the action of boron trifluoride diethyl etherate (BF_3OEt_2) or lithium tetrafluoroborate/dimethoxyethane (LiBF_4/DME) complex, insoluble cross-linked polymers are formed (yields 80 - 100%) (Scheme II-22).



Scheme II-22: Cationic cross-linking of a vinyl derivatives

4.3. Radical approach

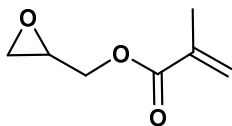
Polyethers were studied as potential materials for vascular prostheses[85]. For this kind of application hydrophilicity and elastomeric behaviour at body temperature are important parameters. Thus, the cross-linking of poly(tetramethylene oxide) (PTMO) with poly(ethylene oxide) (PEO) was performed. The PEO ($\overline{M}_w = 4,5.10^5$ g/mol) was purchased and the PTMO ($\overline{M}_w = 4,5.10^5$ g/mol) was synthesized by cationic polymerization of tetrahydrofuran in presence of antimony pentachloride SbCl_5 .

The cross-linking reaction was allowed by blending these polymers with dicumylperoxide as cross-linker. Initiated under UV at 20°C and 60°C this method enabled to get cross-linked polyether-based materials, however this curing step is far from being controlled. As mentioned by the authors, the cross-linking system was not intensively studied but seemed dependant on the polymer physical state (below or upper the melting temperature). As expected, a decrease of the crystallinity was observed and these cross-linked materials exhibited elastomeric behaviour at 37°C.

4.4. Anionic polymerization approach of epoxide monomers

As compared to all the previous examples, the polyether structure appears to be limited mainly due to the polymerization method. The anionic polymerization of epoxides derivatives bearing reactive moieties toward cross-linking is therefore a way to extend the scope of polyethers with cross-linkable units introduced during the polymerization step with all the benefits that such a polymerization present (functionalisation, block copolymerisation, ...).

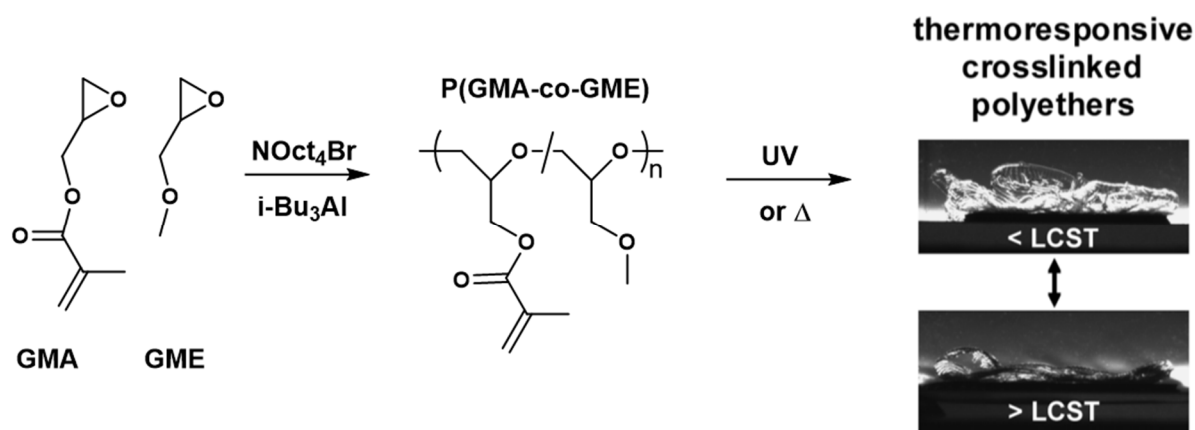
One more time, only few examples are available in the literature based on the use of two monomers, i.e glycidyl methacrylate and furfuryl glycidyl ether.



❖ **Glycidyl methacrylate**

Glycidyl methacrylate (GMA) is a monomer of particular interest since it possesses two polymerizable groups: the epoxide and the methacrylate functions. GMA can be selectively polymerized or copolymerized via one of the two functions, reactive polymers of interest for many applications such as epoxy resins[75], biopolymers immobilization[86], reactive supports[87], etc., can be obtained. The major concern is to use the suitable polymerization conditions that allow a selective reaction of one of the functional groups, thus avoiding cross-linking reaction and the formation of ill-defined materials. Indeed, the literature data report almost exclusively reaction mechanisms involving, more or less selectively, the methacrylate function while the epoxide ring remains unreacted. As an example the use of nucleophilic *s*-BuLi as initiator results in very low conversions and uncontrolled GMA polymerization[88], whereas hindered alkyl lithium systems allow selectively polymerized GMA by the methacrylate function[89].

Thanks to the monomer activated methodology presented in the chapter I regarding the epoxide polymerization[90–93], Carlotti and coll. performed the selective ring-opening polymerization of glycidyl methacrylate distributed in a fully polyether backbone by copolymerization with methyl glycidyl ether[94]. In presence of tetraoctylammonium bromide and triisobutylaluminium, they synthesized statistical copolymers in few hours with molar masses controlled up to 20 000 g/mol and narrow dispersity. The side methacrylate groups were therefore attractive reactive functions owing to the high reactivity of this group toward free radicals[95]. By cross-linking of the pendant double bond (either under heating or UV irradiations) they highlighted the preparation of thermoresponsive polyether hydrogels (Scheme II-23).



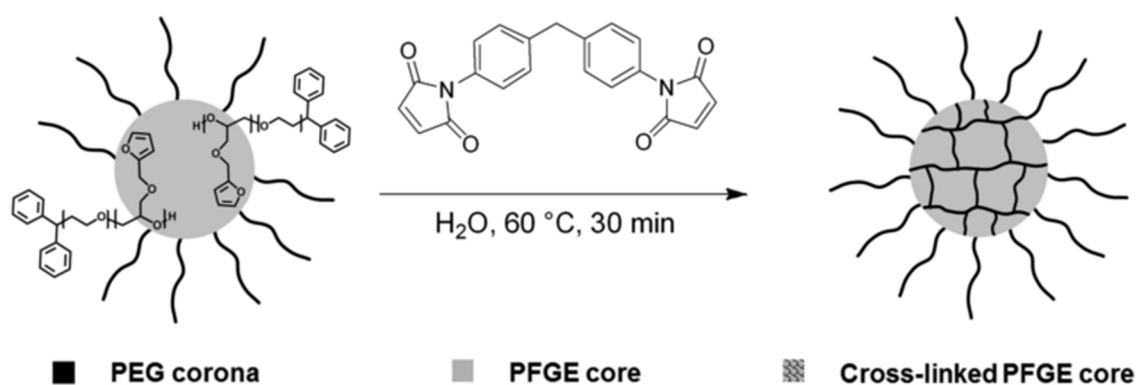
Scheme II-23: Synthesis of poly(glycidyl methacryate-co-glycidyl methyl ether) followed by curing of the pendant methacrylate under UV or heating.



As can be seen in the paragraph 2 of this chapter, the furfuryl glycidyl ether (FGE) is also an interesting monomer as it is composed of an epoxide and a furan moiety, but this monomer was firstly involved in condensation reactions for the preparation of epoxy-thermosets[21–23].

Then, since 2012, Schubert's group paid attention on this monomer and especially by aiming at synthesizing block copolymers able to self-assemble. The homopolymerization in THF was first studied using diphenylmethylpotassium (DPMK) as initiator. For this system, lower molar masses than expected were observed, even if longer reaction times (48 h) were used. Consequently a general study of the FGE homopolymerization was performed focusing on different initiators for the AROP (DPMK, sodium hydride (NaH), cesium hydroxide (CsOH), and potassium tert-butoxide (t-BuOK) in solution THF as well as in bulk[96]. t-BuOK led to poly(furfuryl glycidyl ether) (PFGE) of higher molar masses than DPMK under bulk conditions. CsOH and NaH led to lower molar masses. However, coupling products were observed in case of t-BuOK, DPMK, and CsOH (bi-modal distributions), as well as a broadening of the molar mass distribution using NaH as initiator. On the basis of these results, they selected potassium as the "least worst" candidate for FGE polymerization but never could get higher apparent molar masses than 3 850 g/mol ($\overline{DP_n} = 25$) for a targeted one at 10 000 g/mol probably due to transfer reactions to this substituted monomer. (refer to chapter 1)

Then, by deprotonation of a mono-hydroxyl terminated PEG with DPMK they performed the AROP of FGE to get PEG-b-PFGE copolymers. Aromatic bismaleimide cross-linker was first encapsulated prior to the cross-linking reaction in order to get micelles composed of a PFGE core and a PEG corona (Scheme II-24). By DA reactions in water they immobilized the structure. Thus, the core-cross-linked micelles retain their structure in nonselective solvents like THF or DMF. However, for the retro-DA process, high temperatures were necessary ($\approx 150\text{ }^{\circ}\text{C}$) and only a conversion of 50% could be observed even after 6 hours.

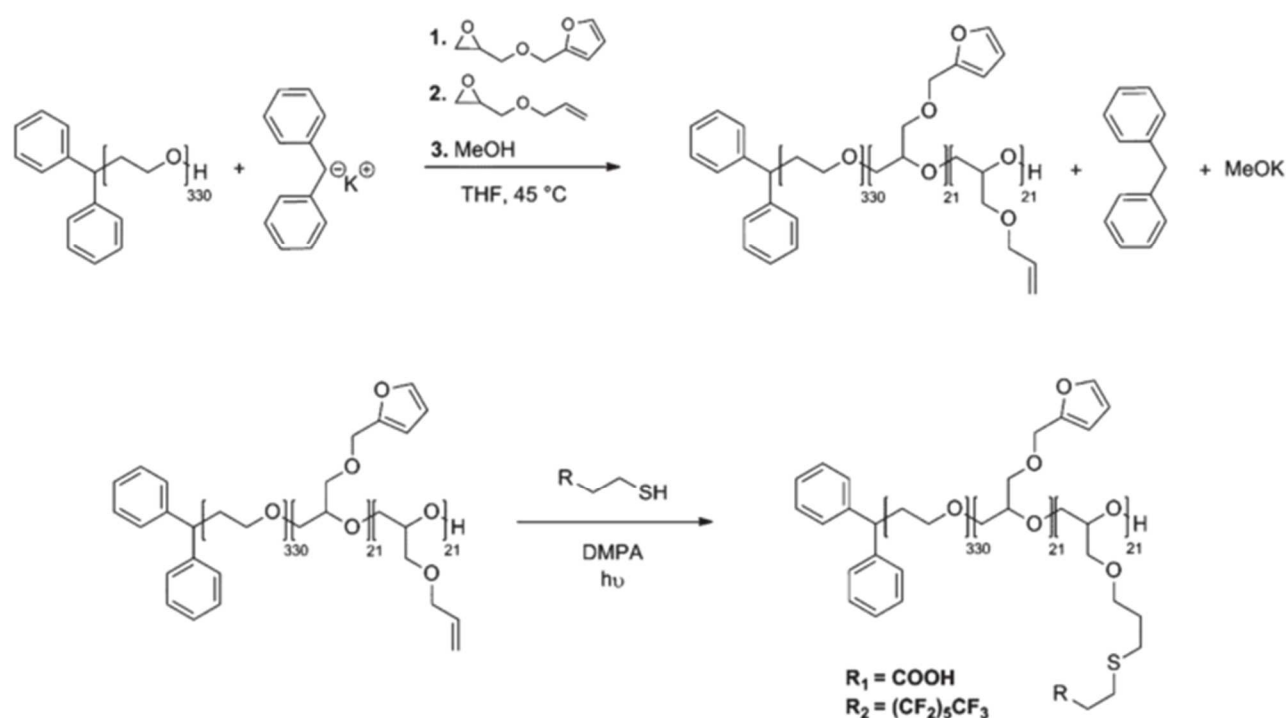


Scheme II-24: Cross-linking by DA reaction of the PEO-b-PFGE under a micellar form

Without the micellization step, this method was also convenient for the preparation of self-healing films.[43]

In a latter article, Shubert and coll. investigated further the copolymerization, and the cross-linking of polyether based materials with the same chemistry intending to extend poly(ethylene oxide) chains with other segments.[97] ABC triblock terpolymer, poly(ethylene oxide)-block-poly(furfuryl glycidyl ether)-block- poly(allyl glycidyl ether) (PEO-b-PFGE-b-PAGE) was synthesized starting from a PEO-OH precursor, deprotonated by DPMK for subsequent anionic polymerization of FGE and AGE (Scheme II-25). The resulting terpolymer exhibited interesting features. Through the pendant double bond provided by AGE monomer, functionalization of the third block was possible by thiol-ene click chemistry. Either a fluorocarbon chain or a carboxy groups were introduced. In the latter case, it has been possible to physically cross-link the terpolymer via of PAGECOOH segment by chelating metal ions (Fe^{3+}). The size of the so-formed objects was shown to be dependent on the pH value and

the polymer/metal ion ratio. With increasing either the amounts of Fe^{3+} or the pH or both, more carboxy groups are complexed, which led to larger particles. However, as compared to the previous example the length of the second and third block had $\overline{DP_n} = 21$ whereas the PEO is composed of 330 repeating units. On the basis of the transfer reaction to substituted epoxides occurring by conventional AROP (see chapter I) we can reasonably assumed that they were limited by the chemistry but it was sufficient for their objective.

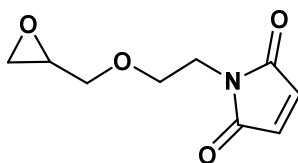


Scheme II-25: Synthesis of the poly(ethylene oxide)-block-poly(furfuryl glycidyl ether)-block-poly(allyl glycidyl ether) (PEO-*b*-PFGE-*b*-PAGE) triblock terpolymer by AROP and the subsequent post-polymerization functionalization using thiol-ene chemistry.

Some other polymerizable epoxides would be interesting to use via anionic ring-opening polymerization in order to get cross-linkable polyethers, i.e allyl glycidyl ether, and maleimide glycidyl ether.



Surprisingly this monomer was only used by AROP to bring reactive vinyl ether side groups along polymer backbones for further functionalization reactions but never for cross-linking using directly the available double-bond.[98]



❖ Maleimide glycidyl ether

This very recent monomer bearing a maleimide moiety was synthesized in 2015 and polymerized by cationic polymerization.[99] The AROP of the epoxide ring would enable to synthesize polyether-based materials with pendant maleimides reactive toward bisfuran cross-linkers. However, as compared to maleic anhydride and due to the high reactivity of the maleimide a side ring-opening may be envisaged.

To conclude this literature review, we have seen that the diversity of cross-linkable polyether-based materials is mainly dependent on the type of chemistry used. Either for a side-chain or an in-chain approach, the activated AROP appears to be a powerful tool to extend the range of accessible materials, especially regarding substituted epoxides. Furthermore, we have also seen that in the furan/maleimide chemistry, even if bismaleimides are used as cross-linkers, they are mainly aromatic which can limit the targeted materials to only rigid cross-links. Thus in the following, we attempted to circumvent some points through the activated copolymerization of propylene oxide and furfuryl glycidyl ether. The so-formed polymers were reacted with an aromatic but also an aliphatic bismaleimide. This work was done in collaboration with Elena Dolci a PhD student under the supervision of Dr Sylvain Caillol in the team “Ingénierie et Architectures Macromoléculaires” (IAM) from Charles Gerhardt Institut in Montpellier. The polymers were synthesized in the LCPO and the cross-linking was performed in Montpellier as they are developing the furan/maleimide chemistry. The results of this study appear in the next part under the form of a submitted article.

Regarding the in-chain approach the introduction of double bonds inside polyether chains was studied by activated AROP of propylene oxide with maleic anhydride. The preliminary results are presented.

5. Activated anionic ring-opening polymerization for the synthesis of reversibly cross-linkable poly(propylene oxide) based on furan/maleimide chemistry

Roos, K.; Dolci, E.; Carlotti, S.; Caillol, S. *Polym. Chem.* **2016**. DOI: 10.1039/c5py01778e [100]

ABSTRACT

The synthesis of cross-linkable random copolyethers of propylene oxide (PO) and furfuryl glycidyl ether (FGE) is firstly discussed. The anionic ring-opening polymerization and monomer activation methodology, based on the combination of tetraoctylammonium bromide and triisobutylaluminum, is used to perform the controlled synthesis of poly(propylene oxide-co-furfuryl glycidyl ether) copolymers with various compositions 95/5, 90/10, 75/25, 50/50, and 25/75 (PO/FGE mol%) and keeping the furfuryl moieties active. Copolymers with molar masses around 10 000 g/mol were obtained in short times. Subsequently, the furfuryl moieties were reacted to aromatic and aliphatic maleimide-based cross-linkers to perform Diels-Alder (DA) “click” reactions. Tridimensional networks were obtained and their swelling ratio and insoluble fraction were determined. Glass transition temperature and retro-Diels-Alder (rDA) transition in the network were determined by differential scanning calorimetry analyses. Gels properties vary with the furan group amount in the initial copolymer and the cross-linker structure. The network disassembly at 110°C was monitored by ^1H NMR and quantitatively recorded by the re-appearance of the copolymer signals due to rDA reaction. The solubility study showed that the gel was able to reform at 20°C leading to reversible cross-linked polyethers.

KEYWORDS

anionic ring-opening polymerization, monomer activation, polyether, reversible cross-linking, Diels-Alder, furan-maleimide

INTRODUCTION

As a part of well-known polymeric materials, polyethers are still today of high importance with a wide range of applications, from the automotive and paper industry to cosmetics and biomedical domains. Polyethers are basically key components used notably in the production of polyurethanes under the form of rigid or flexible foams, adhesives, sealants, coatings and many other applications. Polyurethanes were and are still intensively studied in particular cross-linked materials due to good mechanical properties, thermal stability, and insolubility in solvents when compared to linear structures. However, cross-linked materials cannot be reprocessed or repaired after fracture which represents a great deal for environmental concerns and mostly for recycling. In response to that concern, remendable polymers have been widely studied over the last decades in many fields of application[10,101–104]. The most efficient way to obtain remendable thermosets is to incorporate reversible bonds which can break on demand using a proper stimulus. Several stimuli are possible: temperature, radiation, pH, etc. Among reversible reactions, the Diels-Alder (DA) reaction is a great tool to create thermoresponsive polymers. Involving diene and dienophile species, the Diels-Alder reaction is a [4+2] cycloaddition leading to an adduct which can dissociate under thermal treatment to turn back into the previous diene and dienophile compounds. In polymer science it is particularly desirable for thermoresponsive polymers preparation since DA reaction allows high yield, few side reactions, and mild reaction conditions[4,9,11,12,21,22]. Most of the time, a furan/maleimide couple is chosen as diene/dienophile because of its good reactivity. Many studies combine furan/maleimide with polyurethanes[25–31] or non-isocyanate polyurethanes[33], but also lignin[34], polystyrene[35,36], polyketones[37], poly(methyl)methacrylates[5,38], polysiloxanes[5], polyoxazolines[8], polyamides[40], polyethylene[41], and some polyethers[42,43,99]. The enthusiasm toward the use of maleimide as dienophile is due to its relatively high reactivity thanks to the electron-deficient C=C bond[11]. In addition, a wide range of furan monomers can be prepared from furfural and hydroxymethylfurfural obtained from bio-based polymers (C5 or C6 sugars in polysaccharides respectively)[105]. Two main approaches integrate DA adducts in a polymer network: the multi-block pathway (including DA adduct polymerization, and also polymerization by DA reaction)[7,13–20], and the cross-linking pathway. The main drawback of the first approach is the damage caused to the polymer backbone during retro Diels-Alder (rDA). Therefore, the second approach is often preferred. Indeed, the cross-linking

of polymer network by DA reaction ensures to go back to a linear system after a thermal treatment. To proceed in that pathway, the better option is to (co)polymerize a monomer bearing either the furan or maleimide function as a side group. Thus, it leads to a polymer with pending DA reactive groups. Since the maleimide reactivity could be difficult to control, furan functionalized monomers are often preferred. For instance, Gandini and his coworkers synthesized reversibly crosslinked elastomers by copolymerizing 2-furfuryl metacrylate with hexylacrylate, to give an acrylic polymer bearing furan groups, and crosslink it by DA reaction using a bismaleimide compound[106]. Thus furfuryl glycidyl ether (FGE) is a promising monomer for making reactive polyethers. Researches were focused on different chemistries for their synthesis. As an example poly(furfuryl glycidyl ether) (PFGE) bearing furfuryl moieties on the side chain were prepared using condensation reactions with limited control over molar masses and dispersity[23]. A two-step synthesis was also proposed. Deprotonation of a monohydroxy-terminated poly(ethylene oxide) (PEO-OH) with diphenylmethylpotassium (DPMK) gave rise to the synthesis of reversible cross-linked micelles and films under the form of copolymers (PEO-b-PFGE or PEO-b-PFGE-b-PAGE)[43,96,107,108]. Synthesized from different alkali initiators (NaH, CsOH, DMPK or t-BuOK), potassium counter-ion was chosen as the best candidate to obtain these polymers, despite low molar mass due to transfer to substituted monomer[109,110] and long reaction times inherent to this chemistry. The few developments of reversibly cross-linked polyethers are mainly focused on ethylene oxide-based materials and an aromatic bismaleimide[43,96,108].

In this article, the anionic ring-opening polymerization of propylene oxide and furfuryl glycidyl ether activated by triisobutylaluminium[90,91,93] is studied as a one-step approach to get the corresponding and reactive statistical copolymers. Two different bismaleimides are also investigated for the curing part in order to evaluate their impact over the final cross-linked polymer properties. Indeed, it has been shown that the length and the chemical composition of such linkers/spacers could influence the physical properties and the DA-rDA cycle efficiency[25,111].

Experimental Section

Chemicals

Furfuryl alcohol (2-(hydroxymethyl)furan, 98%), epichlorhydrin (1-chloro-2,3-epoxypropane, 99%), tetrabutylammonium bromide (TBABr, 98%), propylene oxide (1,2-epoxypropane, PO, 99%), tetraoctylammonium bromide (N(Oct)₄Br, 98%), triisobutylaluminum (iBu₃Al, 1M in toluene), 1,1'-(methylenedi-4,1-phenylene)bismaleimide (95%), toluene (99.5%), tetrahydrofuran (THF, 99.9%) and chloroform (99%) were purchased from Sigma Aldrich. Polyether bismaleimide (PEO-PPO-bm) was synthesized by SPECIFIC POLYMERS (product reference SP-1P-9-015). Propylene oxide was purified over CaH₂ and freshly distilled before use in graduated glass tubes. Toluene was stored over polystyryllithium seeds and kept under vacuum for further distillation until use. Triisobutylaluminum was used as received.

Instrumentations

Size Exclusion Chromatography

Polymer molar masses were determined by Size Exclusion Chromatography (SEC) using THF as the eluent. Measurements in THF were performed on a PL GPC50 integrated system with RI and UV detectors and four TSK columns: HXL-L (guard column), G4000HXL (particles of 5mm, pore size of 200Å, and exclusion limit of 400 000g/mol), G3000HXL (particles of 5mm, pore size of 75Å, and exclusion limit of 60 000g/mol), G2000HXL (particles of 5mm, pore size of 20Å, and exclusion limit of 10 000g/mol) at an elution rate of 1mL/min. Polystyrene was used as the standard.

Nuclear Magnetic Resonance

¹H NMR spectra were recorded on a Bruker AC-400 spectrometer in appropriate deuterated solvents.

Thermal analysis

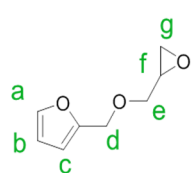
Differential scanning calorimetry (DSC) measurements were carried out with a Q100 apparatus from TA Instruments. DSC experiments were performed with aluminum sealed pans. A constant heating/cooling rate of 10°C/min and gas purging (N₂) at a flow rate of 100

mL/min was used for all experiments. The glass transition temperatures were calculated from the second heating run. DSC traces showed that all the polymers were amorphous. Measurements by modulated DSC were carried out on the same apparatus in modulated mode ($\pm 0.64^{\circ}\text{C}$ every 60 seconds) between -140°C (with an isotherm of 5min) and 250°C with a ramp of $5^{\circ}\text{C}/\text{min}$.

Experimental procedure

Synthesis and purification of furfuryl glycidyl ether (FGE)

Epichlorohydrin (102g, 1.1mol) and tetrabutylammonium bromide (4.5g) were charged into a 500mL two-necked round-bottom flask equipped with an inlet for dry nitrogen. The system temperature was kept at room temperature while furfuryl alcohol (98g, 1mol) was added dropwise over a period of 45min. The reaction was stirred for 4h and then 150mL of aqueous sodium hydroxide (40%w/w) was poured into the system at 0°C . The reaction was left overnight, then the product was extracted with ethyl acetate and washed with water several times. The organic layers were collected, dried and the solvent was removed using rotary evaporator. A light yellow liquid was collected and then purified by distillation at 110°C under 700mbar. A colorless liquid was obtained in a 60% total yield and a final purity superior to 99% purity.

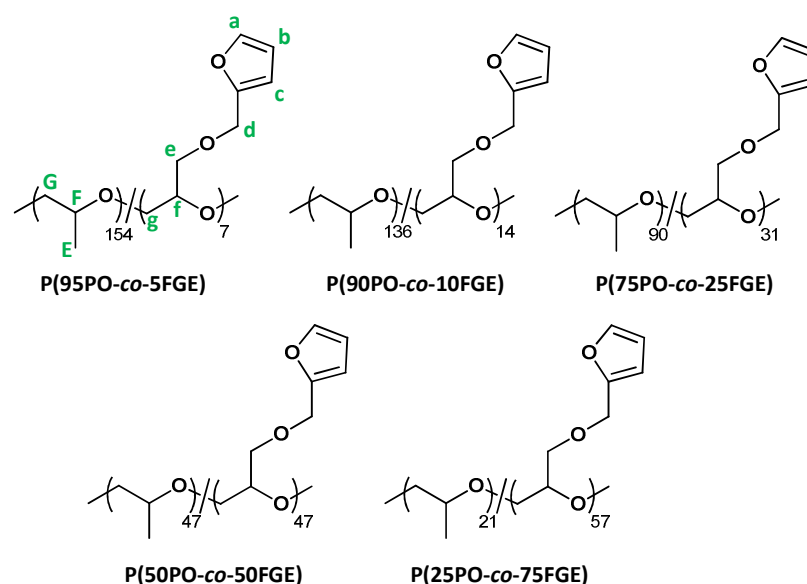


^1H NMR (400MHz, $\text{DMSO}-d_6$) δ ppm: 7.63 (s, 1 H, H_a), 6.43 (b.s, 2 H, H_b and H_c), 4.41 - 4.54 (s, 2 H, H_d), 3.73 (dd, $J=11.5$, 2.6Hz, 1 H, H_e), 3.29 (dd, $J=11.5$, 6.4Hz, 1 H, H_e), 3.11 (m, 1 H, H_f), 2.72 (dd, $J=5.1$, 4.2Hz, 1 H, H_g), 2.54 (dd, $J=5.1$, 2.3Hz, 1 H, H_g)

General procedure for the synthesis of poly(propylene oxide-co-furfuryl glycidyl ether) P(PO-co-FGE) (Scheme 1)

All the polymerizations were initiated at -30°C under argon atmosphere in a glass reactor equipped with a magnetic stirrer and fitted with Teflon stopcocks. As an example for the targeted composition of 90/10 mol% (PO/FGE) a polymerization reactor was flamed under vacuum and cooled down prior to the introduction of 4.33mL of dried toluene through a connected glass tube. Then 0.13mL of furfuryl glycidyl ether (0.96mmol) and 0.6mL of

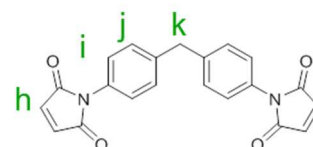
propylene oxide (8.62mmol) were added to the 4.33mL of toluene. 0.23mL of a 0.276M solution of tetrabutylammonium bromide in toluene were added via syringes under dynamic argon flow. Finally 0.22mL of triisobutylaluminum were added to start the polymerization. The starting yellow solution turns immediately to a deeply reddish coloration. The polymerization was started at -30°C and let to go to 20°C for 24h. Methanol was used to stop the reaction. Theoretical \overline{Mn} = 10 000g/mol and SEC (PS standards) \overline{Mn} = 19 900g/mol. \overline{D} = 1.12. The integrations of d (or b+c) protons are in agreement with 2 protons. The experimental composition was calculated in mol% with the following calculation (FGE content (mol%) = $(I_d/2)/(I_d/2 + I_E/3) \times 100$), I_d and I_E being the integration values of the methylene group d and the methyl group E respectively.



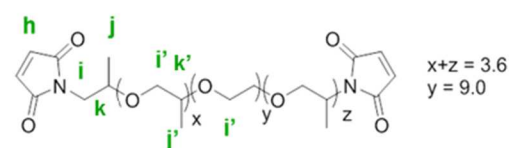
Scheme 1: Targeted copolymers structures

Cross-linkers ^1H -NMR signals

1,1'-(methylene-di-4,1-phenylene)bismaleimide (dPhbm): ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ ppm 7.34 - 7.38 (d, $J=8.6$ Hz, 4 H, H_i) 7.26 (d, $J=8.6$ Hz, 4 H, H_j) 7.1 (s, 4 H, H_h) 4.03 (s, 2 H, H_k)



PEO-PPO-bm: ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ ppm 6.82 - 7.04 (br.s., 4 H, H_h) 4.21 (m, 2 H, H_i) 3.20 - 3.74 (m, 49 H, $H_{i'}$ and H_k and $H_{k'}$) 0.90 - 1.25 (m, 11 H, H_j and $H_{j'}$)



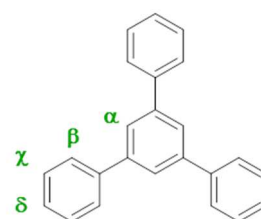
Diels-Alder : cross-linking reaction

The copolymer P(PO-*co*-FGE) (1.00 equivalent of furanic functions) is dissolved in chloroform, and a cross-linker is added (0.90 equivalent of maleimide functions). The mixture is stirred at 20°C for 2 days. The obtained gel is put in the oven at 35°C under vacuum to remove chloroform.

¹H-NMR retro Diels-Alder

A sample of the cross-linked polymer is put in DMSO-*d*₆ with a precise amount of 1,3,5-terphenylbenzene as standard. The system remains at room temperature for 2 days in order to soak the cross-linked polymer. The tube is put at 110°C and ¹H-NMR spectra are recorded frequently to report the composition of the liquid phase.

1,3,5-terphenylbenzene standard: ¹H NMR (400 MHz, DMSO-*d*₆) δppm 7.86 (s, 3 H, H_α) 7.82 (d, *J*=7.09 Hz, 6 H, H_β) 7.51 (t, *J*=7.46 Hz, 6 H, H_χ) 7.41 (t, *J*=7.46 Hz, 3 H, H_δ)



Swelling ratio and insoluble fraction determination

Swelling measurements of the polymer network were carried out using THF as diffusing agent. The swelling percentage was calculated from the differences in weight between dried and swollen networks. For each material, 3 samples (written m_0^i and ranging from 20 to 30mg) were separately dipped into the solvent (THF, 30mL). After 24h, the samples were removed from the solution and their surfaces were dried superficially with filter paper and their weights were measured (m_1^i). For each sample, a swelling ratio (SR_i) was calculated according to the equation below:

$$SR_i = \frac{(m_1^i - m_0^i)}{m_0^i}$$

After the swelling ratio measurements, the samples were dried in a vacuum oven at 40°C during 2 days. Their resulting weights were written (m_2^i) and the insoluble fraction (IF_i) was calculated according to the equation below:

$$IF_i = \frac{m_2^i}{m_0^i}$$

RESULTS & DISCUSSION

Synthesis of poly(propylene oxide-co-furfuryl glycidyl ether) P(PO-co-FGE)

According to Table 1 (run 1 and 2) the homopolymerization of furfuryl glycidyl ether proceeds in a similar way than other oxiranes using anionic ring-opening polymerization and monomer activation[90,91,112,113]. This monomer requires higher amount of $i\text{Bu}_3\text{Al}$ as compared to propylene oxide or ethylene oxide. Indeed a slight excess of aluminum compound is not sufficient because no polymerization is observed for a $[\text{Al}]/[\text{I}]$ ratio equal to 1.7. Almost complete or complete furfuryl glycidyl ether (FGE) conversion is achieved at a higher ratio (3.4). In the simplest case of ethylene oxide for instance, aluminum can only coordinate to the oxygen of the epoxide ring, thereby withdrawing electron density of the methylene groups, which facilitates a nucleophilic attack. By analogy to ethoxyethyl glycidyl ether (EEGE)[93] and glycidyl methyl ether (GME)[114], FGE monomer contains three oxygens that can coordinate to aluminium. As a result the aluminum compound basically designed to activate the epoxide moiety is believed to be “trapped” in a secondary coordination between the others FGE oxygen atoms (Scheme 2) which inhibits the polymerization. The aluminum amount must be increased to trigger the polymerization of FGE and reach higher conversion within longer reaction times as compared to PO[90]. Then, when propylene oxide was involved for the copolyether synthesis, the ratio was kept to 3.4 to prevent aluminum trapping by FGE. Reactions were let to go for 24h even though the polymerization can be completed in shorter times when a high PO content is expected and in comparison with previous works on copolymerization[93,112,115]. The obtained experimental compositions determined by ^1H NMR closely match with the targeted ones. In the case of PO-rich polymers (run 3 and 4 Table 1) the molar mass values seem higher than expected. A 0.6 corrective factor on molar masses of PPO measured by SEC with PS calibration were already reported[90]. Regarding the FGE-rich polymers (run 2, 6 and 7, Table 1), a dispersity broadening is observed probably due to more transfer to reactions to FGE. The P(50PO-co-50FGE) and P(25PO-co-75FGE) exhibits also lower molar masses which can be attributed to a different hydrodynamic radius than other PO-rich compositions.

CHAPTER II. Synthesis of cross-linkable polyethers by anionic polymerization

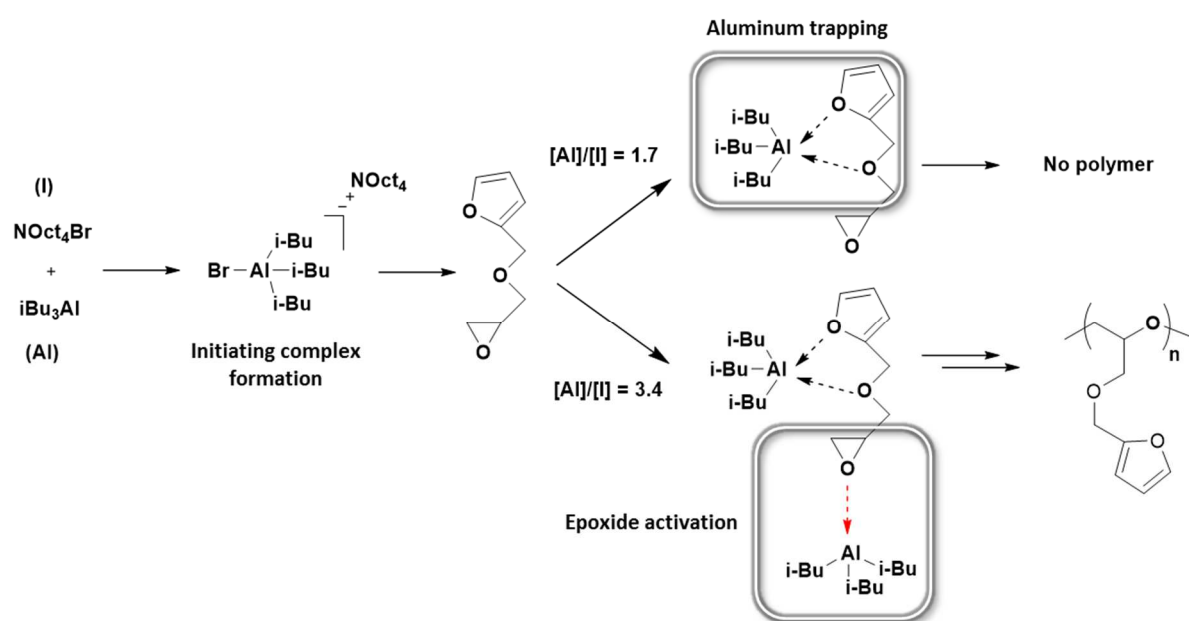
Table 1: Polymerization of furfuryl glycidyl ether and its copolymerization with propylene oxide initiated by NOct₄Br (I) in the presence of *i*-Bu₃Al (Al) in toluene (24h)

Run	Theoretical Composition (PO/FGE) (mol%)	[Al]/[I]	Experimental composition ^a (PO/FGE) (mol%)	Conv ^{a,b} %	\overline{Mn}_{calcd} ^c (g/mol)	\overline{Mn}_{exp} ^d (g/mol)	\overline{D} ^d	T _g ^e (°C)
1	0/100	1.7/1	-/-	0	-	-	-	-
2	0/100	3.4/1	-/100	93	9 300	21 000	1.45	-40
3	95/5	3.4/1	95.7/4.3	100	10 000	21 700	1.11	-64
4	90/10	3.4/1	90.6/9.4	100	10 000	19 900	1.12	-61
5	75/25	3.4/1	72.5/27.5	100	10 000	18 300	1.22	-53
6	50/50	3.4/1	49.5/50.5	100	10 000	10 100	1.46	-45
7	25/75	3.4/1	25.3/74.7	100	10 000	11 720	1.40	-40

^aDetermined by ¹H NMR. ^bDetermined gravimetrically. ^c $\overline{Mn}_{calcd} = ([FGE]_0/[NOct_4Br]_0 \times M_{FGE} + [PO]_0/[NOct_4Br]_0 \times M_{PO}) \times \text{conv.}$

^dDetermined by size exclusion chromatography in tetrahydrofuran using a calibration with polystyrene standards.

^eDetermined by Differential Scanning Calorimetry.



Scheme 2: Polymerization of furfuryl glycidyl ether initiated by tetraoctylammonium bromide in the presence of triisobutylaluminum and depending on the ratio [Al]/[I]

As an example, the ¹H NMR spectrum (**Erreur ! Source du renvoi introuvable.**) confirms the synthesis of P(9PO-co-5FGE). The experimental composition is calculated and agrees with the theoretical one. Every peak was assigned, F, G and e, g, f protons from 3.3 to 3.7ppm belong to the polyether backbone from PO and FGE units respectively. Protons E represent the

resonance from the methyl group of PO units at 1.15ppm. Then a, b, c and d labels are attributed to the pendant furfuryl moiety. Except in the case of homo poly(furfuryl glycidyl ether) no peak from residual FGE monomer are observed meaning a complete monomer consumption.

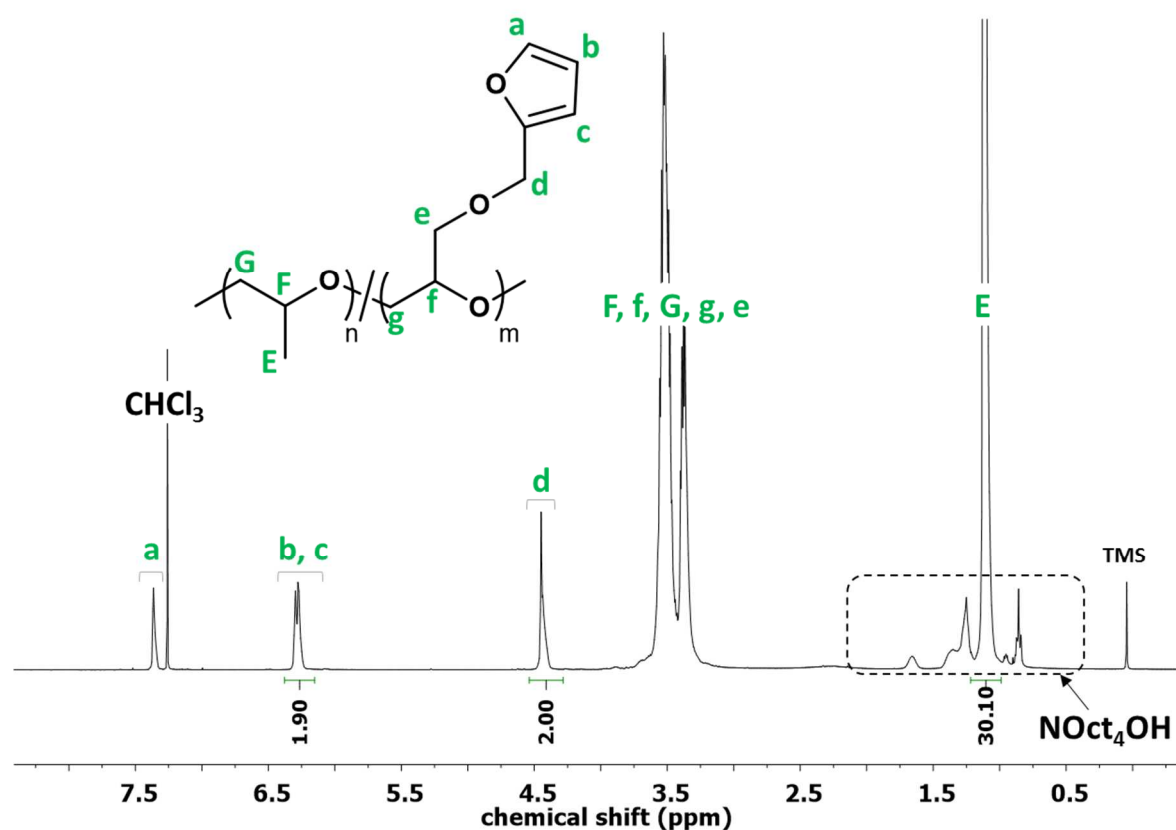


Figure 1: ^1H NMR spectrum in CDCl_3 of P(90PO-co-10FGE) (run 4 table 1) initiated by NOct_4Br in the presence of 3.4eq $i\text{Bu}_3\text{Al}$

The other compositions were calculated and the superposition of ^1H NMR spectra for the different compositions (Figure 2) enables to highlight the expected decrease of the PO unit signals (especially from the CH_3 signal). Residual unreacted monomer is only present in the spectrum of the 100% FGE polymer (uncomplete conversion was observed) and represented by asterisks.

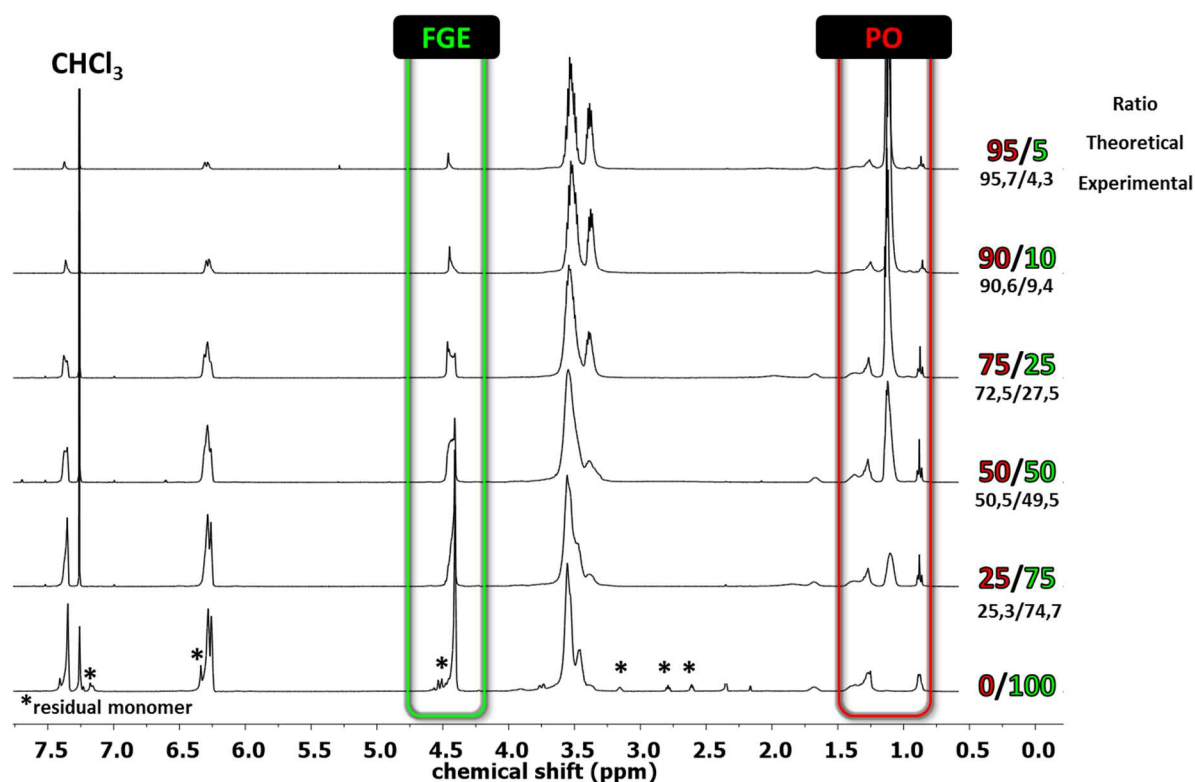


Figure 2: ^1H NMR spectra of $\text{P}(\text{PO-co-FGE})$ copolymers depending on PO/FGE compositions

The polymers were characterized by differential scanning calorimetry (DSC). Their thermograms (Figure 3) show a clear evolution of the glass transition temperature to higher values when increasing the FGE content. Indeed, the incorporation of FGE units to the poly(propylene oxide) backbone is believed to decrease the macromolecular mobility due to more numerous interactions between the furan moieties and an enhanced entanglement involved by the bulky pendant furan groups. Based on the ammonium salt / triisobutylaluminum chemistry, statistic copolymers were already demonstrated[115,116]. Here, all the DSC profiles are exhibiting only one T_g , which can agree with the synthesis of random copolyethers with T_g values (Table 1) in between the one of PPO (-75°C [47]) and the one of PFGE (-40°C [43]) (Figure 3). A precise study of unit sequences by ^{13}C NMR were not successful to corroborate this observation.

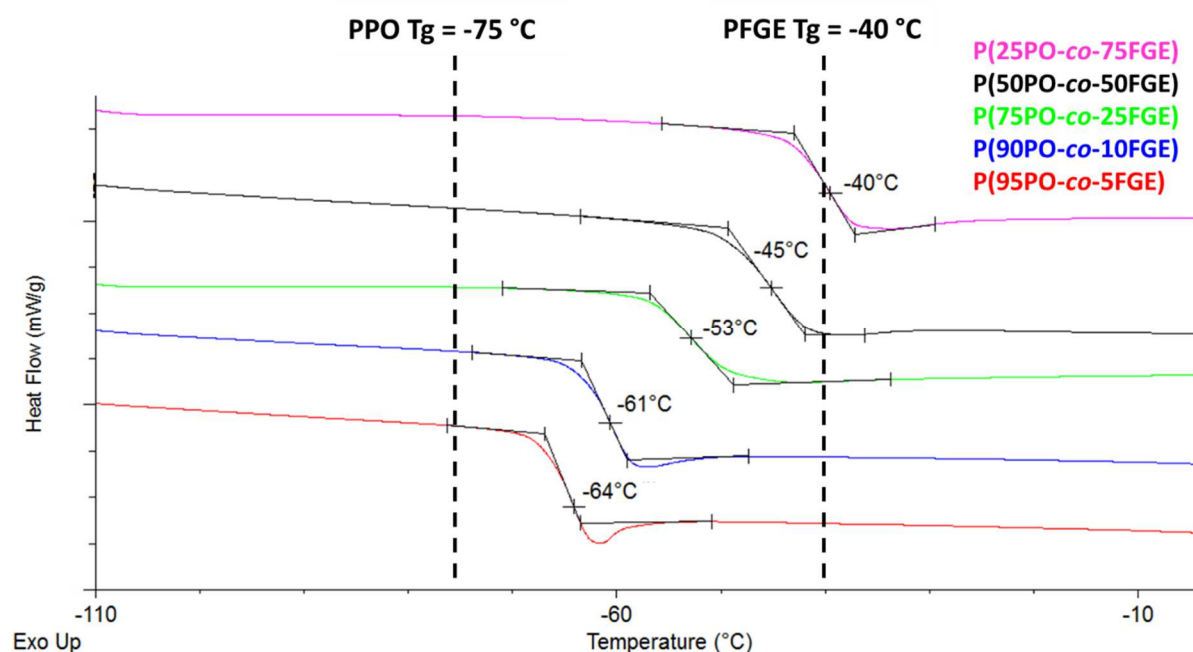
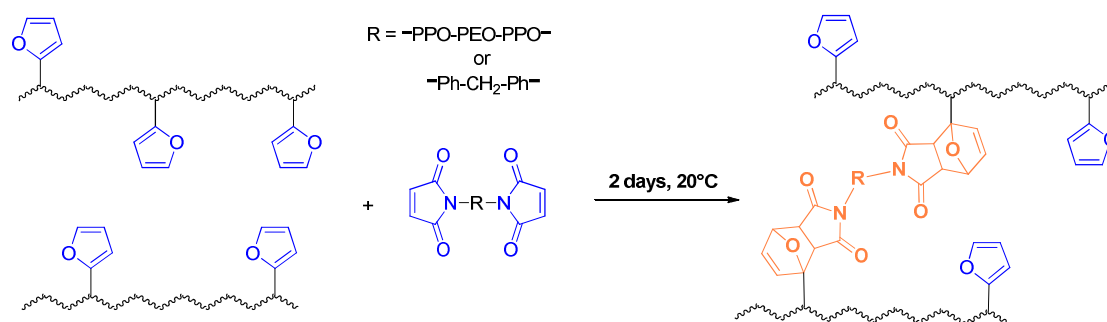


Figure 3: T_g evolution of P(PO-co-FGE) copolymers with various FGE content

Cross-linking by Diels-Alder reaction and reversibility study

Polyethers with pendant furan groups were successfully synthesized. These polymers can react by Diels-Alder reaction (DA) with a bismaleimide to give a cross-linked material (Scheme 3). The study is focused on the furan-rich copolymers P(90PO-co-10FGE) and P(50PO-co-50FGE) to have enough and separate furan moieties on the polyether backbone. Two bismaleimides were chosen as cross-linkers to compare their effect, *i.e.* diphenylene bismaleimide (dPhbm), and an oligoether bismaleimide (PEO-PPO-bm). The first one has a short aromatic structure that is expected to bring rigidity to the networks, whereas the second one has a long aliphatic structure, similar to the PO-furan polymer, and could bring some flexibility. Reaction was performed in chloroform at room temperature and a gel was obtained each time (Table 2).



Scheme 3: Cross-linking Diels-Alder reaction of poly(propylene oxide) bearing furan moieties with bismaleimides

All initial mixtures were liquid at room temperature, whereas rubber solids were obtained after DA reaction. Swelling ratios and insoluble fractions of those materials were measured and reported in Table 2. As expected, swelling ratios are higher for P(90PO-co-10FGE) than for P(50PO-co-50FGE) as they are directly linked to the mesh size of the network. Less furan groups in P(90PO-co-10FGE) means that the cross-linking nodes in the network are more distant from one to another. In the same logic, swelling ratio varies with the cross-linker length: PEO-PPO-bm is longer and more flexible than dPhbm which is short and aromatic. The materials G(x-y) (G for gel, x for the % of FGE, and y for aromatic or aliphatic polyether) exhibit relatively high insoluble fractions (80-87%) whatever the composition and the nature of the cross-linker, which is in agreement with a good accessibility of the reactive functions.

Table 2: Cross-linked P(PO-co-FGE) characterizations

Gel name	Mixture	Swelling ratio	Insoluble fraction (%)	T _g (°C) ^a	T _{rDA} ^a ENDO/EXO (°C)
G(10-Al)	P(90PO-co-10FGE) PEO-PPO-bm	138	85	-61	100/135
G(10-Ar)	P(90PO-co-10FGE) dPhbm	116	85	-61	100/130
G(50-Al)	P(50PO-co-50FGE) PEO-PPO-bm	60	80	-17	100/150
G(50-Ar)	P(50PO-co-50FGE) dPhbm	26	87	66 ^b	90/130

^a Determined by Differential Scanning Calorimetry. ^b determined by modulated DSC.

The glass transition temperatures of the cross-linked materials were measured by DSC (Table 2). In the case of G(10-Al) and G(10-Ar), T_g (-61°C) is similar to the initial copolymer P(90PO-co-10FGE). On the contrary, G(50-Al) and G(50-Ar) have higher T_g . The value of 66°C , corresponding to the G(50-Ar) network, was determined by modulated DSC as it was hidden by the endothermic retro Diels-Alder reaction (rDA). These results can be correlated to the observations made from swelling ratios and insoluble fractions. Cross-linking from P(90PO-co-10FGE) does not induce changes on the polymer entanglement because of the low number of cross-linking nodes in the network. On the contrary, when cross-linking nodes are numerous, the polymer entanglement is denser and chains cannot move freely, resulting in higher T_g .

Retro Diels-Alder reaction is endothermic and thus can be observed by DSC. As shown Figure 4, the rDA transition is broad. Temperature values are measured for the maximum peak transition which corresponds to the temperature where rDA reactions are preponderant (temperatures also given Table 2). For G(10-Al) and G(10-Ar), the rDA peak intensity is low because DA adducts are very diluted in the polymer network. G(50-Al) and G(50-Ar) thermograms exhibit two endothermal transitions corresponding to rDA. Indeed, DA reaction produces two adduct forms which are diastereoisomers: the endo-adduct and the exo-adduct[111]. Exo-adduct is thermally more stable than the endo form, resulting in higher T_{rDA} . The first peak is thus attributed to endo-adduct rDA, and the second one to exo-adduct rDA. Here, these temperatures are globally around 110°C . Thus, thermal treatment will be carried out at 110°C to study rDA-de-cross-linking.

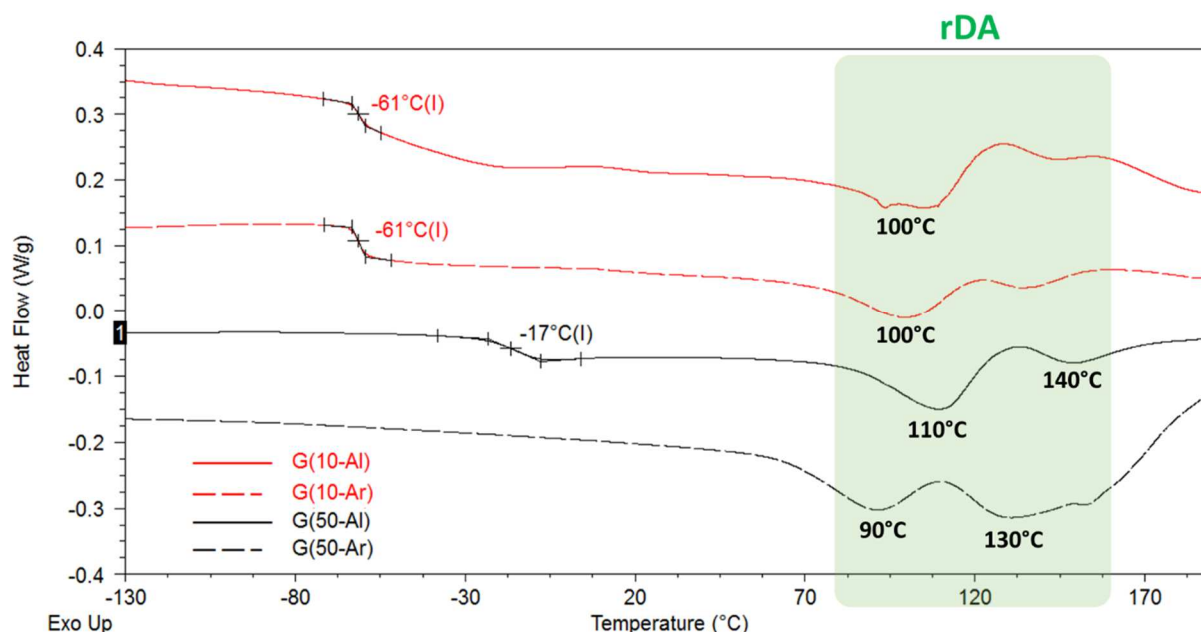


Figure 4: DSC thermograms of P(PO-co-FGE) gels

When heated, the polymer network de-cross-links by rDA reaction. At macromolecular scale, this can be seen by a change in solubility. To observe this evolution, G(50-Al) and G(50-Ar) were put in DMSO at 110°C under magnetic stirring. After 2 hours, the liquid phase is homogeneous; the polymer sample is entirely solubilized (Figure 5). The system can return to its previous form by letting it react by DA reaction at 20°C. DA reaction is slow and it takes 2 days to obtain again a cross-linked network (gel formation). The cross-linking system by DA reaction is thus reversible, allowing disassembly by thermal treatment, and then able to cross-link again at 20°C.

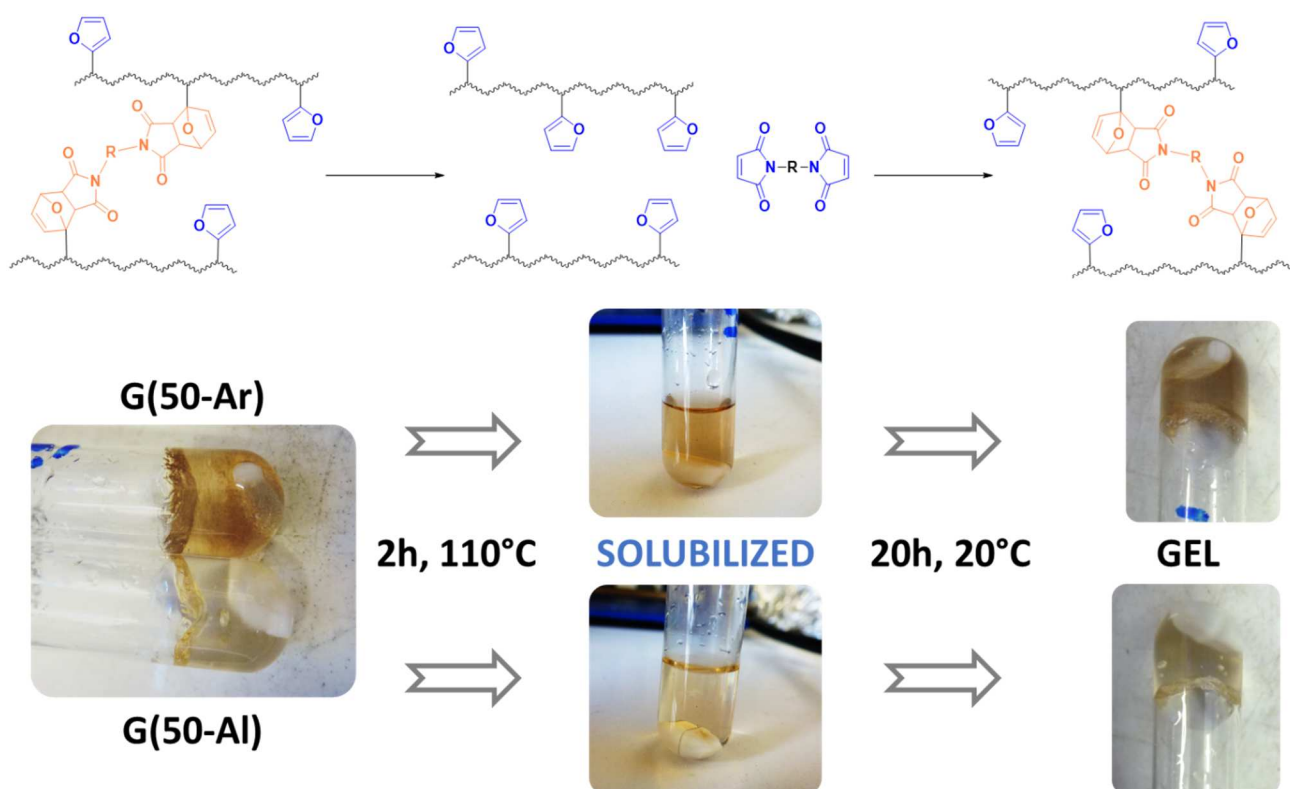


Figure 5: Solubility evolution of G(50-Al) and G(50-Ar) in DMSO

It has been demonstrated by Froidevaux et al[6] that an aromatic N-substituent on the maleimide speeds up rDA reaction. A ^1H -NMR study has been conducted at 110°C in order to compare G(50-Ar) and G(50-Al) rDA reaction rates. A sample of the cross-linked polymer was put in DMSO- d_6 with a precise amount of standard (1,3,5-terphenylbenzene). ^1H -NMR spectra were recorded frequently to report the composition of the liquid phase. At the beginning, only the standard is soluble in DMSO, and by heating, polymer and cross-linker solubilize in DMSO and can be quantified from the standard amount. The integration of the standard peak at 7.8ppm was fixed and the evolution of the h signal at 7.0ppm belonging to the maleimide was monitored. This evolution is reported on Figure 6. The increase of maleimide amount is reaching a plateau after 80 min for G(50-Ar) and 100 min for G(50-Al). This observation confirms that using an aromatic maleimide cross-linker enables to speed up rDA de-bonding of the poly(propylene oxide) chains.

Moreover, ^1H -NMR enables to identify the species formed by thermal treatment. After 2h at 110°C, the material in the ^1H -NMR tube is completely solubilized and can be analyzed. When compared to the initial copolymer and cross-linker spectra (Figure 7), it is clear that this

spectrum is a superposition of those two. Moreover furan and maleimide functions are recovered as indicated by their characteristic signals at 7.6 and 7.0ppm for a and h protons respectively on G(50-Al) NMR spectrum. This proves that thermal treatment and rDA reaction preserve the integrity of the polyether backbone and the furan/maleimide functionality, allowing the system to cross-link again when left at room temperature (as shown Figure 5).

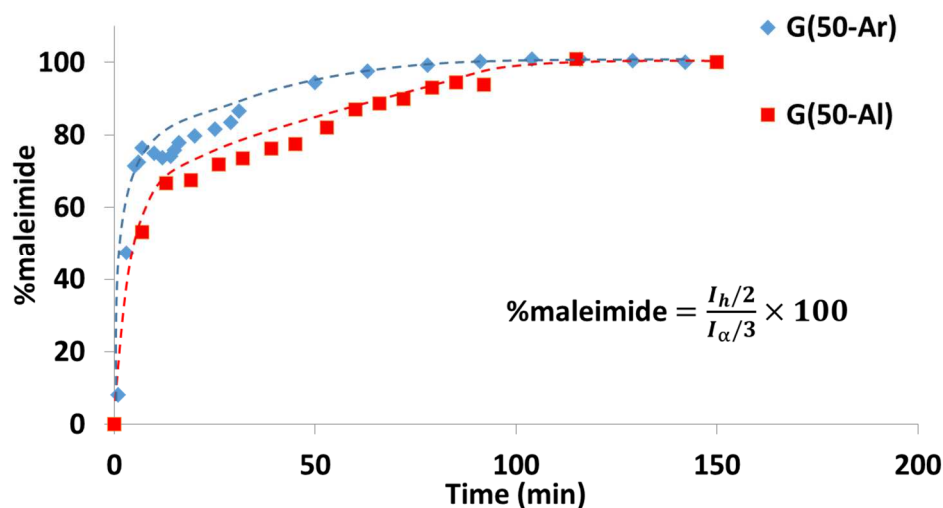


Figure 6: Increase of maleimide amount (mol%) at 110°C for G(50-Al) and G(50-Ar) (monitored by $^1\text{H-NMR}$ in DMSO-d_6)

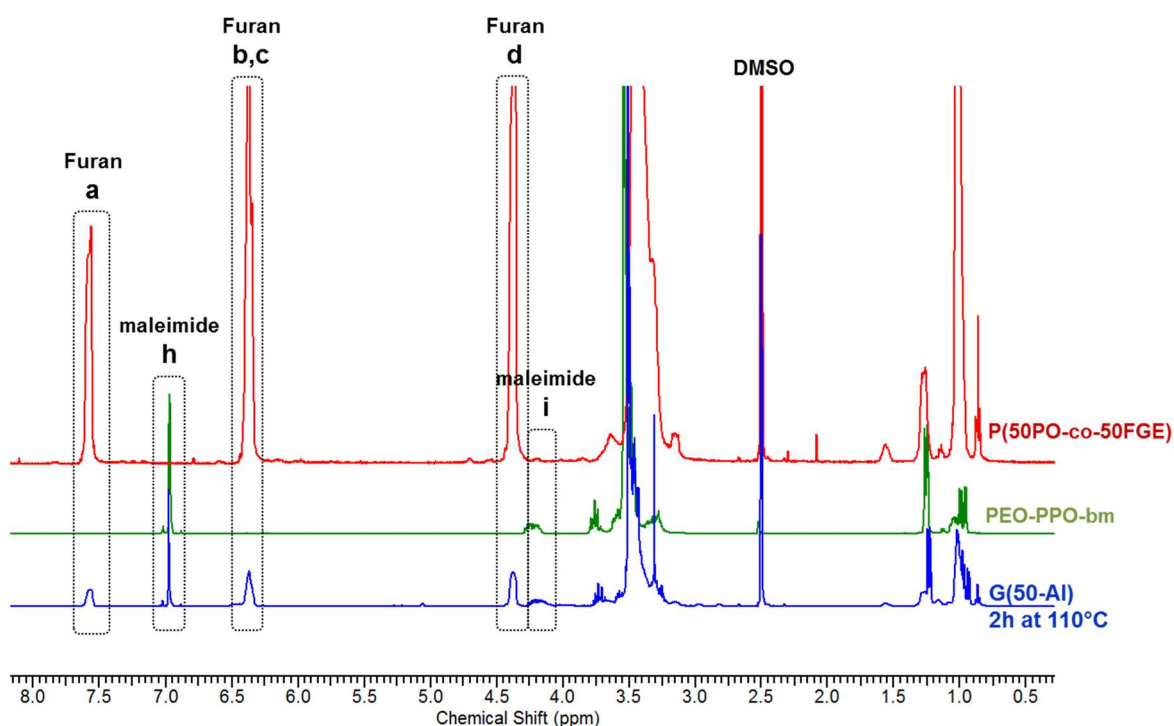


Figure 7: Superposition of G(50-Al) $^1\text{H-NMR}$ spectrum after thermal treatment with initial copolymer and cross-linker spectra

CONCLUSION

The copolymerization of propylene oxide with furfuryl glycidyl ether was investigated by anionic ring-opening polymerization and monomer activation methodology using a combination of tetraoctylammonium bromide and triisobutylaluminum. Copolymers were synthesized with controlled compositions and molar masses around 10 000g/mol. Glass transition temperatures were measured from -64°C to -40°C which agree with a random distribution of furfuryl groups along the polyether chains. Those well-defined copolymers were subsequently reacted with aliphatic or aromatic bis-maleimide compounds by Diels-Alder reaction leading to cross-linked polyether-based gels. The gel structural properties were investigated by measuring their swelling ratio and insoluble fraction in THF, and the T_g were determined by DSC. Denser networks were obtained with furan-rich copolymers characterized by lower swelling ratios, higher insoluble fractions and higher T_g (up to 66°C). DSC analysis enables to observe retro Diels-Alder reaction as an endothermic transition around 100°C. Finally the ability of these systems to de-cross-link was investigated by a solubility study. The initial gel can be completely solubilized in DMSO after 2h at 110°C. This property enables to kinetically follow retro-Diels-Alder reaction by quantitative ^1H NMR, which showed that aromatic bismaleimide used as cross-linker speeds up the de-cross-linking process.

6. Activated copolymerization of propylene oxide with maleic anhydride for the synthesis of cross-linkable poly(propylene oxide)

Here appear the preliminary results of the study aiming to introduce double bonds inside a polyether backbone. This work will be further investigated but few conclusions can still be drawn. With the combination of tetraoctylammonium bromide (I) and triisobutylaluminum (Al) the activated copolymerization of maleic anhydride (MA) and propylene oxide (PO) proceeded quantitatively in 2-methyltetrahydrofuran (Table 1). The increasing content of MA (from 5% to 50%) decreases the molar masses of the resulting polymers and no homopolymerization of maleic anhydride was observed even with an higher [Al]/[I] ratio.

Table 1: Copolymerization of propylene oxide (PO) with maleic anhydride (MA) initiated by NOct₄Br (I) in the presence of *i*-Bu₃Al (Al) in 2-methyltetrahydrofuran

Run	Theoretical Composition (PO/MA) (%)	[Al]/[I]	Experimental Composition ^a (PO/MA) (%)	Time (h)	Conv ^{a,b} (%)	\overline{Mn}_{calcd}^c (g/mol)	\overline{Mn}_{exp}^d (g/mol)	\overline{D}^c
1	100/0	1.5	-/-	4	100 ^b	10 000	19 300	1.12
2	95/5	3	96/4	24	100	5 000	4 700	1.54
3	75/25	3	68/32	24	100	5 000	1 300	1.09
4	63/37	3	57/43	24	100	5 000	1 500	1.09
5	50/50	3	54/46	24	100	5 000	1 400	1.21
6	0/100	4	-/-	24	0 ^a	-	-	-

^aDetermined by ¹H NMR. ^bDetermined gravimetrically. ^c $\overline{Mn}_{calcd} = ([MA]_0/[NOct_4Br]_0 \times M_{MA} + [PO]_0/[NOct_4Br]_0 \times M_{PO}) \times \text{conv.}$

^dDetermined by size exclusion chromatography in tetrahydrofuran using a calibration with polystyrene standards.

By ¹H NMR, a, c and b proton signals at 6.25, 5.2 and 4.2 ppm respectively are attributed to alternated MA and PO units. b' and c' proton signals are assigned to methylene and methine groups from homo PPO units (figure 1). The percentages of maleic anhydride in the polymers were calculated according the formula $MA(\%) = \frac{Ia/2}{\frac{Ia}{2} + Ic + \frac{I(b'c')}{3}} \times 100$ and the results were found to be in a good agreement with the theoretical values.

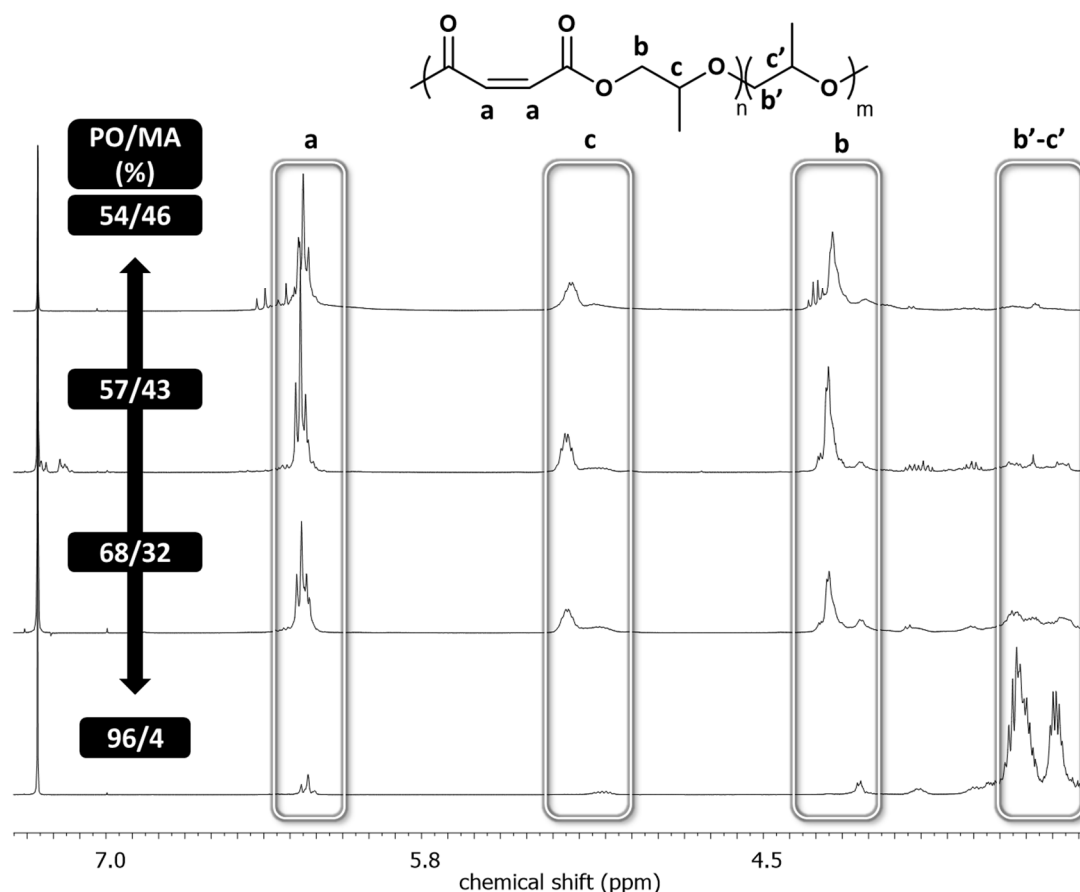


Figure 1: ^1H NMR spectra (CDCl_3) of $\text{P}(\text{PO-co-MA})$ copolymers depending on PO/MA compositions

In order to check the sustainability of this approach, the MA-rich copolymer (run 5) was involved in a subsequent thermally induced vulcanization in presence of sulfur and N-tert-butyl-2-benzothiazolesulfenamide (TBBS) as accelerator. By DSC measurements, after one heating run, a broad exotherm peak is observed with a maximal intensity at 185 °C and attributed to the cross-linking reaction involving the polymer double bonds (figure 2). After cooling and a second heating run no further exotherm was observed and the final material was shown to be insoluble. The T_g of the cross-linked material is observed to be similar with the linear one, but higher than a homo PPO ($T_g = -75^\circ\text{C}$). Indeed, by increasing the MA content an increase of the T_g was observed in the range of - 68 °C to 3°C corresponding to 5% to 50% of MA incorporated in the material.

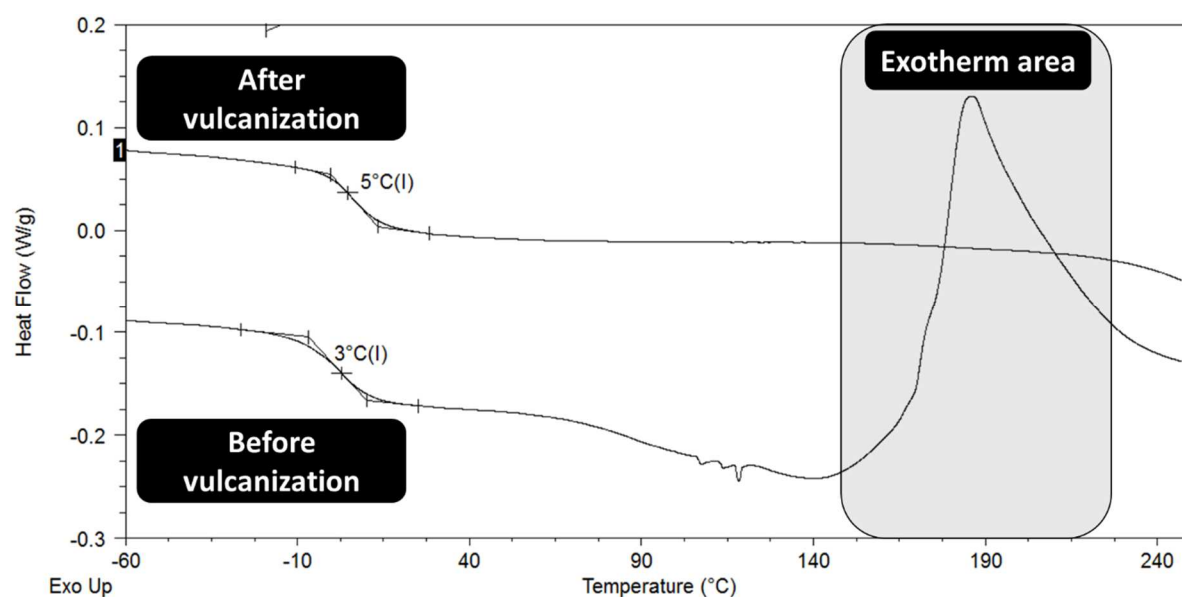


Figure 2: DSC thermogram of the polymer sample (run 5), before and after vulcanization

Based on these preliminary results, the incorporation of double-bonds inside the polyether backbone is demonstrated. Using a common vulcanization process a cross-linked materials was obtained. As cyclic anhydrides and epoxides are known to react alternatively (see paragraph 3.1) the determination of the distribution of MA units in the polymer chains could be investigated. Materials with lower contents of MA will be further studied and cross-linked in order to get cross-linked polyether-based materials expected to have an elastomeric behaviour.

REFERENCES

1. Diels, O.; Alder, K. Synthesen in der hydroaromatischen Reihe. *Justus Liebig's Ann. der Chemie* **1928**, *460*, 98–122.
2. Nicolaou, K. C.; Snyder, S. A.; Montagnon, T.; Vassilikogiannakis, G. The Diels-Alder Reaction in Total Synthesis. *Angew. Chemie Int. Ed.* **2002**, *41*, 1668–1698.
3. Brieger, G.; Bennett, J. N. The intramolecular Diels-Alder reaction. *Chem. Rev.* **1980**, *80*, 63–97.
4. Peterson, A. M.; Jensen, R. E.; Palmese, G. R. Reversibly cross-linked polymer gels as healing agents for epoxy-amine thermosets. *ACS Appl. Mater. Interfaces* **2009**, *1*, 992–995.
5. Gandini, A. The application of the Diels-Alder reaction to polymersyntheses based on furan/maleimide reversible couplings. *Polímeros Ciência e Tecnol.* **2005**, *15*, 95–101.
6. Froidevaux, V.; Borne, M.; Laborbe, E.; Auvergne, R.; Gandini, A.; Boutevin, B. Study of the Diels-Alder and retro-Diels-Alder reaction between furan derivatives and maleimide for the creation of new materials. *RSC Adv.* **2015**, *5*, 37742–37754.
7. Goussé, C.; Gandini, A. Synthesis of 2-furfurylmaleimide and preliminary study of its Diels-Alder polycondensation. *Polym. Bull.* **1998**, *40*, 389–394.
8. Chujo, Y.; Sada, K.; Saegusa, T. Reversible gelation of polyoxazoline by means of Diels-Alder reaction. *Macromolecules* **1990**, *23*, 2636–2641.
9. Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. A thermally re-mendable cross-linked polymeric material. *Science* **2002**, *295*, 1698–1702.
10. Wu, D. Y.; Meure, S.; Solomon, D. Self-healing polymeric materials: A review of recent developments. *Prog. Polym. Sci.* **2008**, *33*, 479–522.
11. Liu, Y.-L.; Chuo, T.-W. Self-healing polymers based on thermally reversible Diels-Alder chemistry. *Polym. Chem.* **2013**, *4*, 2194–2205.
12. Liu, Y.-L.; Hsieh, C.-Y. Crosslinked epoxy materials exhibiting thermal remendability and removability from multifunctional maleimide and furan compounds. *J. Polym. Sci. Part A Polym. Chem.* **2006**, *44*, 905–913.
13. Mikroyannidis, J. A. Synthesis and diels-alder polymerization of furfurylidene and furfuryl-substituted maleamic acids. *J. Polym. Sci. Part A Polym. Chem.* **1992**, *30*, 125–132.
14. Mikroyannidis, J. A. Furyl-maleimidein situ generated ab-monomers: Synthesis, characterization, and Diels-Alder polymerization. *J. Polym. Sci. Part A Polym. Chem.* **1992**, *30*, 2017–2024.
15. Gandini, A.; Silvestre, A. J. D.; Coelho, D. Reversible click chemistry at the service of

macromolecular materials. *Polym. Chem.* **2011**, 2, 1713–1719.

16. Tesoro, G. C.; Sastri, V. R. Synthesis of siloxane-containing bis(furans) and polymerization with bis(maleimides). *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, 25, 444–448.

17. Teramoto, N.; Arai, Y.; Shibata, M. Thermo-reversible Diels–Alder polymerization of difurfurylidene trehalose and bismaleimides. *Carbohydr. Polym.* **2006**, 64, 78–84.

18. Kuramoto, N.; Hayashi, K.; Nagai, K. Thermoreversible reaction of diels—alder polymer composed of difurfuryladipate with bismaleimidodiphenylmethane. *J. Polym. Sci. Part A Polym. Chem.* **1994**, 32, 2501–2504.

19. Vilela, C.; Cruciani, L.; Silvestre, A. J. D.; Gandini, A. A double click strategy applied to the reversible polymerization of furan/vegetable oil monomers. *Macromol. Rapid Commun.* **2011**, 32, 1319–1323.

20. Chen, X.; Wudl, F.; Mal, A. K.; Shen, H.; Nutt, S. R. New Thermally Remendable Highly Cross-Linked Polymeric Materials. *Macromolecules* **2003**, 36, 1802–1807.

21. Tian, Q.; Rong, M. Z.; Zhang, M. Q.; Yuan, Y. C. Synthesis and characterization of epoxy with improved thermal remendability based on Diels–Alder reaction. *Polym. Int.* **2010**, 59, 1339–1345.

22. Tian, Q.; Yuan, Y. C.; Rong, M. Z.; Zhang, M. Q. A thermally remendable epoxy resin. *J. Mater. Chem.* **2009**, 19, 1289–1296.

23. Pratama, P. A.; Peterson, A. M.; Palmese, G. R. Diffusion and Reaction Phenomena in Solution-Based Healing of Polymer Coatings Using the Diels–Alder Reaction. *Macromol. Chem. Phys.* **2012**, 213, 173–181.

24. Bai, N.; Simon, G. P.; Saito, K. Investigation of the thermal self-healing mechanism in a cross-linked epoxy system. *RSC Adv.* **2013**, 3, 20699.

25. Zhong, Y.; Wang, X.; Zheng, Z.; Du, P. Polyether-maleimide-based crosslinked self-healing polyurethane with Diels–Alder bonds. *J. Appl. Polym. Sci.* **2015**, 132, DOI:10.1002/app.41944.

26. Du, P.; Liu, X.; Zheng, Z.; Wang, X.; Joncheray, T.; Zhang, Y. Synthesis and characterization of linear self-healing polyurethane based on thermally reversible Diels–Alder reaction. *RSC Adv.* **2013**, 3, 15475–15482.

27. Du, P.; Wu, M.; Liu, X.; Zheng, Z.; Wang, X.; Joncheray, T.; Zhang, Y. Diels–Alder-based crosslinked self-healing polyurethane/urea from polymeric methylene diphenyl diisocyanate. *J. Appl. Polym. Sci.* **2014**, 131, DOI: 10.1002/app.40234.

28. Du, P.; Wu, M.; Liu, X.; Zheng, Z.; Wang, X.; Sun, P.; Joncheray, T.; Zhang, Y. Synthesis of linear polyurethane bearing pendant furan and cross-linked healable polyurethane containing Diels–Alder bonds. *New J. Chem.* **2014**, 38, 770–776.

29. Gaina, C.; Ursache, O.; Gaina, V.; Varganici, C. D. Thermally reversible cross-linked poly(ether-urethane)s. *Express Polym. Lett.* **2013**, *7*, 636–650.
30. Nguyen, L.-T. T.; Devroede, J.; Plasschaert, K.; Jonckheere, L.; Haucourt, N.; Du Prez, F. E. Providing polyurethane foams with functionality: a kinetic comparison of different “click” and coupling reaction pathways. *Polym. Chem.* **2013**, *4*, 1546–1556.
31. Rivero, G.; Nguyen, L.-T. T.; Hillewaere, X. K. D.; Du Prez, F. E. One-Pot Thermo-Remendable Shape Memory Polyurethanes. *Macromolecules* **2014**, *47*, 2010–2018.
32. Varganici, C.-D.; Ursache, O.; Gaina, C.; Gaina, V.; Rosu, D.; Simionescu, B. C. Synthesis and Characterization of a New Thermoreversible Polyurethane Network. *Ind. Eng. Chem. Res.* **2013**, *52*, 5287–5295.
33. Dolci, E.; Michaud, G.; Simon, F.; Boutevin, B.; Fouquay, S.; Caillol, S. Remendable thermosetting polymers for isocyanate-free adhesives: a preliminary study. *Polym. Chem.* **2015**, DOI: 10.1039/C5PY01213A.
34. Duval, A.; Lange, H.; Lawoko, M.; Crestini, C. Reversible crosslinking of lignin via the furan–maleimide Diels–Alder reaction. *Green Chem.* **2015**, DOI: 10.1039/C5GC01319D.
35. Canary, S. A.; Stevens, M. P. Thermally reversible crosslinking of polystyrene via the furan–maleimide Diels–Alder reaction. *J. Polym. Sci. Part A Polym. Chem.* **1992**, *30*, 1755–1760.
36. Goussé, C.; Gandini, A.; Hodge, P. Application of the Diels–Alder Reaction to Polymers Bearing Furan Moieties. 2. Diels–Alder and Retro-Diels–Alder Reactions Involving Furan Rings in Some Styrene Copolymers. *Macromolecules* **1998**, *31*, 314–321.
37. Toncelli, C.; De Reus, D. C.; Picchioni, F.; Broekhuis, A. A. Properties of Reversible Diels–Alder Furan/Maleimide Polymer Networks as Function of Crosslink Density. *Macromol. Chem. Phys.* **2012**, *213*, 157–165.
38. Syrett, J. A.; Becer, C. R.; Haddleton, D. M. Self-healing and self-mendable polymers. *Polym. Chem.* **2010**, *1*, 978–987.
39. Kavitha, A. A.; Singha, N. K. Atom-Transfer Radical Copolymerization of Furfuryl Methacrylate (FMA) and Methyl Methacrylate (MMA): A Thermally-Amendable Copolymer. *Macromol. Chem. Phys.* **2007**, *208*, 2569–2577.
40. Liu, Y.-L.; Chen, Y.-W. Thermally Reversible Cross-Linked Polyamides with High Toughness and Self-Repairing Ability from Maleimide- and Furan-Functionalized Aromatic Polyamides. *Macromol. Chem. Phys.* **2007**, *208*, 224–232.
41. Magana, S.; Zerroukhi, A.; Jegat, C.; Mignard, N. Thermally reversible crosslinked polyethylene using Diels–Alder reaction in molten state. *React. Funct. Polym.* **2010**, *70*, 442–448.

42. Dispinar, T.; Van Camp, W.; De Cock, L. J.; De Geest, B. G.; Du Prez, F. E. Redox-responsive degradable PEG cryogels as potential cell scaffolds in tissue engineering. *Macromol. Biosci.* **2012**, *12*, 383–394.
43. Barthel, M. J.; Rudolph, T.; Teichler, A.; Paulus, R. M.; Vitz, J.; Hoeppener, S.; Hager, M. D.; Schacher, F. H.; Schubert, U. S. Self-Healing Materials via Reversible Crosslinking of Poly(ethylene oxide)-Block-Poly(furfuryl glycidyl ether) (PEO-*b*-PFGE) Block Copolymer Films. *Adv. Funct. Mater.* **2013**, *23*, 4921–4932.
44. Haas, H. C. Maleimide polymers. II. Radical polymerization kinetics. *J. Polym. Sci. Polym. Chem. Ed.* **1973**, *11*, 315–318.
45. Peterson, A. M.; Palmese, G. R. Reaction Kinetics and Thermodynamic Aspects of Thermoreversibly Cross-Linked Polymer Networks. *Macromol. Chem. Phys.* **2013**, *214*, 1798–1805.
46. Penczek, P.; Czub, P.; Pielichowski, J. Unsaturated Polyester Resins: Chemistry and Technology. **2005**, *184*, 1–95.
47. Fischer, R. F. Polyesters from epoxides and anhydrides. *J. Polym. Sci.* **1960**, *44*, 155–172.
48. Inoue, S.; Kitamura, K.; Tsuruta, T. Alternating copolymerization of phthalic anhydride and propylene oxide by dialkylzinc. *Die Makromol. Chemie* **1969**, *126*, 250–265.
49. Hsieh, H. L. Terpolymerization of Cyclic Ethers with Cyclic Anhydride. *J. Macromol. Sci. Part A - Chem.* **1973**, *7*, 1525–1535.
50. Kern, R. J.; Schaefer, J. Catalyst-controlled monomer distributions in copolymers. Copolymerization of propylene oxide and maleic anhydride. *J. Am. Chem. Soc.* **1967**, *89*, 6–14.
51. Lustoň, J.; Maňásek, Z. Character of Active Centers in the Copolymerization of Epoxides with Cyclic Anhydrides. *J. Macromol. Sci. Part A - Chem.* **1978**, *12*, 983–994.
52. Lustoň, J.; Maňásek, Z. Ammonium salt catalyzed copolymerization of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone with phthalic anhydride. *Die Makromol. Chemie* **1980**, *181*, 545–555.
53. Schaefer, J.; Katnik, R. J.; Kern, R. J. The monomer distributions of propylene oxide-maleic anhydride copolymers. *J. Am. Chem. Soc.* **1968**, *90*, 2476–2480.
54. Aida, T.; Sanuki, K.; Inoue, S. Well-controlled polymerization by metalloporphyrin. Synthesis of copolymer with alternating sequence and regulated molecular weight from cyclic acid anhydride and epoxide catalyzed by the system of aluminum porphyrin coupled with quaternary organic salt. *Macromolecules* **1985**, *18*, 1049–1055.
55. Takenouchi, S.; Takasu, A.; Inai, Y.; Hirabayashi, T. Effects of Geometrical Difference of Unsaturated Aliphatic Polyesters on Their Biodegradability II. Isomerization of Poly(maleic

anhydride-co-propylene oxide) in the Presence of Morpholine. *Polym. J.* **2002**, 34, 36–42.

56. Hua, Z.; Qi, G.; Chen, S. Ring-opening copolymerization of maleic anhydride with propylene oxide by double-metal cyanide. *J. Appl. Polym. Sci.* **2004**, 93, 1788–1792.

57. Jeske, R. C.; DiCiccio, A. M.; Coates, G. W. Alternating copolymerization of epoxides and cyclic anhydrides: an improved route to aliphatic polyesters. *J. Am. Chem. Soc.* **2007**, 129, 11330–1.

58. Maleic Anhydride Chain - World Market Overview. *Tecnon OrbiChem* **2015**, Chemical Committee Meeting at APIC, Seoul.

59. Severini, F.; Pegoraro, M.; Ricca, G.; Audisio, G.; Dainese, D.; Gallo, R. Synthesis and characterization of maleic anhydride oligomers. *Br. Polym. J.* **1990**, 23, 23–28.

60. Deng, X.; Li, Z.; Yuan, M.; Hao, J. Anionic ring-opening polymerization of adipic anhydride initiated by potassium poly(ethylene glycol)ate. *J. Appl. Polym. Sci.* **2003**, 88, 2194–2201.

61. Krüger, S.; Krah, F.; Arndt, K. F. Random cross-linked poly(styrene-co-maleic anhydride): Characterization of cross-linking intermediates by size exclusion chromatography. *Eur. Polym. J.* **2010**, 46, 1040–1048.

62. Bianchi, E.; Ciferri, A.; Parodi, R.; Rampone, R.; Tealdi, A. Ethylene-maleic anhydride copolymers and derivatives. Potentiometric titrations and interactions with polypeptides. *J. Phys. Chem.* **1970**, 74, 1050–1056.

63. Heo, K.-B.; Lee, H.-J.; Kim, H.-J.; Kim, B.-S.; Lee, S.-Y.; Cho, E.; Oh, I.-H.; Hong, S.-A.; Lim, T.-H. Synthesis and characterization of cross-linked poly(ether sulfone) for a fuel cell membrane. *J. Power Sources* **2007**, 172, 215–219.

64. Oh, Y.-S.; Lee, H.-J.; Yoo, M.; Kim, H.-J.; Han, J.; Kim, T.-H. Synthesis of novel crosslinked sulfonated poly(ether sulfone)s using bisazide and their properties for fuel cell application. *J. Memb. Sci.* **2008**, 323, 309–315.

65. Zhuo, Y. Z.; Nan Lai, A.; Zhang, Q. G.; Zhu, A. M.; Ye, M. L.; Liu, Q. L. Highly ionic-conductive crosslinked cardo poly(arylene ether sulfone)s as anion exchange membranes for alkaline fuel cells. *J. Memb. Sci.* **2015**, 491, 138–148.

66. Sridhar, S.; Suryamurali, R.; Smitha, B.; Aminabhavi, T. M. Development of crosslinked poly(ether-block-amide) membrane for CO₂/CH₄ separation. *Colloids Surfaces A Physicochem. Eng. Asp.* **2007**, 297, 267–274.

67. Gresham, W. F.; Connolly, D. J. Fluorocarbon vinyl ether polymers 1964, US patent 3,282,875.

68. Scott, K.; Taama, W. .; Argyropoulos, P.; Sundmacher, K. The impact of mass transport and methanol crossover on the direct methanol fuel cell. *J. Power Sources* **1999**, 83, 204–216.

69. Zhong, S.; Cui, X.; Cai, H.; Fu, T.; Zhao, C.; Na, H. Crosslinked sulfonated poly(ether ether ketone) proton exchange membranes for direct methanol fuel cell applications. *J. Power Sources* **2007**, *164*, 65–72.
70. Wang, J.; He, G.; Wu, X.; Yan, X.; Zhang, Y.; Wang, Y.; Du, L. Crosslinked poly (ether ether ketone) hydroxide exchange membranes with improved conductivity. *J. Memb. Sci.* **2014**, *459*, 86–95.
71. Bhide, B. D.; Voskericyan, A.; Stern, S. A. Hybrid processes for the removal of acid gases from natural gas. *J. Memb. Sci.* **1998**, *140*, 27–49.
72. Chung, C. M.; Lee, J. H.; Cho, S. Y.; Kim, J. G.; Moon, S. Y. Preparation of porous thin films of a partially aliphatic polyimide. *J. Appl. Polym. Sci.* **2006**, *101*, 532–538.
73. Wind, J. D.; Paul, D. R.; Koros, W. J. Natural gas permeation in polyimide membranes. *J. Memb. Sci.* **2004**, *228*, 227–236.
74. Bondar, V. I.; Freeman, B. D.; Pinnau, I. Gas transport properties of poly(ether-b-amide) segmented block copolymers. *J. Polym. Sci. Part B Polym. Phys.* **2000**, *38*, 2051–2062.
75. May, C. *Chemistry and Technology of Epoxy Resins*; Marce Dekker: New York, 1988.
76. Fernández-Francos, X.; Ramis, X.; Serra, À. From curing kinetics to network structure: A novel approach to the modeling of the network buildup of epoxy-anhydride thermosets. *J. Polym. Sci. Part A Polym. Chem.* **2014**, *52*, 61–75.
77. Brash, J. L.; Uniyal, S. Dependence of albumin-fibrinogen simple and competitive adsorption on surface properties of biomaterials. *J. Polym. Sci. Polym. Symp.* **1979**, *66*, 377–389.
78. Ratner, B. D.; Hoffman, A. S.; Hanson, S. R.; Harker, L. A.; Whiffen, J. D. Blood-compatibility-water-content relationships for radiation-grafted hydrogels. *J. Polym. Sci. Polym. Symp.* **1979**, *66*, 363–375.
79. Sung Wan, K.; Randy G. Lee Applied Chemistry at Protein Interfaces. **1975**, *145*, 218–229.
80. Sa Da Costa, V.; Brier-Russell, D.; Salzman, E. W.; Merrill, E. W. Esca studies of polyurethanes: blood platelet activation in relation to surface composition. *J. Colloid Interface Sci.* **1981**, *80*, 445–452.
81. Bruins, P. *Polyurethane technology*; Interscience Publishers: New York, 1969.
82. Hattori, H. Heterogeneous Basic Catalysis. *Chem. Rev.* **1995**, *95*, 537–558.
83. Trofimov, B. A.; Nosyreva, V. V.; Mal'kina, A. G. The Role of Potassium Cation in the Favorskii Ethynylation of Acetone: Effekt of Dibenzo-18-crown-6. *Russ. J. Org. Chem.* **2005**, *41*, 1254–1259.
84. Trofimov, B. A.; Morozova, B. V.; Mikhaleva, A. I.; Tatarinova, I. V.; Markova, M. V.;

Henkelmann, J. Synthesis of cross-linked polyethylene oxide-acetal macrocycles for solid superbase catalysts. *J. Appl. Polym. Sci.* **2011**, *120*, 3363–3369.

85. Pol, B. J. M.; van der Does, L.; Bantjes, A. Tetrahydrofuran (co)polymers as potential materials for vascular prostheses. *Clin. Mater.* **1993**, *13*, 57–60.

86. Danisman, T.; Tan, S.; Kacar, Y.; Ergene, A. Covalent immobilization of invertase on microporous PHEMA–GMA membrane. *Food Chem.* **2004**, *85*, 461–466.

87. Biçak, N.; Bulutçu, N.; Şenkal, B. F.; Gazi, M. Modification of crosslinked glycidyl methacrylate-based polymers for boron-specific column extraction. *React. Funct. Polym.* **2001**, *47*, 175–184.

88. Antoun, S.; Wang, J. S.; Jérôme, R.; Teyssié, P. Anionic polymerization of various methacrylates initiated with LiCl-complexed sBuLi. *Polymer (Guildf)*. **1996**, *37*, 5755–5759.

89. Antoun, S.; Teyssié, P.; Jérôme, R. Lithium Diisopropylamide as Initiator for the Anionic Polymerization of Methacrylates. *Macromolecules* **1997**, *30*, 1556–1561.

90. Labbé, A.; Carlotti, S.; Billouard, C.; Desbois, P.; Deffieux, A. Controlled High-Speed Anionic Polymerization of Propylene Oxide Initiated by Onium Salts in the Presence of Triisobutylaluminum. *Macromolecules* **2007**, *40*, 7842–7847.

91. Labbé, A.; Carlotti, S.; Deffieux, A.; Hirao, A. Controlled Polymerization of Glycidyl Methyl Ether Initiated by Onium Salt/Triisobutylaluminum and Investigation of the Polymer LCST. *Macromol. Symp.* **2007**, *249-250*, 392–397.

92. Gervais, M.; Labbé, A.; Carlotti, S.; Deffieux, A. Direct Synthesis of α -Azido, ω -hydroxypolyethers by Monomer-Activated Anionic Polymerization. *Macromolecules* **2009**, *42*, 2395–2400.

93. Gervais, M.; Brocas, A.-L.; Cendejas, G.; Deffieux, A.; Carlotti, S. Synthesis of Linear High Molar Mass Glycidol-Based Polymers by Monomer-Activated Anionic Polymerization. *Macromolecules* **2010**, *43*, 1778–1784.

94. Labbé, A.; Brocas, A. L.; Ibarboure, E.; Ishizone, T.; Hirao, A.; Deffieux, A.; Carlotti, S. Selective ring-opening polymerization of glycidyl methacrylate: Toward the synthesis of cross-linked (co)polyethers with thermoresponsive properties. *Macromolecules* **2011**, *44*, 6356–6364.

95. Horak, D.; Shapoval, P. Reactive poly(glycidyl methacrylate) microspheres prepared by dispersion polymerization. *J. Polym. Sci. Part A Polym. Chem.* **2000**, *38*, 3855–3863.

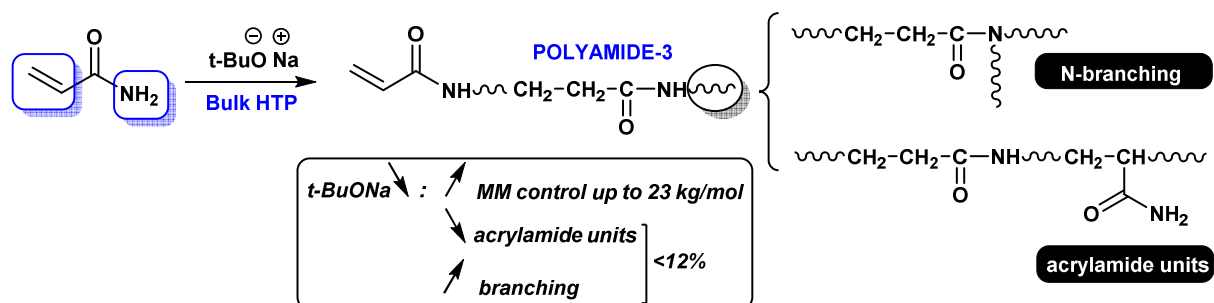
96. Barthel, M. J.; Rudolph, T.; Crotty, S.; Schacher, F. H.; Schubert, U. S. Homo- and diblock copolymers of poly(furfuryl glycidyl ether) by living anionic polymerization: Toward reversibly core-crosslinked micelles. *J. Polym. Sci. Part A Polym. Chem.* **2012**, *50*, 4958–4965.

97. Wagner, M.; Barthel, M. J.; Freund, R. R. A.; Hoeppener, S.; Traeger, A.; Schacher, F. H.; Schubert, U. S. Solution self-assembly of poly(ethylene oxide)-block-poly(furfuryl glycidyl ether)-block-poly(allyl glycidyl ether) based triblock terpolymers: a field-flow fractionation study. *Polym. Chem.* **2014**, *5*, 6943–6956.
98. Mangold, C.; Dingels, C.; Obermeier, B.; Frey, H.; Wurm, F. PEG-based Multifunctional Polyethers with Highly Reactive Vinyl-Ether Side Chains for Click-Type Functionalization. *Macromolecules* **2011**, *44*, 6326–6334.
99. Klein, R.; Übel, F.; Frey, H. Maleimide Glycidyl Ether: A Bifunctional Monomer for Orthogonal Cationic and Radical Polymerizations. *Macromol. Rapid Commun.* **2015**, DOI: 10.1002/marc.201500400.
100. Roos, K.; Dolci, E.; Carlotti, S.; Caillol, S. Activated anionic ring-opening polymerization for the synthesis of reversibly cross-linkable poly(propylene oxide) based on furan/maleimide chemistry. *Polym. Chem.* **2016**.
101. Zhang, X.; Chen, G.-C.; Collins, A.; Jacobson, S.; Morganelli, P.; Dar, Y. L.; Musa, O. M. Thermally degradable maleimides for reworkable adhesives. *J. Polym. Sci. Part A Polym. Chem.* **2009**, *47*, 1073–1084.
102. Bergman, S. D.; Wudl, F. Mendable polymers. *J. Mater. Chem.* **2008**, *18*, 41–62.
103. Hillewaere, X. K. D.; Du Prez, F. E. Fifteen Chemistries for Autonomous External Self-Healing Polymers and Composites. *Prog. Polym. Sci.* **2015**, *49*, 121–153.
104. Delaittre, G.; Guimard, N. K.; Barner-Kowollik, C. Cycloadditions in Modern Polymer Chemistry. *Accounts Chem. Res.* **2015**, *48*, 1296–1307.
105. Gandini, A. The irruption of polymers from renewable resources on the scene of macromolecular science and technology. *Green Chem.* **2011**, *13*, 1061–1083.
106. Rana Gheneim; Catalina Perez-Berumen, and; Gandini*, A. Diels–Alder Reactions with Novel Polymeric Dienes and Dienophiles: Synthesis of Reversibly Cross-Linked Elastomers. **2002**.
107. Barthel, M. J.; Schacher, F. H.; Schubert, U. S. Poly(ethylene oxide) (PEO)-based ABC triblock terpolymers - synthetic complexity vs. application benefits. *Polym. Chem.* **2014**, *5*, 2647–2662.
108. Hörenz, C.; Rudolph, T.; Barthel, M. J.; Günther, U.; Schacher, F. H. Amphiphilic polyether-based block copolymers as crosslinkable ligands for Au-nanoparticles. *Polym. Chem.* **2015**, *6*, 5633–5642.
109. Hans, M.; Keul, H.; Möller, M. Chain transfer reactions limit the molecular weight of polyglycidol prepared via alkali metal based initiating systems. *Polymer (Guildf)*. **2009**, *50*, 1103–1108.

110. Keul, H.; Möller, M. Synthesis and degradation of biomedical materials based on linear and star shaped polyglycidols. *J. Polym. Sci. Part A Polym. Chem.* **2009**, *47*, 3209–3231.
111. Gandini, A. The furan/maleimide Diels–Alder reaction: A versatile click–unclick tool in macromolecular synthesis. *Prog. Polym. Sci.* **2013**, *38*, 1–29.
112. Rejsek, V.; Sauvanier, D.; Billouard, C.; Desbois, P.; Deffieux, A.; Carlotti, S. Controlled Anionic Homo- and Copolymerization of Ethylene Oxide and Propylene Oxide by Monomer Activation. *Macromolecules* **2007**, *40*, 6510–6514.
113. Gervais, M.; Brocas, A.-L.; Deffieux, A.; Ibarboure, E.; Carlotti, S. Rapid and controlled synthesis of hydrophobic polyethers by monomer activation. *Pure Appl. Chem.* **2012**, *84*, 2103–2111.
114. Müller, S. S.; Moers, C.; Frey, H. A Challenging Comonomer Pair: Copolymerization of Ethylene Oxide and Glycidyl Methyl Ether to Thermoresponsive Polyethers. *Macromolecules* **2014**, *47*, 5492–5500.
115. Carlotti, S.; Labbé, A.; Rejsek, V.; Doutaz, S.; Gervais, M.; Deffieux, A. Living/Controlled Anionic Polymerization and Copolymerization of Epichlorohydrin with Tetraoctylammonium Bromide–Triisobutylaluminum Initiating Systems. *Macromolecules* **2008**, *41*, 7058–7062.
116. Labbé, A.; Brocas, A.-L.; Ibarboure, E.; Ishizone, T.; Hirao, A.; Deffieux, A.; Carlotti, S. Selective Ring-Opening Polymerization of Glycidyl Methacrylate: Toward the Synthesis of Cross-Linked (Co)polyethers with Thermoresponsive Properties. *Macromolecules* **2011**, *44*, 6356–6364.

CHAPTER III.

Synthesis of polyamide-3 by anionic polymerization



CHAPTER III. Synthesis of polyamide-3 by anionic polymerization

1. Introduction	142
2. Synthesis of aliphatic polyamides by polycondensation.....	143
2.1. Common polyamides.....	143
2.2. Polyamide-3 by polycondensation of β -alanine and its derivatives	144
3. Anionic ring-opening polymerization of cyclic amides (lactams)	146
3.1. Mechanism of the anionic polymerization of lactams	147
3.1.1. Initiating and activating systems.....	147
3.1.2. Propagation reaction.....	150
3.1.3. Side reactions	151
3.2. Polymerization of β -lactams.....	154
3.2.1. Substituted β -lactams	154
3.2.2. Unsubstituted β -lactam	155
4. Hydrogen-Transfer Polymerization	158
4.1. Polymerization of acrylamide.....	158
4.1.1. Initiation and propagation steps.....	158
4.1.2. Sides reactions.....	162
4.2. Polymerization of other precursors.....	164
5. Solvent-free anionic polymerization of acrylamide, a mechanistic study for the rapid and controlled synthesis of polyamide-3	169
SUPPORTING INFORMATION.....	185
REFERENCES.....	188

1. Introduction

Polyamides (PA) are a wide range of polymers usually present in markets such as fibers, engineering plastics and specialties due to specific and various properties depending on their structures. Obtained from different precursors polyamides are named PA6-6, PA6-10, PA-11, PA-12, PA-6 etc The latter being one of the most versatile engineering thermoplastic. The strong interchain interaction derived from the polarity of amide (CONH) groups by hydrogen-bondings provide excellent properties to PA-6 such as high impact strength, stiffness and resistance to chemicals. PA-6 is therefore a remarkable candidate as a lightweight material for metal replacement applications. However and despite their attractive properties, aliphatic polyamides have relatively low glass transition temperature ($40^{\circ}\text{C} < T_g < 60^{\circ}\text{C}$) which limits their use at mainly “room temperature”.

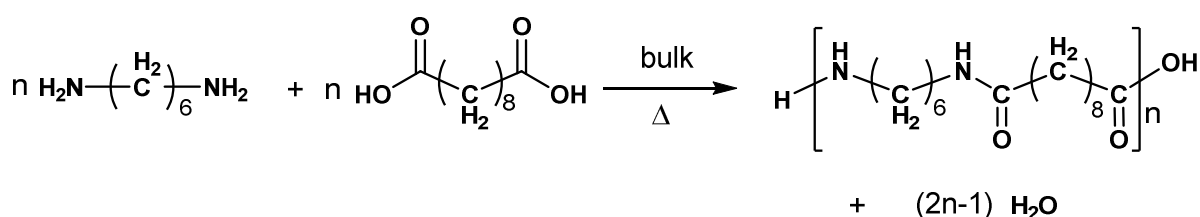
Moisture absorption of the amide groups causes also some drawbacks, this plasticizing effect reduces tensile strength and modulus. As a result, PA-6 components for example are not used successfully in all engineering applications because of a lack of rigidity. Modification of the moisture absorbance of PA-6 but also the increase of the T_g are therefore actual fields of research toward this kind of polymers. Of course some improvements of the mechanical and thermal properties can be performed by formulation or blending polyamides with numbers of modifiers such as glass fibers, glass beads, and carbon fibers. But another approach may require some changes in the polymer functional groups. Thus this can be performed by monomer preparation or by post-polymerization modifications of the polymer. This would end up with different types of polymer structures (block, random, crosslinked etc.).

Changing the length of the aliphatic repeating unit appears also to be interesting. Thus, often compared to the silk, the polyamide-3 (PA-3) exhibits a higher T_g (up to 126°C) but also a higher moisture uptake and sensitivity to hydrolysis, both derived from the higher proportions of hydrogen bondings due to the higher proportions of amide groups. However due to some synthetic limitations[1–10] this polymer is not commercially available. The different synthetic pathways and the interest around this polymer are referenced below. In the following, we focus the literature review on the different ways to synthesize aliphatic polyamides with a close link with polyamide-3.

2. Synthesis of aliphatic polyamides by polycondensation

2.1. Common polyamides

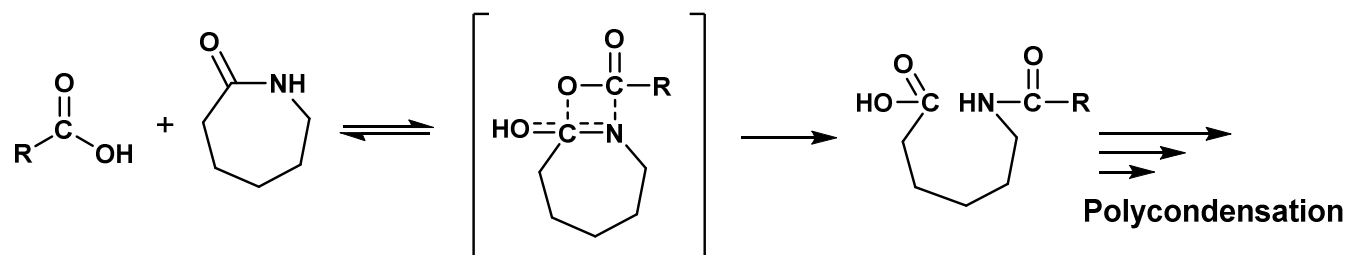
Polycondensation is one of the methods used to obtain aliphatic polyamides. It is generally conducted at higher temperatures than the melting point of the resulting polymers to get homogeneous reaction medium. At this temperature the released volatile by-products such as water or alcohol are eliminated. Synthesis of aliphatic polyamides is carried out by reaction of difunctional carboxylic acids or acid chloride groups with amino groups. For example, polyamide 6-6 (PA6-6) is synthesized by polycondensation reaction of adipic acid and hexamethylenediamine by eliminating water. Other polyamide examples are polyamide 6-10 (PA6-10) from hexamethylenediamine and sebacic acid (Scheme III-1) and polyamide 4-6 (PA4-6) from butane-1,4-diamine and adipic acid. Resulting polymers have still some water in the polymerization atmosphere even though the polymerization is carried out at higher temperature. The presence of water after polycondensation reduced the thermal and mechanical properties because of its plasticizing effect. However by using hexamethylenediamine in presence of sebacyl chloride and sodium chloride, the synthesis of PA-6-10 is allowed (sodium chloride being there to trap the so-formed hydrochloric acid). This enables a PA6-10 synthesis at room temperature and constitutes a perfect academic example as the polymerization can be performed through an interfacial process.



Scheme III-1: Polycondensation of hexamethylenediamine with sebacic acid for PA6-10 synthesis

In presence of water, hydrolytic polymerization reaction of ϵ -caprolactam (ϵ -CL) occurs at 250 °C for 72 hours and gives PA-6. The aminolytic and acidolytic polymerization of ϵ -CL was also investigated (Scheme III-2).[11] Even though the previously mentioned polyamides (PA-6, PA6-6, etc ...) seem to have close chemical structures, their thermal and mechanical

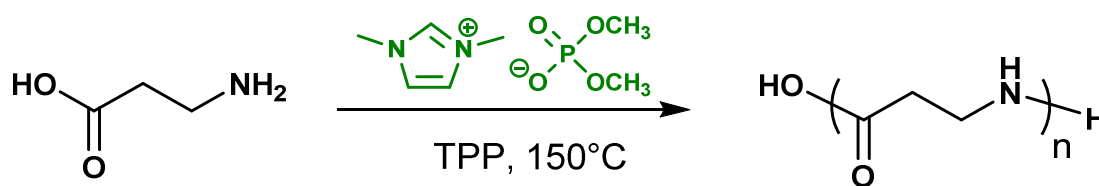
properties are different. For example, PA6-6 has a higher crystallinity and a lower water uptake and therefore a higher chemical resistance, than PA-6. However, PA-6 has a lower melting temperature which makes it attractive for an easy processability in the industrial area.



Scheme III-2: Initiation specie for the acidolytic ring-opening of ϵ -caprolactme

2.2. Polyamide-3 by polycondensation of β -alanine and its derivatives

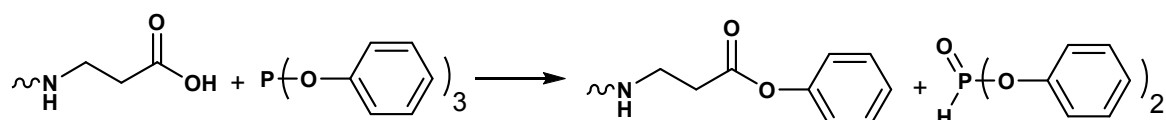
The polycondensation of β -alanine could be a straightforward method for poly(β -alanine) (another name for polyamide-3) synthesis. This polymer is insoluble in most organic solvents and undergoes degradation reactions before melting (mp= 320-355 °C) and, therefore, cannot be prepared by conventional polycondensation. However, Fradet and coll. recently reported PA-3 synthesis in ionic liquids in presence of triphenyl phosphite (TPP) (Scheme III-3).[12]



Scheme III-3: Synthesis of Poly(β -alanine) in 1,3-dimethylimidazolium dimethyl phosphate in the presence of TPP

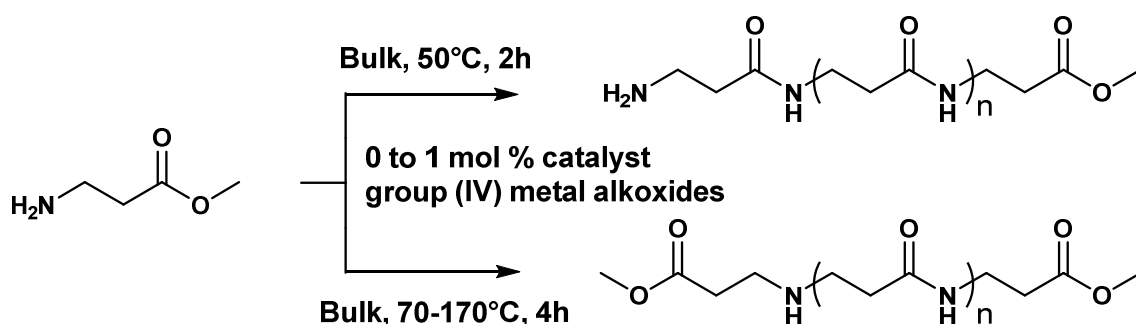
They based their work on the previous synthesis of aromatic polyamide in ionic liquids obtained by polycondensation of aromatic diamines and aromatic diacid chlorides at low temperatures (0–60 °C) or from diamines and diacids with addition of triphenyl phosphite at higher temperatures.[13–16] Polyamide-3 with a maximum degree of polymerization $\overline{DP}_n =$

43.5 could be obtained in 1,3-dimethylimidazolium dimethyl phosphate in 8 to 18 hours corresponding to 3 550 g/mol. At that time this is the first example of direct polycondensation of β -alanine for the PA-3 synthesis. Macrocycles formation and reaction of β -alanine with triphenyl phosphite were reported as side reactions leading to the presence of phenyl ester-terminated PA-3 chains and diphenyl phosphite (DPP) (Scheme III-4). One can note that the β -alanine was also copolymerized with ϵ -caprolactone to yield quasi alternating polyesteramides and very low proportions of poly(β -alanine) were observed[17].



Scheme III-4: Formation of Phenyl Ester and DPP during β -Alanine Polymerization

One year later, Scott and coll. reported another way for the PA-3 synthesis by performing ester-amide exchange with β -alanine derivatives (β -alanine esters) catalysed by titanium or hafnium alkoxides (Scheme III-5).[18] The obtained molar masses were quite similar to the method established in ionic liquids but in shorter times (1 to 4 h). The introduction of different chemical groups at the PA-3 chain ends was possible.

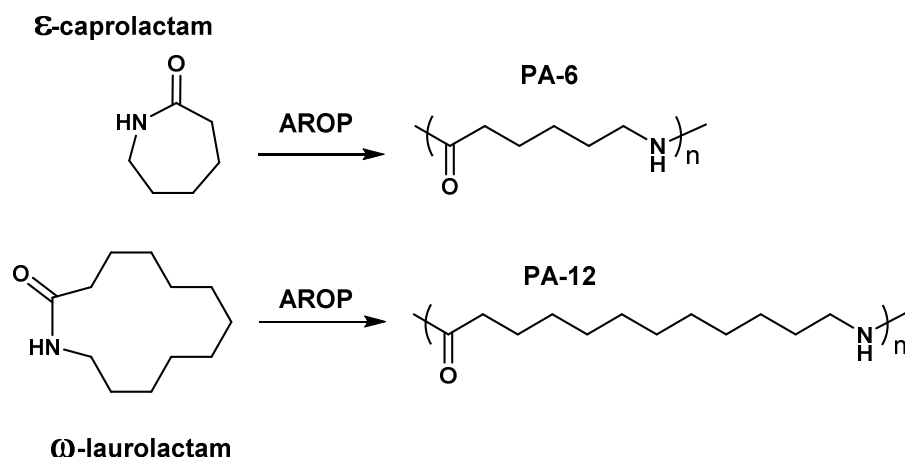


Scheme III-5: Formation of PA-3 by amide ester exchange from β -alanine-OMe

3. Anionic ring-opening polymerization of cyclic amides (lactams)

We have seen that polycondensation could lead to the synthesis of aliphatic polyamides, which usually involves high temperature (at least higher than the melting temperature of the yielding polymer) and the removal of the by-product which can have a negative effect in the final material. Regarding polyamide-3, only a few examples are referenced and are limited to low degrees of polymerization.

Anionic ring-opening polymerization (AROP) of lactams can be envisaged to overcome such drawbacks. In the following, mechanistic aspects and some key features of such a polymerization are presented. Depending on the nature of cyclic lactams available and on their ring strain, several polyamides can be obtained. Industrially an anionic initiation followed by an activated monomer mechanism is mainly used for the polymerization in molds in order to prepare polyamides PA-6 and PA-12 directly from the corresponding lactams (Scheme III-6)[19]. Polymerization mechanism of lactams, their polymerizability, and the properties of the resulting polymers were largely investigated. Fundamental reviews published by Reimschuessel[20], Sebenda[21], Sekiguchi[22], Hashimoto[23], Roda[24] Russo[25], and Carlotti[26] can be found and precise this presented overview. The anionic route is the fastest method for producing polyamides due to a low activation energy needed. This fast kinetic makes nowadays this route of high interest for industrial processes producing lightweight composite materials for automotive industry and wind energy. The anionic polymerization of lactams may be accomplished in solution or in bulk either below or above the melting point of the polymer for the latter.



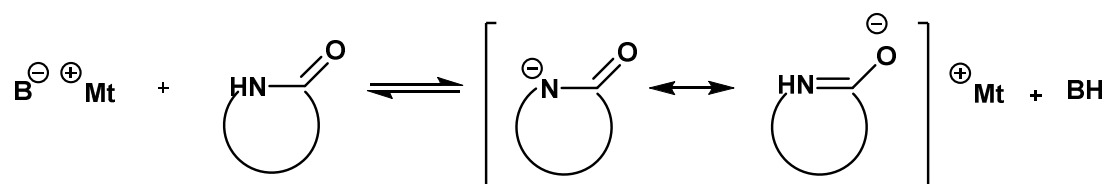
Scheme III-6: Example of resulting polyamides from the AROP of their corresponding lactams

3.1. Mechanism of the anionic polymerization of lactams

The mechanism differs from the anionic polymerization of most of unsaturated and heterocyclic monomers because the growth center is not an anionically activated end-group, but is represented by an N-acylated neutral chain. The anionic polymerization of lactams is initiated, under anhydrous conditions, by formation of a lactamate anion. Strong bases are able to deprotonate lactams and produce N anion of lactam effective for initiating the polymerization.

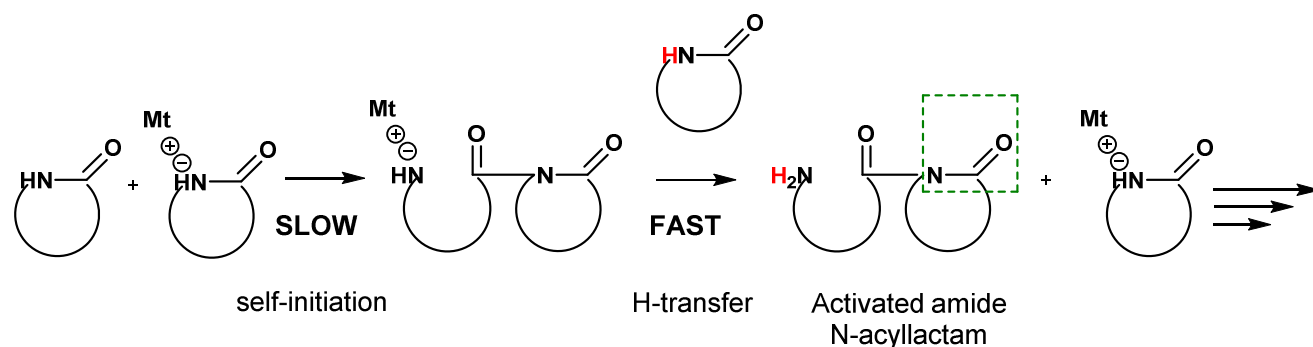
3.1.1. Initiating and activating systems

The anionically activated species is the monomer in the form of lactamate anion which is a very strong nucleophile generated by the deprotonation of a lactam monomer with a strong base such as $t\text{-BuONa}$, $t\text{-BuOK}$, EtMgBr , Et_2Mg etc. (Scheme III-7). The negative charge is delocalized on the amide group due to resonance stabilization by conjugation with the carbonyl group.



Scheme III-7: Structures of the anionically activated monomer

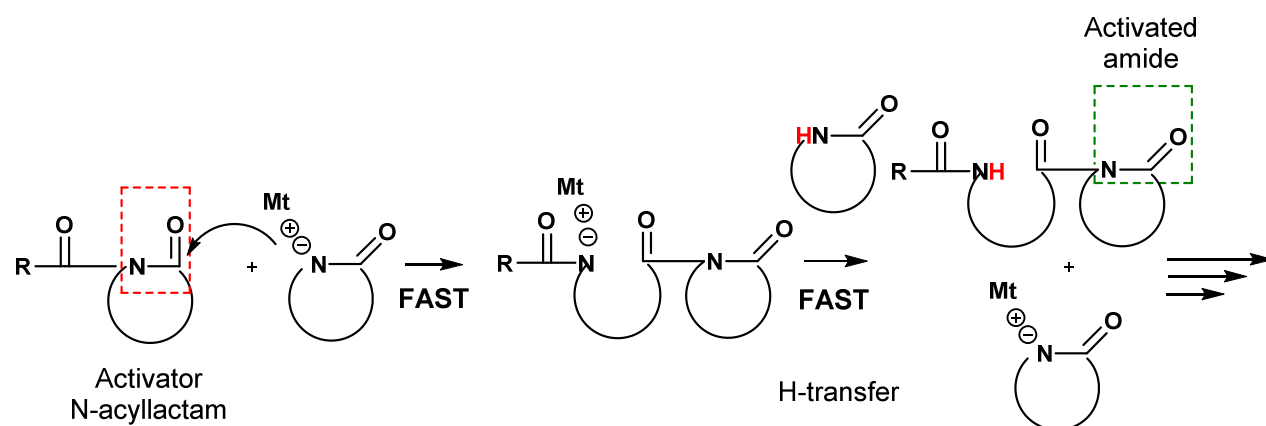
The lactamate anion is acylated by a lactam monomer, although the acylating ability of the latter is poor, with the amide group being stabilized by resonance. The lactamate anion reacts with the monomer by a ring-opening transamidation reaction forming N-acyl lactam structures carrying primary amine anions. Assuming a free ion mechanism,[21] the imide anion is formed, in the first slow step, by nucleophilic attack of the lactamate on the carbonyl of the lactam molecule (Scheme III-8). As it is not stabilized by resonance, rapid proton exchange undergoes with lactam monomer, yielding imide dimer (N-acyllactam) and regenerating the lactamate. Result of these two combined reactions is the disproportionation between two amide groups (present in lactam monomer and in lactamate anion) to give amine and acyl lactam moieties (in the N-acyllactam species) and the reaction rate is dependent on factors like the nature of the counter-ion, the reaction medium, the lactam ring-size, the kind of substituents and the structure of the resulting linear monomeric unit. N-substituted lactam are observed to react with lactamate anion with a rate significantly higher than that of the initial reaction, depending on the size and the electrophilicity of the substituent, and are generally used as activators in the activated anionic polymerization. The use of high reaction temperatures ($> 250^{\circ} \text{C}$) is required in the absence of activator and only the more reactive lactams, such as ϵ -caprolactam, undergo polymerization in the presence of a strong base in a non-activated method (see paragraph 2.1).



Scheme III-8: Nucleophilic attack of lactamate anion to lactam (self-initiation step) followed by H-transfer

The initiators, which are the monomers carrying the anionic charge able to attack the chain end, were investigated by reaction of a lactam with strong bases such as mainly metal alkoxide[27], metal halide[28], alkali metal[22], Grignard reagent[29] but also ammonium salts[30] and phosphazene bases[31]. The association of a strong base (NaH, LiH, BuLi) with a reducing agent such as metal dialkyl/dialkoxy aluminium hydrides or metal dialkylboron hydride can also be used also precursors of lactamates.[32,33]

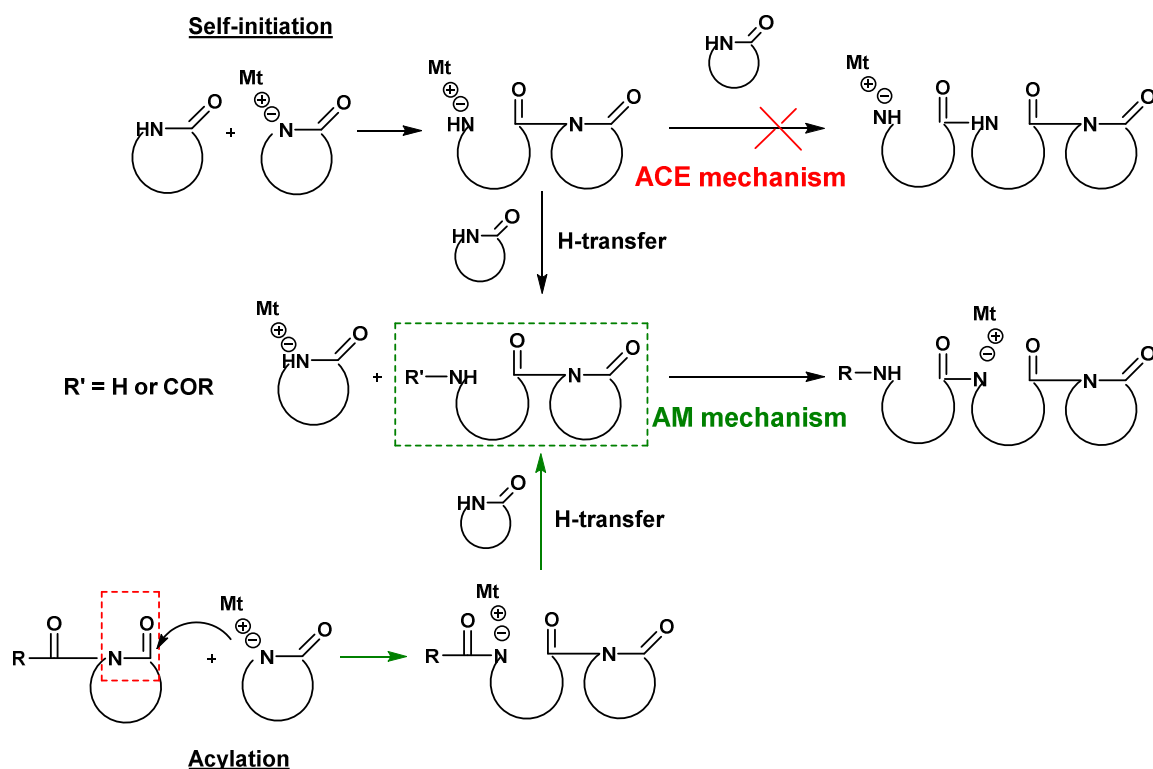
With non-activated anionic polymerization of lactams an induction period and slow kinetics are observed (Scheme III-8). Opposite behaviours are obtained when an activator is added. AROP can be performed at much lower temperatures (e.g 130-180 °C for ϵ -CL)(Scheme III-9). Addition of an acylating agent was therefore shown to trigger the polymerization by favouring fast acylation reaction and propagation step to the detriment of a slow self-initiation step. Here, attention is given on N-acyllactam derivatives as they are well-known activators, but many others can be used such as carbon dioxide[34], isocyanates[35] and esters derivatives[36–38].



Scheme III-9: Nucleophilic attack of lactamate anion to N-acyllactam (acylation step) followed by H-transfer

3.1.2. Propagation reaction

The self-initiation and the acylation step are both followed by an extremely fast H-transfer step by deprotonation of a monomer. As a consequence this directly refers to the growth of the polymer chains via an Activated Monomer (AM) mechanism as the monomer is carrying the anion[26]. The neutral N-acyllactam acts as the growth center at the chain end and comes contrasts with an Active Chain End mechanism (ACE). (Scheme III-10)



Scheme III-10: Formation of active species in anionic ring-opening polymerization of lactam: Activated Monomer (AM) mechanism vs Active Chain-End (ACE) mechanism

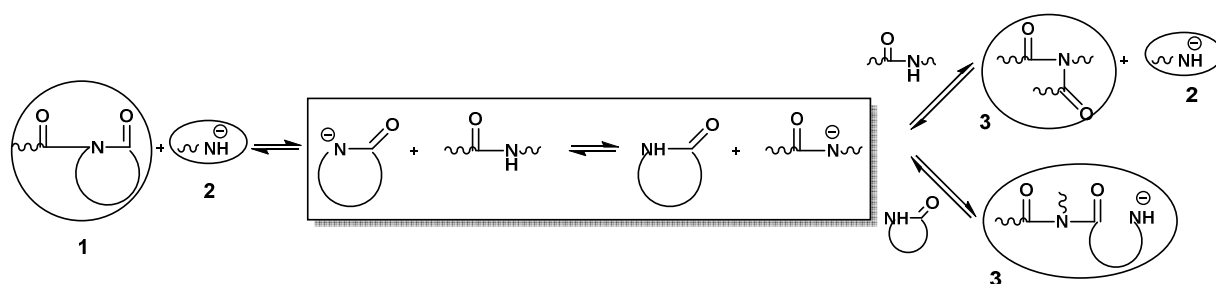
In this activated polymerization the polymer molar mass are controlled by the concentration of activator (N-acyllactam) as compared to monomer concentration (lactam). However such a polymerization is not living because of side reactions usually observed in the lactam ring-opening chemistry.

3.1.3. Side reactions

Species involved in anionic polymerization are in general highly reactive and lead to a series of side reactions, in particular when using high temperatures and/or long polymerization times. Reversible and irreversible side reactions can occur in which both the growth centers and the monomer anions are consumed. The strongly basic conditions in AROP of lactams promote mainly polymer branching and β -keto compounds, yielding to side products and chain irregularities. Reactivities are nevertheless related to numbers of factor such as the lactam size and their substituents, the nature of the activator, the initial ratio of initiator and activator concentrations, the permittivity of the reaction medium, and the reaction temperature as well as the nature of the counter-ion[26].

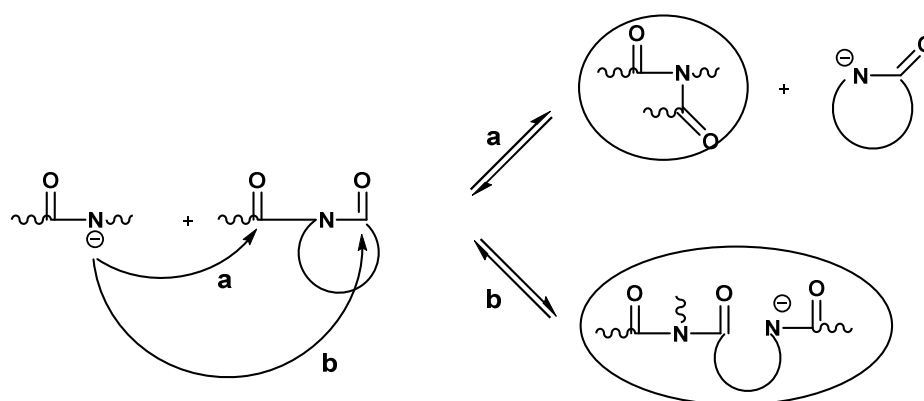
❖ **Formation of acyllactams, amines and imides**

The polymer amide groups may be involved in the formation of acyllactams and amine end groups. Indeed, the presence of amide N anions along the polymer chain and derived from equilibrium reactions with lactam anions in strongly basic medium, may produce imide groups and polymer branching (Scheme III-11).



Scheme III-11: Formation of acyllactam (1), amine (2), and imide (3) groups during AROP of lactams

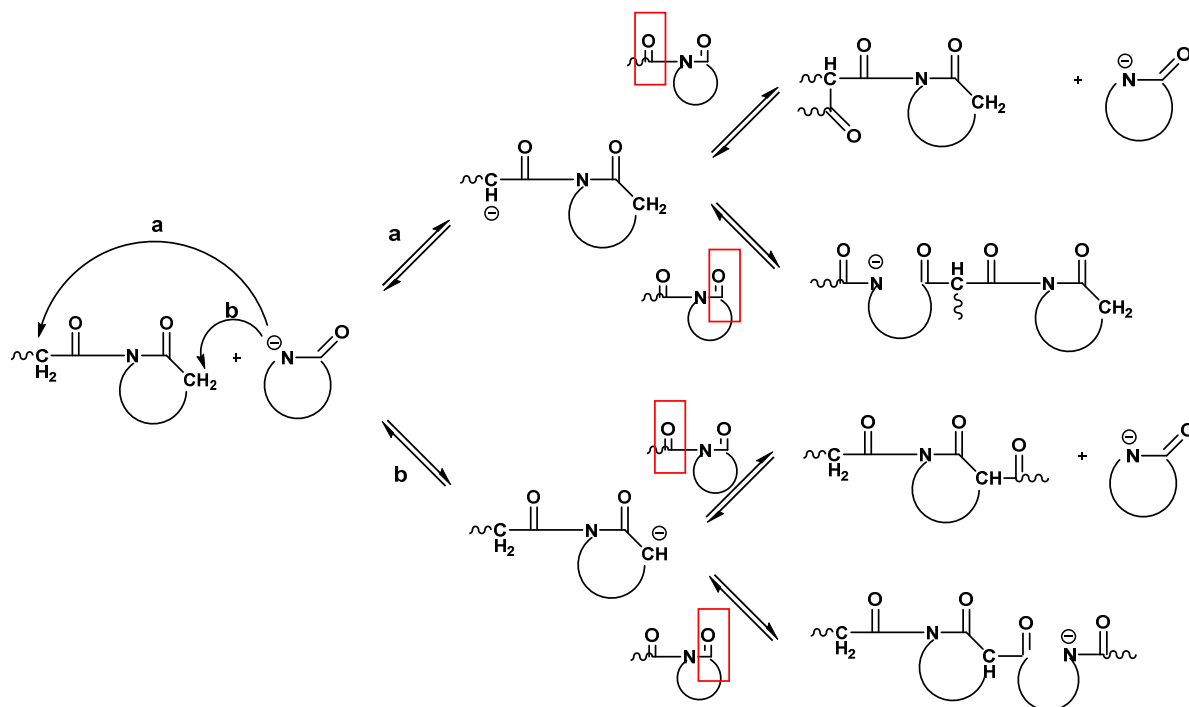
Transacylation reactions between polymer amide anions and acyllactams (N-acylations) may cause depolymerisation (pathway a) or incorporation of a lactam unit (pathway b) (Scheme III-12).



Scheme III-12: Formation of imide groups by N-acylation

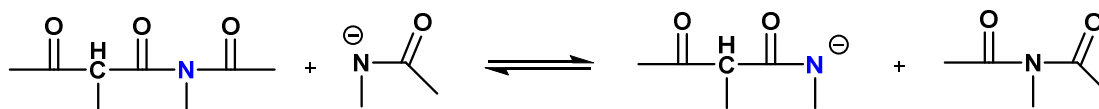
❖ **Formation of β -ketoimides and β -ketoamides**

The acidity of the hydrogen atoms in α position of the carbonyl of the imide group in the N-acyllactam chain end is comparable to that of hydrogen in an amide group. As a consequence, in the presence of lactamate, deprotonation may occur by leading to the formation of two distinct carbanions (pathway a and b) which can both give rise to the formation of two β -ketoimides. Claisen-type condensation reactions can then happen, giving four different β -ketoimide structures (Scheme III-13).



Scheme III-13: Formation of carbanions giving β -ketoimides during AROP of lactams

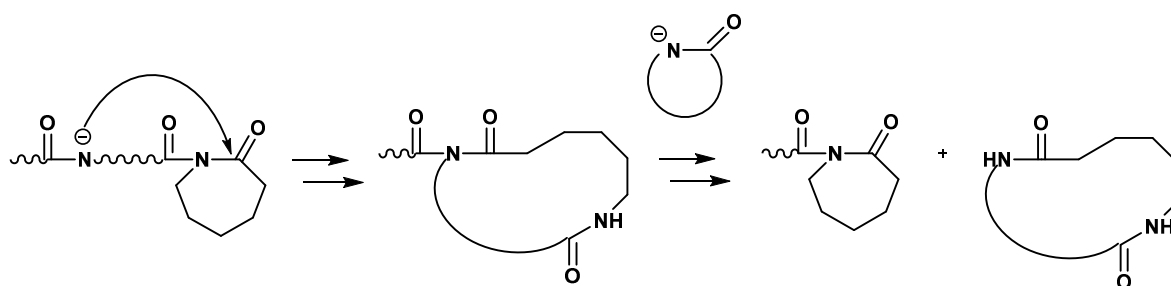
Neutral β -ketoimides are also strong acylating agents and may be involved in reactions, acting as growth centers and leading to either linear or branched chains. β -Ketoimides may be converted to β -ketoamides by nucleophilic attack of the N- anion on the carbonyl of the imide group (Scheme III-14).



Scheme III-14: Formation of a β -ketoamide from acylation of β -ketoimide

❖ Formation of cyclic oligomers

The formation of cyclic oligomers was particularly investigated by Russo et al. for ϵ -caprolactam[39,40] and the amount depends particularly on the polymerization temperature (e.g. 3.5% at 280 °C). The main reaction leading to cyclic oligomers is a back-biting reaction which is an intramolecular reaction of the neutral end groups with amidic groups inside the chain (Scheme III-15). The counter-ion involved in the polymerization is also directly influencing the occurrence of such a side reaction[41]. Using magnesium salts of ϵ -CL, cyclization reactions are strongly reduced both below and above the melting temperature of the polymer formed as compared with sodium systems. The existence of coordination between magnesium-based compounds with end groups of polyamides is suggested. Cyclic structures can have a negative influence on processing or applications as they are able to modify the crystalline structure in the solid phase[39]



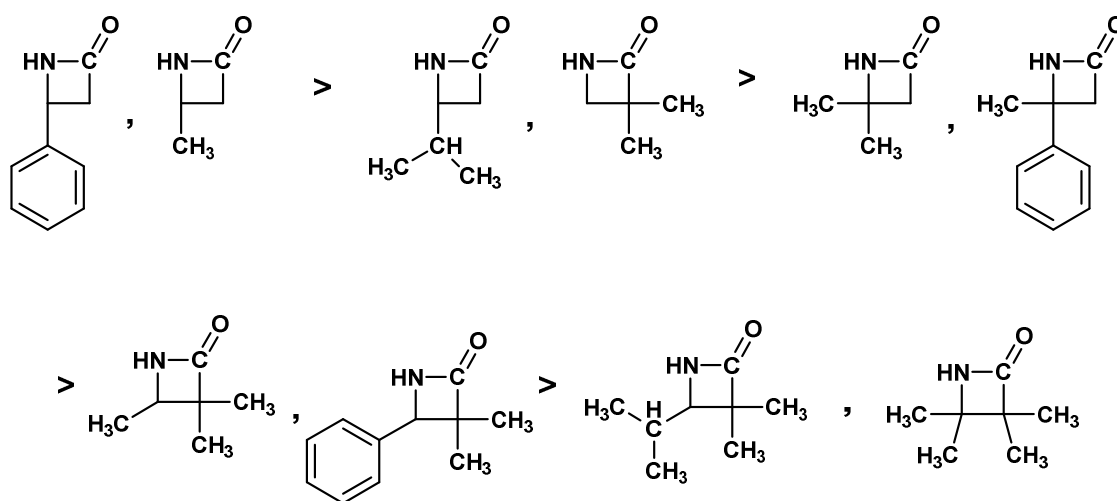
Scheme III-15: Formation of cyclic oligomers by intramolecular reactions.

3.2. Polymerization of β -lactams

3.2.1. Substituted β -lactams

The β -lactams represent the four-membered ring cyclic amide family. Based on the same mechanistic background presented previously, living anionic polymerization can nevertheless be reached when substituted β -lactams (or β -propiolactams) are used. Indeed they are highly reactive due a high ring strain and thus enable the use of low polymerization temperatures and rates. The review of Hashimoto published in 2000 describes in details the specificities of the ring-opening polymerization of such monomers[23]. Sebenda et al. showed first that the activated anionic polymerization of a bulky β -lactam, i.e. 3-butyl-3-methyl-2-azetidinone, has a living character giving a monodisperse polyamide of molar mass very close to the theoretical value[42,43]. Other substituted monomers were also

polymerized in a controlled manner in homogeneous solution, using aprotic and apolar solvents like N,N-dimethylacetamide, DMF, or DMSO, and in the presence of lithium salts[44–46]. The apparent polymerizability of β -lactams was found to decrease with the number and bulkiness of substituents in the following order: 4-phenyl-, 4-methyl- > 4-isopropyl-, 3,3-dimethyl- > 4,4-dimethyl, 4-methyl-4-propyl- > 3,3,4-trimethyl-, 3,3-dimethyl-4-phenyl-, 3,4,4-trimethyl- > 4-isopropyl-3,3-dimethyl-, 3,3,4,4-tetramethyl-2-azetidinone (Scheme III-16). Nevertheless, depolymerization and transamidation reactions are known to occur both at the acyllactam chain end, and on the polyamide chain and therefore to broaden the molar mass distribution[23]. Stopping the reaction before complete conversion minimizes transamidation reactions enabling the preparation of block and graft copolymers, or other structures taking advantage of the living character of the polymerization.



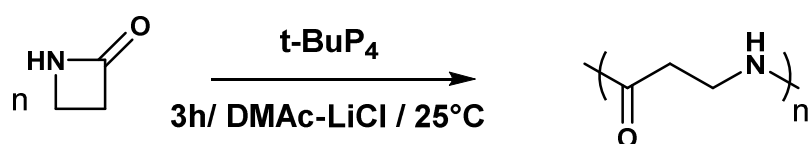
Scheme III-16: Decrease of apparent polymerizability depending on the β -lactam structure

The possibilities to play with the substituents of β -lactams offer nowadays PA-3-like materials with amphiphilic character and exhibiting bioactivity for instance[47–51].

3.2.2. Unsubstituted β -lactam

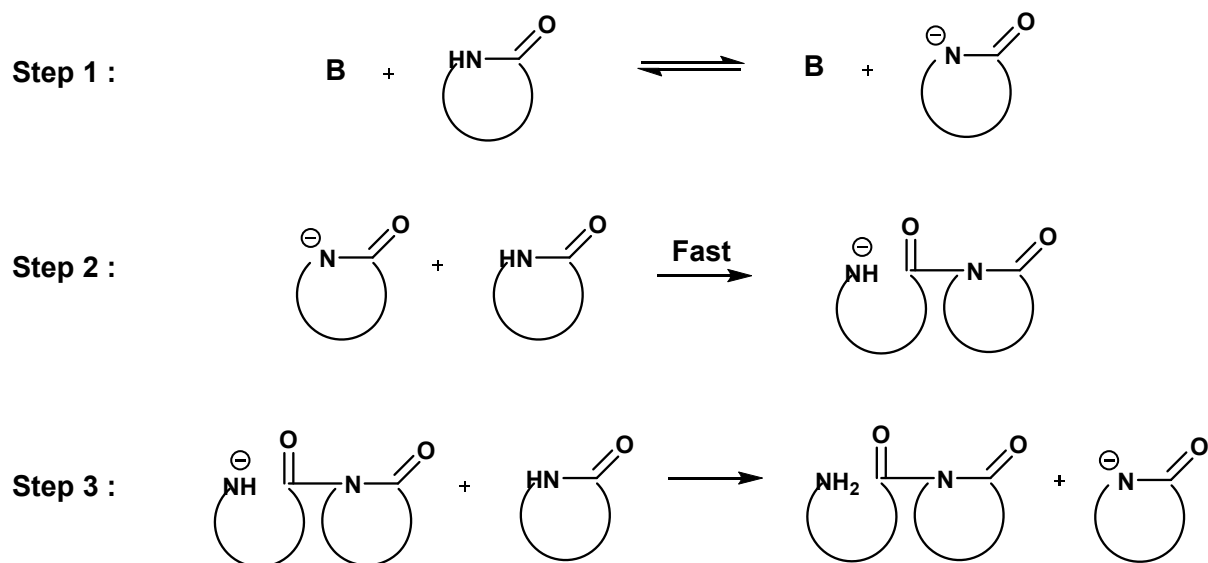
Polyamides cohesion comes in general from the strong intra- and intermolecular interactions which are formed within linear structures. Thus, and based on the benefits that

the anionic ring-opening polymerization (AROP) of lactams provide, it appears interesting if polyamide-3 could be synthesized from the unsubstituted β -lactam. However this is barely achieved as only few exceptions (referenced below) can claim such a synthesis. Indeed, aliphatic polyamide-3 cannot be synthesized by AROP of 2-azetidinone (the unsubstituted β -lactam) with metal catalyst due to predominant depolymerisation and transamidation reactions. Using the organic phosphazene base $t\text{-BuP}_4$, Zhang and coll. were able to perform such a synthesis in a N,N -dimethylacetamide and lithium chloride mixture (Scheme III-17)[2]. An increase in temperature was shown to increase the polymerization rate to the detriment of the molar mass and yield. As $t\text{-BuP}_4$ concentration increases, the yield and molar masses of the polyamide-3 decrease. As a consequence the initiation of the polymerization is proposed to follow an anionic ring-opening mechanism.



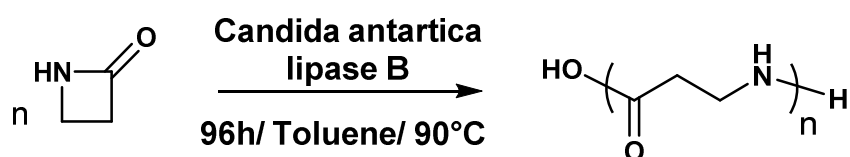
Scheme III-17: Ring-opening polymerization of 2-azetidinone by phosphazene base $t\text{-BuP}_4$

An interesting point is that this polymerization is carried out without any addition of activator such as N -acyllactam and no induction period was observed (see paragraph 3.1.1). A mechanism is suggested, the initiation involves the following steps (Scheme III-18). **Step 1:** at the beginning, lactam reacts with $t\text{-BuP}_4$ (B) to yield a lactamate anion. **Step 2:** the lactamate anion reacts with the monomer to form an aminic anion with ring opening. **Step 3:** the unstable aminic anion quickly abstracts a proton from β -lactam to yield dimeric lactam and regenerate lactamate anion, which acts as the growth centre of the polymerization. Note that unlike the case of anionic ring-opening polymerization with metal catalysts, the lactamate anion transforms immediately into an aminic anion, so that no apparent induction period is observed.

Scheme III-18: Initiation process for the *t*-BuP₄-catalyzed

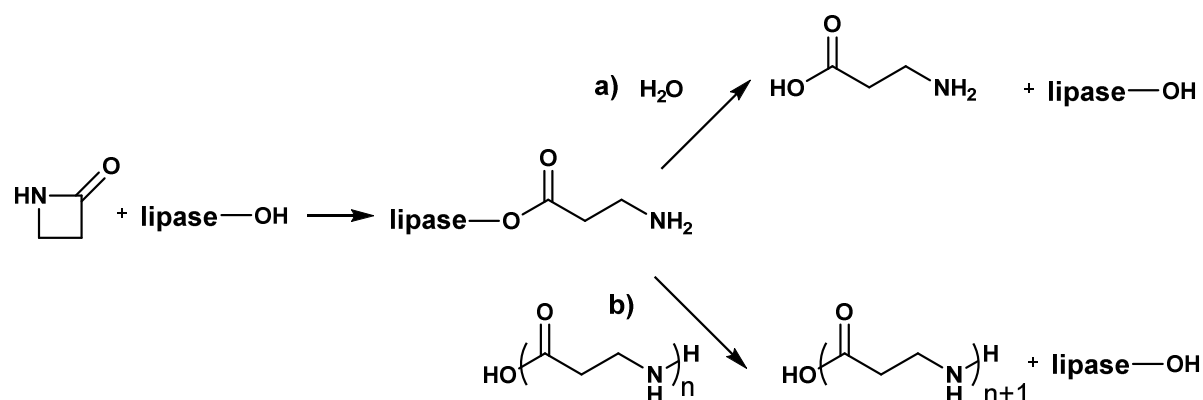
Even if an initiation mechanism is proposed, the propagation step remains unclear and coarsely discussed. Despite the molar mass dependence with the amount of *t*-BuP₄, the monomer conversion is never completed and tends to decrease with the increase of the molar masses. Such a system enables the synthesis of linear polyamide-3 in 3 hours with molar masses up to 10⁵ g/mol. The glass transition temperature is found to be as high as 126 °C and a crystallinity around 40 %.

Far from the anionic method an alternative pathway was reported by Loos and coll. (Scheme III-19)[52]. They performed the synthesis of polyamide-3 by enzyme-catalyzed ring-opening polymerization of 2-azetidinone as the Lipase B from *Candida Antarctica* was shown to ring open some β-lactams[53].



Scheme III-19: Ring-opening polymerization of 2-azetidinone by enzyme

An acyl-enzyme intermediate is formed and attacked. By following either the pathway **a)** the reaction with water releases β -alanine and the initial enzyme or the pathway **b)** the reaction with a growing oligomer ($n = 1, 2, \dots$) yield to a linear polyamide-3 (Scheme III-20). Unfortunately the molar mass obtained was very low with $DP_n = 18$.



Scheme III-20: Proposed pathways for the ring-opening polymerization of 2-azetidinone catalysed by an enzyme

Those last examples demonstrated the possible synthesis of linear polyamide-3 but still with some limitations.

4. Hydrogen-Transfer Polymerization

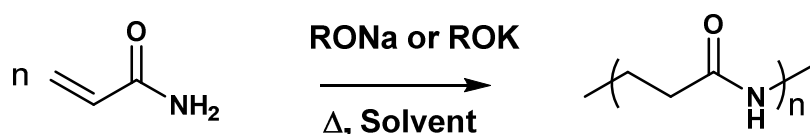
4.1. Polymerization of acrylamide

4.1.1. Initiation and propagation steps

Aiming to synthesize β -alanine by subsequent hydrolysis of poly- β -alanine (polyamide-3) Matlack firstly patented in 1954 the polymerization of acrylamide in the presence of various metal catalysts to get polyamide-3[54]. Three years later he proposed with Breslow and Hulse the first anionic mechanism for such a polymerization[55] which was rapidly called hydrogen-transfer polymerization as it was involving an anion transferring its charge from a carbon to a nitrogen by a proton transfer[56]. It can also be found under the name of transition polymerization or migrational polymerization but refers exactly to the same features[1,57]. This alternative method for the synthesis of PA-3 is of great interest as

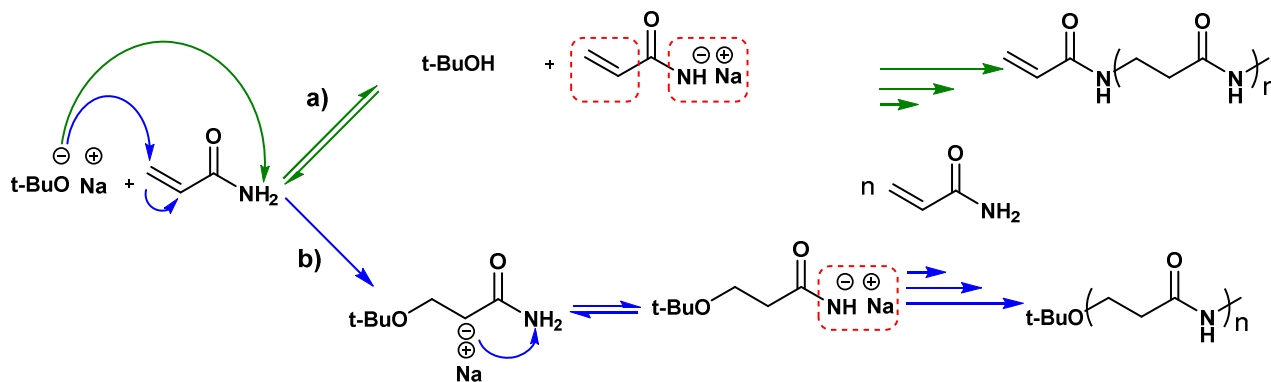
the acrylamide double bond is activated by the withdrawing effect of the carbonyl group and the amide can be easily deprotonated.

Basically, the protocol is as simple as the reaction presented Scheme III-21. The mixture of acrylamide with mainly alkoxides of alkali metal such as sodium or potassium *tert*-butoxide in aprotic or even protic solvents lead to the synthesis of polyamide-3.



Scheme III-21: Synthesis of polyamide-3 by anionic polymerization of acrylamide initiated by sodium or potassium alkoxides

However the mechanism appears to be rather complex. On the one hand, Breslow et al. believed that the polymerization was initiated by abstraction of a primary amide proton from acrylamide by a *tert*-butoxide anion to yield the corresponding amide anion $\text{CH}_2=\text{CHCONH}^-$ (pathway a. Scheme III-22)[55]. On the other hand, Ogata and coll. favoured an initiation by 1,4 addition (Michael-type addition) of the *tert*-butoxide anion to acrylamide followed by intramolecular proton transfer to yield the reactive species $(\text{CH}_3)_3\text{COCH}_2\text{CHCONH}^-$ (pathway b. Scheme III-22)[58]. In both mechanisms the primary amide anion end could participate in chain growth, but in that of Breslow growth could also occur at the olefinic end, whereas Ogata's mechanism does not allow for growth at the *t*-butoxy end. However, Tani and coll. isolated from the reaction mixture different oligomers having olefinic and ether end groups, demonstrating that both types of initiation occur[59]. Breslow, et al. favoured a chain-transfer mechanism for chain growth, whereas Ogata favoured continuation by poly(1,4-addition) mechanism. In a latter work Breslow stated that anionic polymerization of acrylamide presented all the attributes of a condensation polymerization (i.e. disappearance of the monomer to be converted into dimer, trimer, etc, and long after monomer has disappeared, high polymer begins to form).

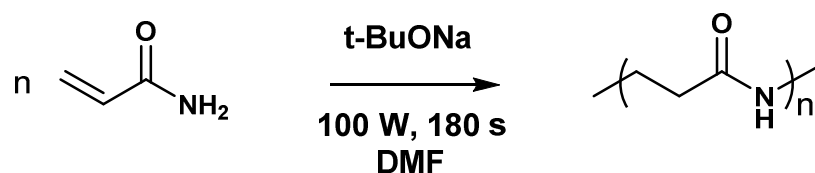


Scheme III-22: Possible initiations and propagations for the hydrogen-transfer polymerization of acrylamide in presence of sodium tert-butoxide

Since, hydrogen-transfer polymerization of acrylamide was further investigated and the opinion as well as the scientific results tend to support the mechanism of Breslow without excluding that both mechanisms can occur depending on the experimental conditions. Indeed, a trend can be highlighted depending on several factors like the nature of initiator, the initiator or monomer concentration, the type of solvent, and the polymerization temperature.[56–64] In contrast with primary alkoxides, tertiary alkoxides of alkali metals were shown to be the best metals catalyst for such a polymerization in the order $t\text{-BuOK} \approx t\text{-BuONa} > t\text{-BuOLi}$ and to be not linked to the polymer chain end. The yield is also higher in solvents of lower dielectric constant and in aromatic than in aliphatic solvents. As expected, the polymerization seldom occurs in protic solvents. Most of the time the polymerizations were performed in pyridine, benzene and its derivatives or still in DMF or DMAc to favour the polymer solubility from 30 minutes to 18 hours between 80 and 150°C yielding either incomplete conversion or low molar masses.

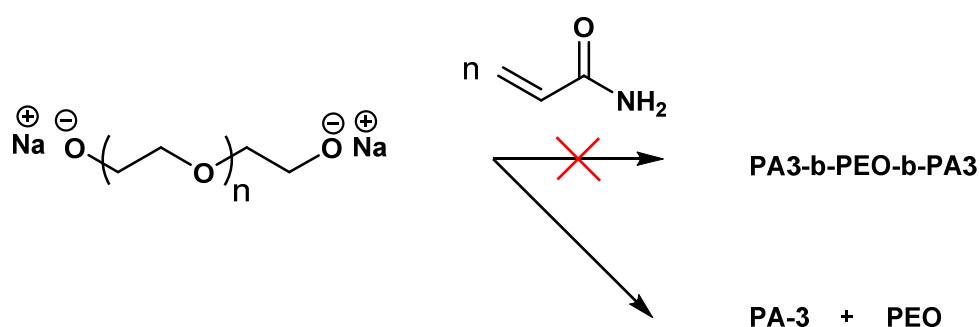
In 2009 Iwamura et al. used microwave irradiations for the “eco-friendly” anionic polymerization of acrylamide (Scheme III-23)[65]. Thus, using the same principles as described previously they obtained polyamide-3 in a few minutes with a maximum yield of 96%. They did not give any indication about the evolution of the molar masses with the amount of base neither about the impact of the microwaves on the possible branching reactions (see paragraph 4.1.2). This so-called green work being done in DMF we can think that the authors were limited by the polymer solubility in the reaction medium. They also

demonstrated the possibility to again use microwaves for the chemical recycling of the polyamide-3 under the form of β -alanine using acidic conditions.



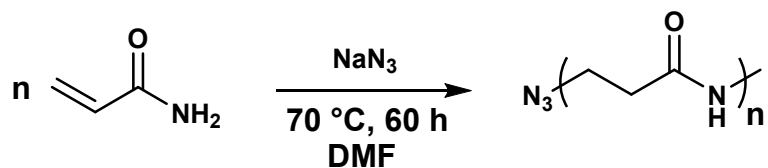
Scheme III-23: Anionic polymerization of acrylamide initiated by sodium tert-butoxide under microwave irradiations

Based on the HTP chemistry, the block copolymerization was also briefly investigated. Indeed, Tagekami and coll. attempted to initiate the HTP of acrylamide by using disodium salt of poly(ethylene oxide) (PEO) in several solvents at various temperatures in order to synthesize PA3-PEO-PA3 block copolymers[66]. The Michael type addition of alkoxide anion of PEO to acrylamide monomer did not occur in the initiation reaction and the polymerization proceeded exclusively via a hydrogen-transfer mechanism (Scheme III-24). The polymer found to be formed was a branched polyamide-3 without covalent linkage with the PEO.



Scheme III-24: Polymerization of acrylamide initiated by disodium salt of poly(ethylene oxide)

In 2015 Krishnamoorthi and coll. succeeded to perform the synthesis of azide-initiated PA-3 in order to form 3-arm polyamide-3 by subsequent click chemistry reactions with alkyne[67]. Sodium azide NaN_3 was therefore used as initiator for the acrylamide HTP (Scheme III-25).



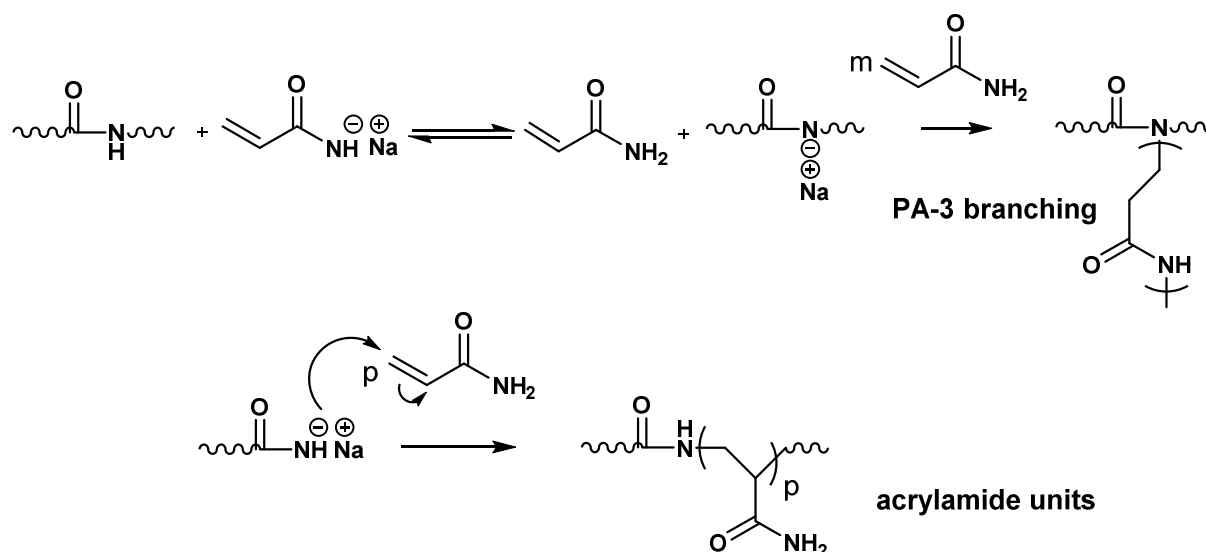
Scheme III-25: Anionic polymerization of acrylamide initiated by sodium azide

This polymerization yielded to 96% polymer ($\overline{Mn}_{\text{exp}} = 4600$ g/mol, $\overline{D} = 1.47$) which is an interesting result as it is similar to the one observed by acrylamide HTP initiated by sodium tert-butoxide (regarding the macromolecular dimensions). The authors then supported a polymerization occurring by Michael type addition as they gave evidences of azide group covalently linked at the polymer chain end. The initiation efficiency was not discussed as they finally get their 3-arm PA-3. However it can be noticed that when performing the click reaction their product yield was 60%. According to this result, incomplete click reaction can be envisaged due to the presence of unfunctionalized PA-3 chains which can be reasonably explained by the previous reports from the literature.

Those two examples therefore support one more time that the initiation conditions remain unclear as in some cases a polymer functionalisation by the initiator may be observed.

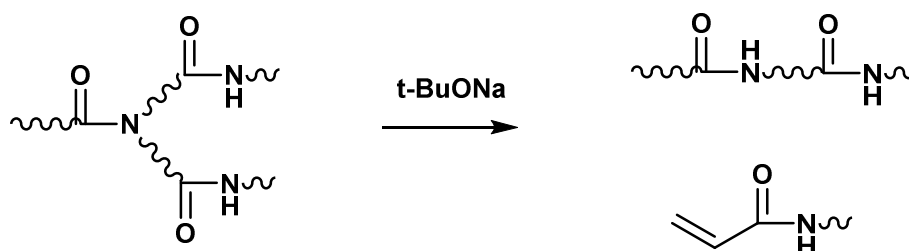
4.1.2. Sides reactions

On the basis of the reactional pathways depicted previously, some works also reported the presence of branching reactions via deprotonation of a secondary amide and the presence of vinyl enchainements via 1,2 addition during the hydrogen-transfer polymerization of acrylamide[8,68,69]. Thus, nitrogen-chain fragments but also acrylamide units are shown to exist along an extended PA-3 backbone (Scheme III-26).



Scheme III-26: Formation of branched polyamide-3 and acrylamide units

One example of acrylamide polymerization via HTP in N-methyl-2-pyrrolidone at 100°C reports also the presence of acid residues without any hydrolysis of the resulting mixture. This result was attributed to elimination reactions of branched units catalyzed by sodium tert-butoxide and coarsely explained by the following mechanism (Scheme III-27)[68]. The authors supported this by the fact that amides could undergo pyrolytic elimination reaction giving the reported example that by heating acrylonitrile with β -phthalimido propionitrile at 200 °C similar acid residues have been formed. This lone result had to be mentioned but can be debated.

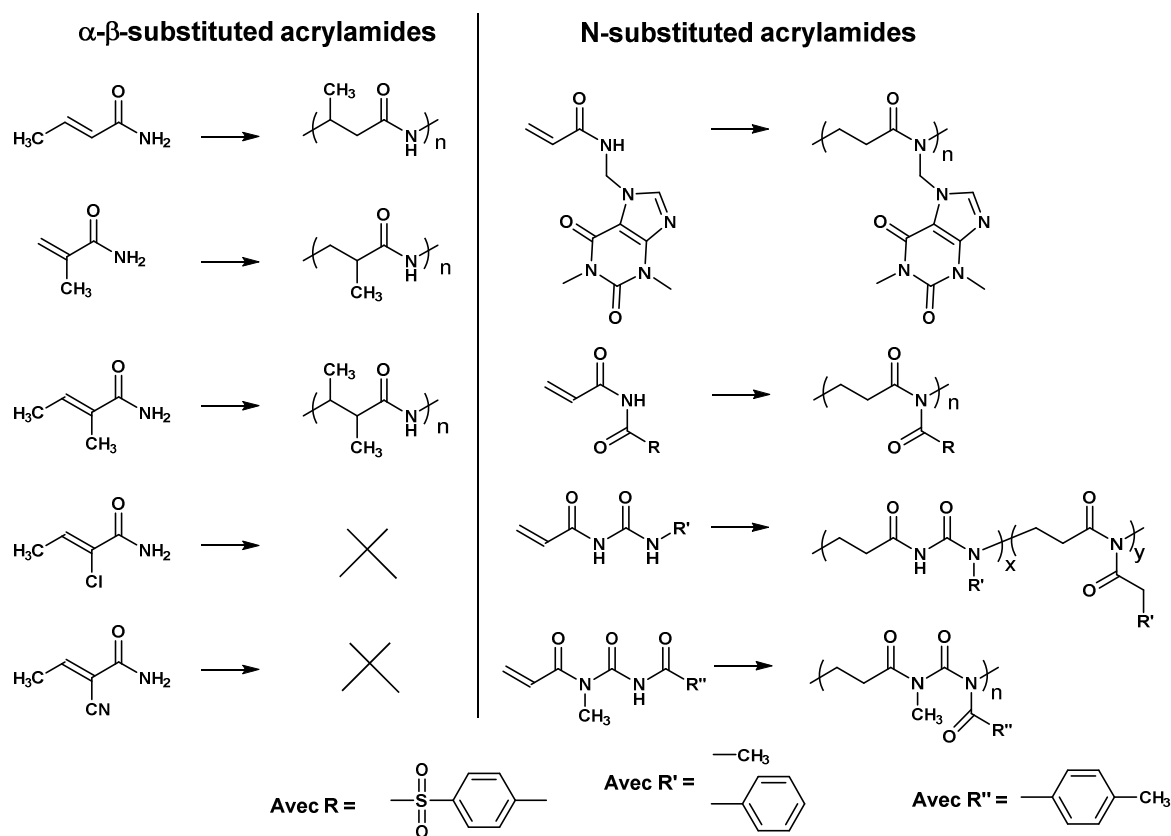


Scheme III-27: The proposed elimination of branched unit catalyzed by t-BuONa

4.2. Polymerization of other precursors

❖ Acrylamide derivatives

Other molecules similar to acrylamide were investigated. Having an activated double bond (by a carbonyl group) and a labile hydrogen, enabled HTP of the following derivatives in presence of *t*-BuONa or *t*-BuOK[69–76]. By analogy with substituted β -lactams, various PA-3-like structures can be prepared. The polymerization rates of the α - and/or β -substituted acrylamide were found to decrease from top to bottom (left column Scheme III-28). Acrylamide gave the polymer with the highest degree of polymerization among the monomers examined. The number and the position of the methyl substituent in acrylamide affected significantly both the rate of polymerization and the molar mass of the polymer. α -Substitution by cyano (CN) and chloro (Cl) groups, which are electron-withdrawing groups, seems to be unfavourable for the hydrogen-transfer polymerization. Some monomers were also found to copolymerize by a hydrogen-transfer mechanism. However, the most reactive one is incorporated first, the less reactive one was incorporated only as a terminal unit.

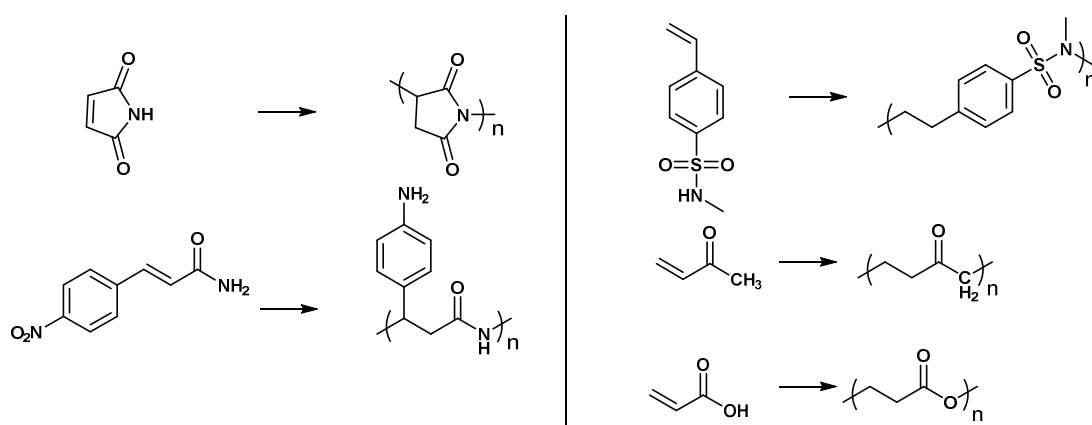


Scheme III-28: HTP of various acrylamide derivatives

It has to be noted that for each monomer only the HTP form of the polymer is presented, vinyl polymerization was also observed and constitutes a part of the repeating units in low proportions. Regarding the N-substituted acrylamide compounds they led to interesting structure in terms of pendant moieties however the presence of several carbonyl groups in the initial monomer led to more numerous side reactions.

❖ Vinyl monomers

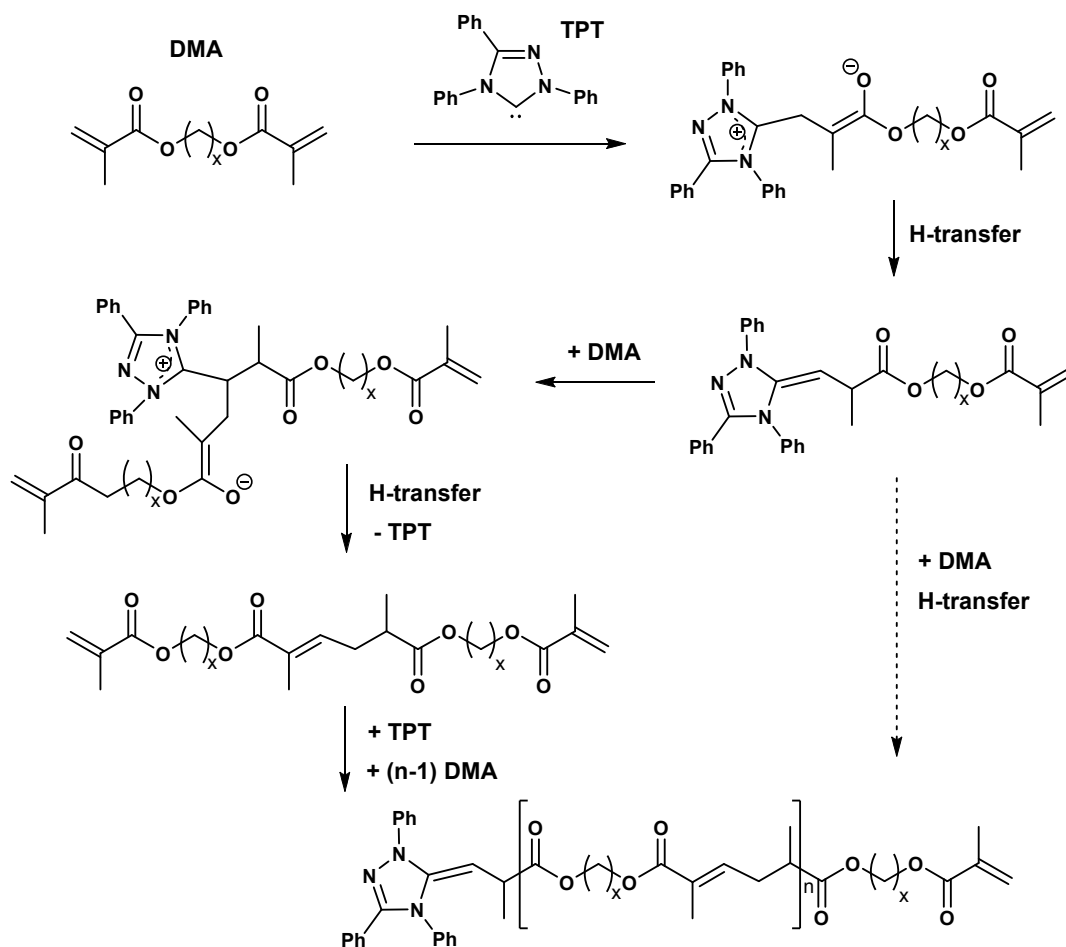
Maleimide[77], cinnamide[78,79], styrenesulfonamide derivatives[80], methyl vinyl ketone[81] and acrylic acid[82] were also investigated as potential candidates for a polymerization via hydrogen-transfer (Scheme III-29). Still with alkoxides of alkali metals, these species were slightly reactive to this method, low molar masses, low conversion, and low selectivity of the polymerization route (vinyl or HTP growth) were mainly observed.



Scheme III-29: HTP from vinyl monomers

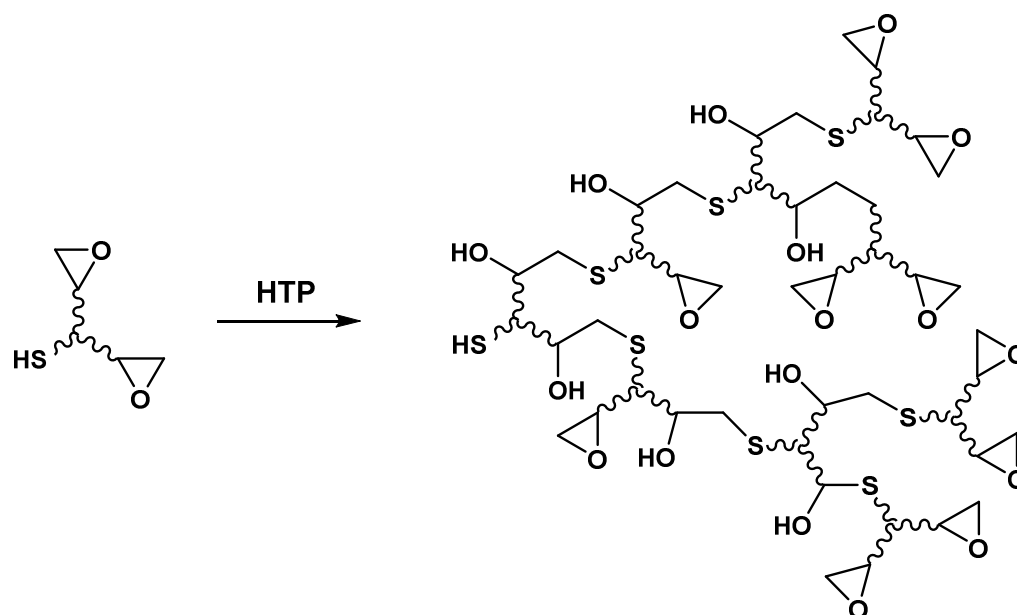
❖ Other examples

As they are also strong base and/or strong nucleophile, N-heterocyclic carbenes were used in HTP. Indeed, in presence of 1,3,4- triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene (TPT), dimethacrylates were shown to polymerize via hydrogen-transfer to give unsaturated polyesters according to the following mechanism proposed by the authors (Scheme III-30)[83].



Scheme III-30: Proposed possible mechanism for HTP of dimethacrylates catalyzed by TPT

Finally the concept of HTP was also applied to an AB₂-type monomer containing thiol and epoxide as reactive moieties. The base-catalyzed hydrogen transfer polymerization of this monomer led to the formation of a polythioether-based hyperbranched polymer (Scheme III-31) [84]



Scheme III-31: Hydrogen transfer thiol-epoxy polymerization

This literature review highlighted the importance of the experimental conditions regarding the synthesis of polyamide-3. The type of polymerization, monomer, initiator, solvent or temperature were shown to deeply influence the yield and the molar masses of the final polymers. On this basis we decided to study the hydrogen-transfer polymerization of acrylamide in bulk conditions intending to overcome the limitations previously described. The results are presented and depicted in the following submitted article.

5. Solvent-free anionic polymerization of acrylamide, a mechanistic study for the rapid and controlled synthesis of polyamide-3

Kevin Roos^{1,2,3}, Mikael Planes^{1,2,3}, Amelie Vax^{1,2,3}, Stephane Carlotti^{*,1,2,3}

ABSTRACT

A synthetic pathway based on hydrogen-transfer polymerization of acrylamide initiated by t-BuONa is proposed in this study where attention is given to the initiation and propagation steps. This anionic polymerization was performed in bulk and led to the synthesis of polyamide-3 with controlled molar mass up to 23 000 g/mol. NMR, SEC, and MALDI-ToF characterizations are supporting the chemical structures and the macromolecular dimensions of branched polyamide-3. The polymerization is completed in 5 to 20 minutes depending on the targeted molar mass as confirmed by a complementary thermal study. By DSC and TGA measurements, glass transition temperatures and degradation temperatures are found to be up to 88 °C and 357 °C respectively. Branching reactions are presented to be dependant with the initiator amount. An equilibrium between branching and deprotonation reactions is therefore proposed. The formation of imide groups is also evoked thanks to the titration of the polymerization atmosphere.

KEY WORDS

acrylamide, polyamide-3, hydrogen transfer polymerization, anionic polymerization, bulk polymerization

INTRODUCTION

Polyamides are one of the major engineering thermoplastics. Their properties can be modified by a number of techniques like copolymerization, incorporation of fillers, or blending with other polymers. The class of polyamides offers a lot of industrial applications in textile, medicine or automobile industry. A large amount of inter- and intramolecular electrostatic interactions provides to polyamides their excellent mechanical properties and resistance to chemicals. Polyamides in general belong to an active field of research where polyamide-3 can show interesting features. Polyamide-3 is also known as nylon-3 or poly(β -alanine) depending on the precursors used. It differs from other commercial polyamides in term of properties due to only two methylene groups for one amide function and thus-exhibits a capacity to up-take moisture, a glass transition temperature at 110-125 °C, a high melting temperature (320-355 °C) and crystallinity (30-40 %) depending on the precursor used and on the synthesis conditions[1–8]. Although polyamide-3 shows properties quite similar to that of silk it has not been commercialized yet. Only a few applications of polyamide-3 and derivatives are referenced such as a formaldehyde scavenger, polyoxymethylene stabilizer or antimicrobial polypeptides-like[6,9,10]. At its earliest stages Matlack and collaborators showed that polyamide-3 can be obtained by hydrogen transfer polymerization (HTP) of acrylamide[54,55]. This polymerization method was then further investigated[3,8,56–62,67–69] and extended to acrylamides derivatives[1,70,72–75,85] or other compounds like maleimide[77,86], cinnamide[78,79], crotonamide[76] and methyl vinyl ketone[81]. In the case of acrylamide, alkali precursors were shown to be the best candidates to turn it into polyamide-3, but the discussion remained opened for a while regarding the initiation step. Indeed the alkali precursors were shown to trigger the polymerization either by the proton abstraction[55] from the amide or by addition on the acrylamide double bond[58] under the form of poly-Mikael addition[87]. The polymerizations were tried in a number of solvent (protic and aprotic)[57] but basically benzene, pyridine and dimethylformamide can be used as inert solvent even under microwave irradiations[65]. Kumar et al. recently performed alkyne/azide click chemistry on PA-3 bearing azide functions and synthesized by anionic polymerization of acrylamide initiated by sodium azide[67]. The synthesis of polyamide-3 was also developed through polycondensation of β -alanine and its derivatives[18,88] or by ring-opening polymerization

of substituted β -lactams[44,48,51,89–91] or unsubstituted β -propiolactam with an enzymatic[52] or an anionic approach[2]. However and depending on the polymerization method, some limitations are observed, i.e. low monomer conversion, low molar masses, long reaction time, or the use of toxic solvent. In the present article we focused on the anionic approach based on hydrogen transfer polymerization of acrylamide in the molten state and mechanistic investigations based on the structure and properties exhibited by the so-formed polymers.

EXPERIMENTAL SECTION

Chemicals

Acrylamide (2-propenamide, AAm, 98%) was purchased from Alfa Aesar and was recrystallized in heptane. Potassium peroxodisulfate (KPS, 99%) and sodium tert-butoxide (t-BuONa, 97%) were purchased from Sigma-Aldrich and used as received.

Instrumentations

Size Exclusion Chromatography

Polymer molar masses were determined by Size Exclusion Chromatography (SEC) using hexafluoroisopropanol (HFIP + 0.05 %mol potassium trifluoroacetate KTFA) as the eluent. Measurements in HFIP were performed on a PL GPC50 integrated system with RI equipped and UV (280 nm) detectors and two PL HFIP gel columns (300 x 7.5 mm) (exclusion limits from 100 Da to 1 500 000 Da) at an elution rate of 1 mL/min. Columns temperature was held at 40°C. Poly(methyl methacrylate) was used as the standard.

Nuclear Magnetic Resonance

^1H NMR, ^{13}C NMR, DEPT135, HSQC ($^1\text{H}/^{13}\text{C}$) NMR spectra were recorded at 298 K on a Bruker Avance 400 spectrometer operating at 400MHz in appropriate deuterated solvents.

Thermal analysis

Thermogravimetric analyses (TGA) were performed using a TGA-Q50 system from TA instruments at a heating rate of 10 °C/min under a nitrogen atmosphere, from room

temperature to 700 °C with platinum pans. The weight loss was recorded as a function of temperature.

Differential scanning calorimetry (DSC) measurements were carried out with a Q100 apparatus from TA Instruments. DSC experiments were performed with aluminum sealed pans. In modulated mode, the sample was heated from –90 °C to 150 °C at a rate of 5 °C/min. Consecutive cooling and second heating run were also performed at 5 °C/min. The glass transition temperatures were calculated from the second heating run.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-Tof-MS)

Analyses were performed by the CESAMO (Bordeaux, France) on a Voyager mass spectrometer (Applied Biosystems). The instrument is equipped with a pulsed N₂ laser (337 nm) and a time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron and with an accelerating voltage of 20 kV. Samples were dissolved in hexafluoroisopropanol (HFIP) at 10 mg/mL. The matrix (α -cyano-4-hydroxy-cinnamic acid) solution was prepared by dissolving 10 mg of polymer sample in 1 mL of HFIP. A MeOH solution of cationisation agent (NaI, 10 mg/mL) was also prepared. The solutions were combined in a 10:1:1 volume ratio of matrix to sample to cationisation agent. One to two microliters of the obtained solution was deposited onto the sample target and vacuum-dried.

Ammonia titration

Ammonia emissions were titrated by acido-basic reaction followed by pH measurements with a pH probe. The gaseous emissions were first collected from the reactor thanks to a dynamic argon flow. The emissions were bubbled into an HCl solution to trap the ammonia under the form of a water soluble salt NH_4^+Cl^- . The purging was allowed to continue 30 minutes after a stabilization of the polymerization medium at 90 °C. The resulting solution was titrated by an adequate NaOH solution. The amount of NH₃ was determined by the difference between the initial amount of HCl (n_{HCl}) and the HCl titrated (equal to the amount of NaOH at the first pH jump). The polymerization reactions were done twice to validate the reproducibility.

Experimental procedure

General procedure for the synthesis of polyamide-3 and recording of the thermal exotherm

Polyamide-3 was prepared in bulk by anionic polymerization of acrylamide in a glass reactor (see supporting information Figure III-S6). As an example this glass reactor equipped with a magnetic stirrer and a temperature probe was pre-heated and degassed under dynamic dry argon flow. Acrylamide (AAM, 2 g, 28 mmol) was added at 90 °C under dry argon atmosphere. After complete melting of acrylamide in a few minutes and temperature stabilized at 90 °C, solid sodium tert-butoxide (t-BuONa, 27.8 mg, 0.28 mmol) was added to the molten mixture, the polymerization started and temperature was recorded thanks to a temperature probe directly dipped in the melted mixture. After reaction, the polymer obtained was crushed and analysed. Conversion (> 98 %) of the monomer was determined by ^1H NMR and confirmed gravimetrically after washing with a THF reflux. ^1H NMR (400 MHz, HFIP/ D_2O): δ (ppm) 2.3-2.5 (m, 2H, $-(\text{NH}-\text{CH}_2\text{CH}_2(\text{CO}))_n-$), 3.3-3.5 (m, 2H, $-(\text{NH}-\text{CH}_2\text{CH}_2(\text{CO}))_n-$), 7.46 (s, 1H, $-(\text{NH}-\text{CH}_2\text{CH}_2(\text{CO}))_n-$). ^{13}C NMR (HFIP/ D_2O) δ (ppm) = 35.1 ($-(\text{NH}-\text{CH}_2\text{CH}_2(\text{CO}))_n-$), 35.7 ($-(\text{NH}-\text{CH}_2\text{CH}_2(\text{CO}))_n-$), 173.4 ($-(\text{NH}-\text{CH}_2\text{CH}_2(\text{CO}))_n-$). Theoretical \overline{Mn} = 7 100 g/mol and SEC \overline{Mn} = 6 900 g/mol. D = 1.8.

Procedure for the synthesis of polyacrylamide

Polyacrylamide was synthesized by free radical polymerization in solution. Acrylamide (AAM, 1 g, 14 mmol) was dissolved in 14 mL of deionized water and bubbled with dynamic dry argon for 30 min. The reaction mixture was then heated to 55 °C and potassium persulfate (KPS, 12 mg, 0.045 mmol) was added under argon (under the form of a 12 mg/mL water solution previously degassed). After 2 h stirring, the mixture was poured in cold methanol. The polymer was filtered out and dried overnight in an oven at 60 °C. ^1H NMR (400 MHz, D_2O): δ (ppm) 2.45-2.1 (1H, $-(\text{CH}_2\text{CH}(\text{CONH}_2))_n-$), 1.9-1.45 (2H, $-(\text{CH}_2\text{CH}(\text{CONH}_2))_n-$). ^{13}C NMR (D_2O) δ (ppm) = 35.4 ($-(\text{CH}_2\text{CH}(\text{CONH}_2))_n-$), 42.3 ($-(\text{CH}_2\text{CH}(\text{CONH}_2))_n-$), 180.3 ($-(\text{CH}_2\text{CH}(\text{CONH}_2))_n-$).

RESULTS & DISCUSSION

Depending on the polymerization method used, polyacrylamide (PAAm) or polyamide-3 (PA-3) are synthesized from acrylamide using a radical initiator like potassium persulfate (KPS) or an alkali initiator like sodium tert-butoxide (t-BuONa) respectively. Polyacrylamide is characterized by the repeated signals at δ 1.7 and 2.2 ppm assigned to CH_2 and CH groups on its ^1H NMR spectrum. On the contrary, in presence of t-BuONa the formation of polyamide-3 is mainly observed and confirmed by the integration values and the different chemical shifts at δ 2.4 and 3.4 ppm attributed to methylene groups (Figure 1). These chemical shifts are in agreement with those observed in the latest synthesis of polyamide-3 in solution by hydrogen transfer polymerization of acrylamide initiated by t-BuONa under microwaves irradiations[65].

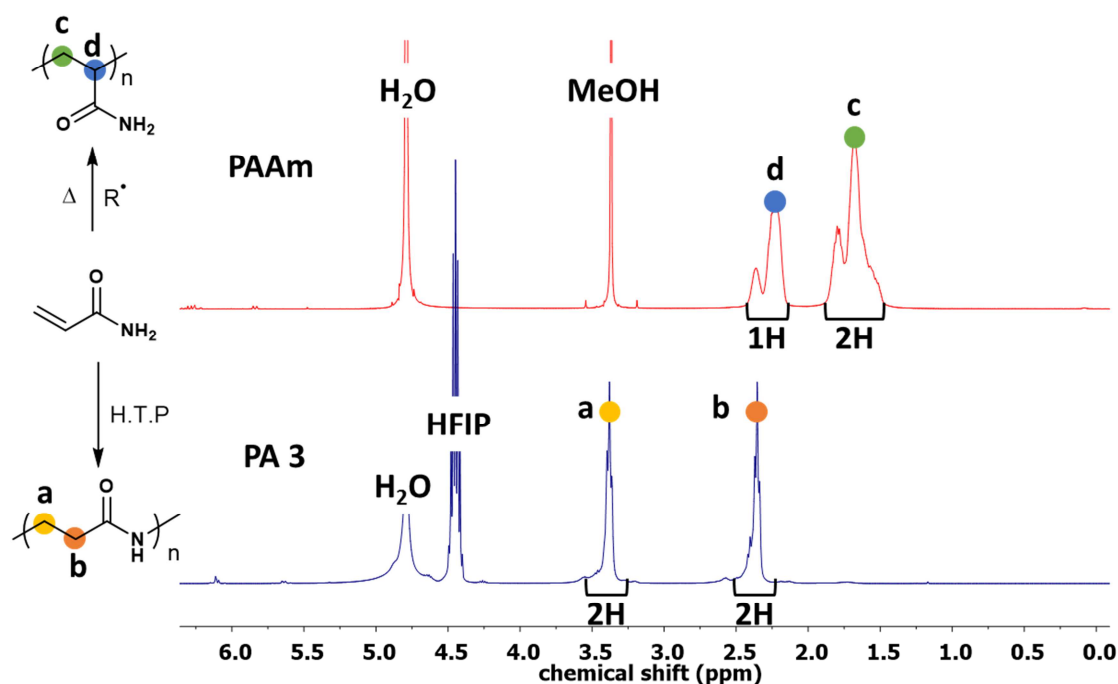


Figure 1 : NMR spectra of polyacrylamide (PAAm, top) and polyamide-3 (PA-3, bottom) using acrylamide as monomer.

Table 1 presents the results obtained by the anionic polymerization of acrylamide in bulk. At first the attempt to control the polymer molar mass by adding N-acetylcaprolactam (NACCLA) as initiator (or activator as referred in polyamide-6 chemistry) was made by changing the ratio $[\text{NACCLA}]_0/[\text{AAm}]_0$ [23]. As shown Table 1 (run 1, 2, 3) no such control was achieved. Only the variation of sodium tert-butoxide amount enabled to influence the molar

mass (runs 4-10 Table 1 and Figure 2). Decreasing this value as compared to the monomer amount enabled to increase the molar mass except for run 11. When t-BuONa amount becomes too low a loss of control is envisaged. This point will be discussed in a following paragraph.

Table 1: Anionic bulk polymerization of acrylamide AAm in the presence of t-BuONa (90°C, conv > 98%)

Run	NAcCLA %mol	t-BuONa %mol	Time (min)	%branching ^a	%PAAm ^a	\overline{Mn}_{calcd} (g/mol)	\overline{Mn}_{exp}^b (g/mol)	\overline{D}^b
1	2.8	5	< 5	2.5	7.5	2 500 ^c	4 000	3.2
2	1.4	5	< 5	5	10	5 000 ^c	2 200	3.4
3	0.7	5	< 5	3.7	7.5	10 000 ^c	2 000	3.4
4	-	10	< 5	5	12	710 ^d	1 600	3.6
5	-	5	< 5	3.7	7.5	1 420 ^d	1 800	3.5
6	-	2.5	< 5	3.5	5	2 840 ^d	2 200	3.5
7	-	2	< 5	3	5	3 550 ^d	3 300	3.1
8	-	1	< 5	3.5	2	7 100 ^d	6 900	1.8
9	-	0.5	< 5	3	3	14 200 ^d	9 700	1.8
10	-	0.25	< 15	6	1.5	28 400 ^d	23 600	2.3
11	-	0.125	< 20	11	< 1	56 900 ^d	4 400	3.1

^aDetermined by NMR: %branching = $(I_a/4)/(I_a/4 + I_b/2)$, %PAAm = acrylamide units = $I_c/(I_c + I_a)$, ^bdetermined by SEC (PMMA calibration), ^c $\overline{Mn}_{calcd} = ([AAm]_0/[NacCLA]_0 \times M_{AAm}) \times \text{conv.}$ ^d $\overline{Mn}_{calcd} = ([AAm]_0/[t\text{-BuONa}]_0 \times M_{AAm}) \times \text{conv.}$

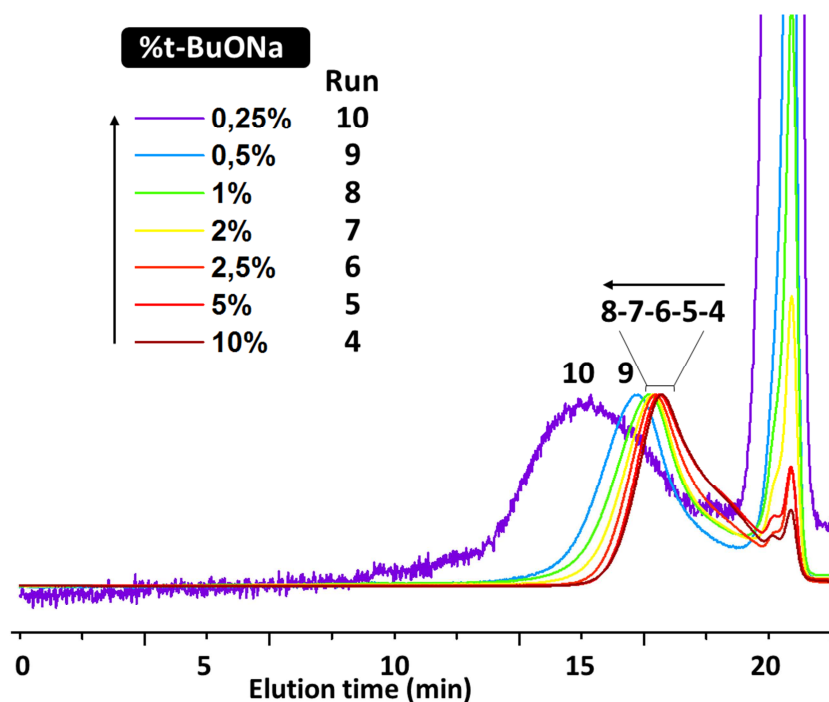


Figure 2: SEC traces of polyamide-3 depending on the amount of t-BuONa, UV detector

The MALDI TOF analysis performed on a PA-3 sample (run 8, Table 1) shows one main population attributed to terminations with a double bond and a hydrogen.

$$P1 = 733.5 \text{ g/mol} = M_{Na} + M_{C_3H_4NO} + n \times M_{C_3H_5NO} + M_H \quad (n = 9).$$

The monomer deprotonation is first envisaged as no initiation by tert-butoxide is observed on the spectrum. This first result agrees with the one obtained by Matlack and coll. as an olefinic end group was found in the polymer[55] but also contrasts with Ogata's mechanism[58] or the result obtained by Tani et al. where a t-butyl group was observed as a chain end[59].

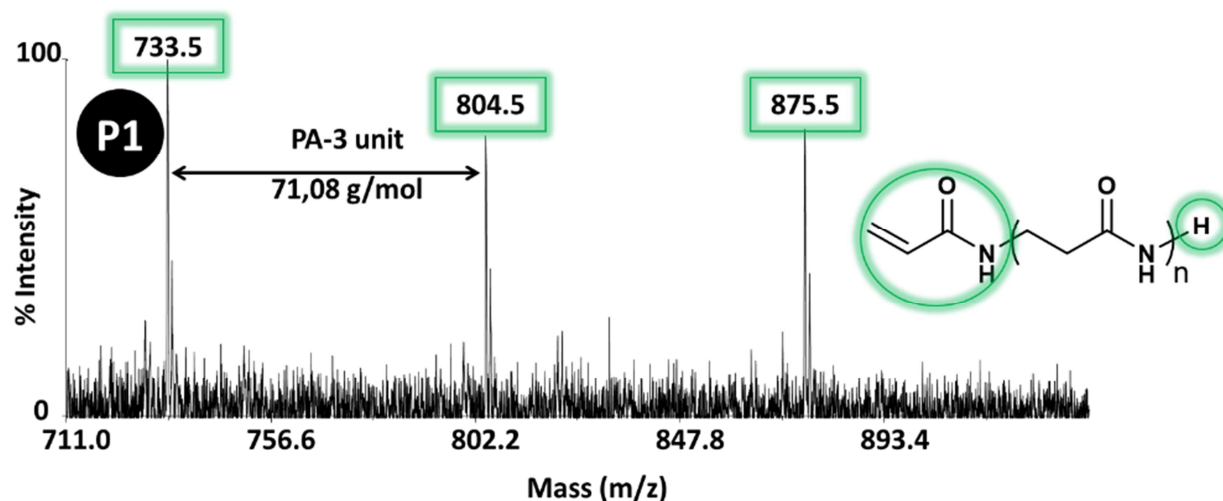
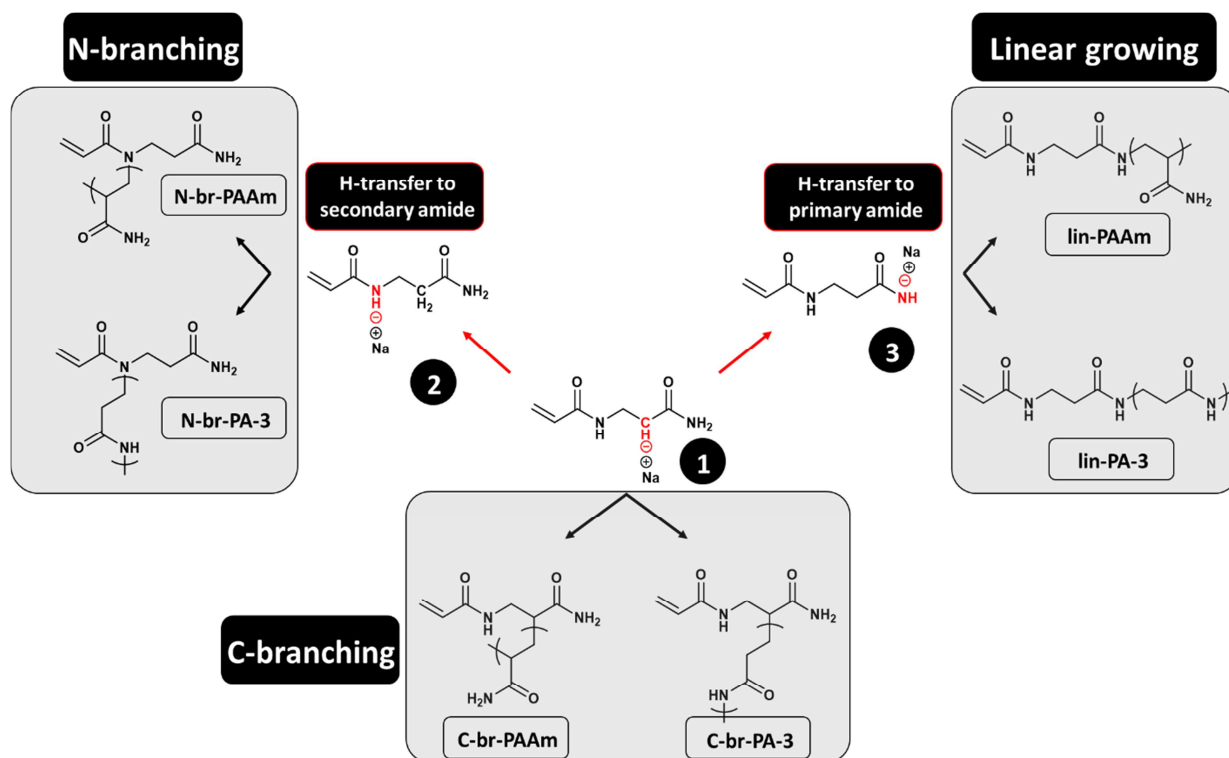


Figure 3: Enlarged MALDI-TOF spectrum of polyamide-3 obtained from acrylamide (run 8, Table 1).

Based on this first indication, different kinds of propagation can be envisaged once an anion is formed. The addition of a deprotonated acrylamide to another monomer first occurs forming intermediate 1 (Scheme 1). Thus, intermediates 2 and 3 can also be generated by hydrogen transfer to the secondary or primary amide. C-branching, N-branching as well as linear growing are expected. In each case, polyacrylamide units (PAAm) or polyamide-3 units (PA-3) can be envisaged.



Scheme 1: Possible hydrogen-transfer and propagation reactions from the intermediate 1

The polymer structure was further investigated by HSQC ($^1\text{H}/^{13}\text{C}$) NMR analysis (Figure 4) showing a correlation map between the ^1H and ^{13}C DEPT 135 spectra of the same polyamide-3 sample (run 8, Table 1). This map obtained without any purification of the polymer enables to calculate the monomer conversion, the percentage of polyacrylamide units, and branching to propose a polymer structure. In analogy to the initial ^1H NMR spectrum, the two broad proton signals at 2.4 and 3.4 ppm are attributed to the main carbon signals between 34 and 36 ppm corresponding exclusively to secondary carbon CH_2 . The backbone is mainly composed of PA-3 units. The presence of acrylamide units is shown by the correlation between PAAm proton signals at 1.7 and 2.2 ppm with secondary (CH_2) and tertiary (CH) carbon signals of low intensity at 24.7 and 45.3 ppm. This single distinguishable tertiary carbon signal (CH) on the DEPT135 spectrum being attributed, we therefore discriminate or consider as very low contribution any form of branching from the carbanion of the intermediate 1 which would have also given a CH signal on this spectrum if present. Meaning that and depending on the chemical shift of the remaining CH_2 at 32 ppm and around 43 ppm, those signals are attributed to branched PA-3 units from secondary amide (N-br-PA-3) which correlate to proton signals b' and a' at 2.6 and 3.5 ppm respectively. This

last result reminds a previous work of Applequist and coll. who reported the chain branching in poly- β -alanine from acrylamide polymerization[8]. Their work done in solution concluded to the presence of short branches along a rather extended backbone and suggested that branch growth was initiated during polymerization by the formation of secondary amide anions on the polymer chain. The envisaged polymer structure is so drawn on the 2D map (Figure 4).

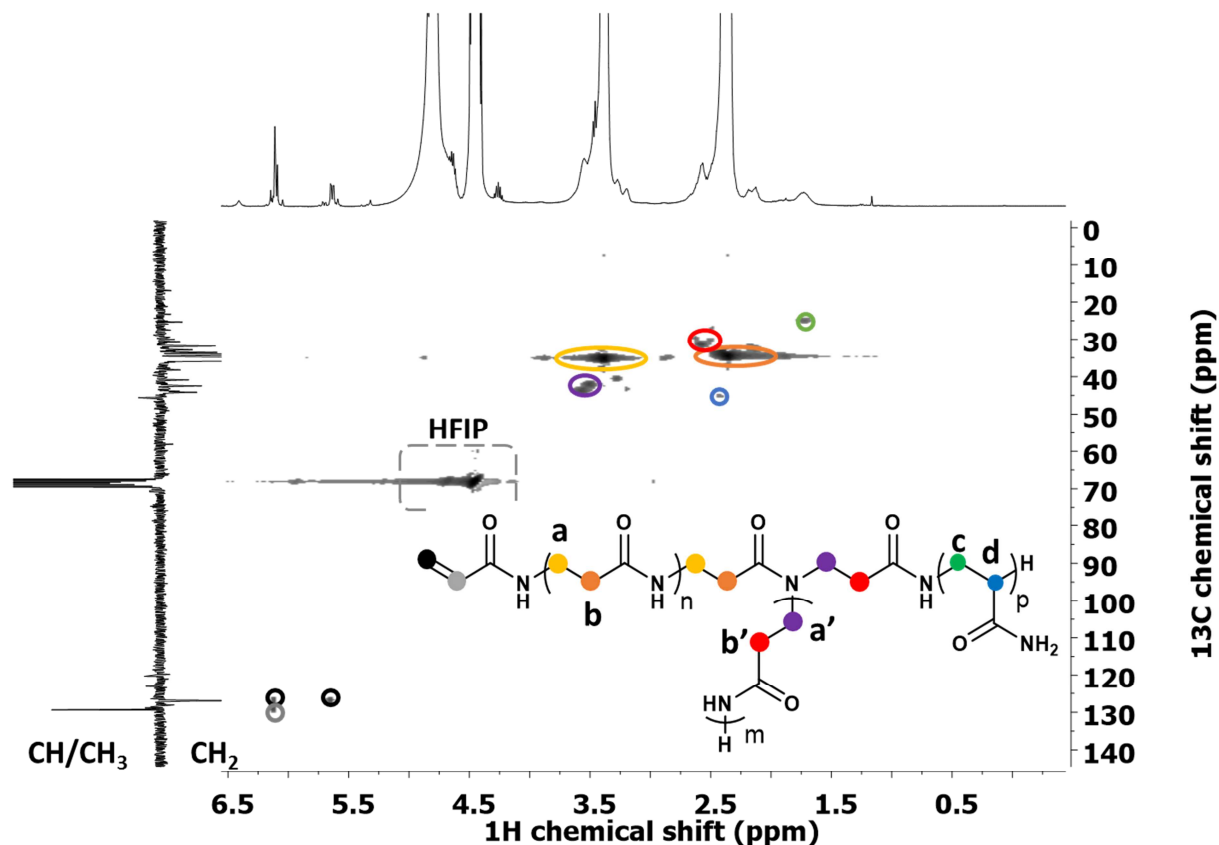


Figure 4: 2D ($^1\text{H}/^{13}\text{C}$ DEPT135) HSQC NMR spectrum of polyamide-3 (run 8, Table 1)

The compilation of the different ^1H NMR spectra of polyamide-3 with different amount of t-BuONa (Figure 5) enables to establish a correlation between the evolution of PAAm and N-br-PA-3 units present. Indeed, as it can be observed at 1.7 ppm, the polyacrylamide content tends to disappear in favor of the branched units at 2.6 and 3.5 ppm when decreasing the amount of base. This observation is also in agreement with the carbon NMR spectra where the signal of a' (43 ppm), b' (32 ppm) and their corresponding carbonyl group (176.5 ppm) are increased for a lower amount of t-BuONa (see supporting information Figure III-S1). Even if a molar mass dependance was observed with the ratio $[\text{AAm}]/[\text{t-BuONa}]$ a limit is observed

with a higher ratio. It was not possible to get molar masses higher than 23 000 – 26 000 g/mol and the dispersity was shown to broaden (Table 1). Based on these results this limitation could be explained by the much higher percentage of branching in these experimental conditions (Table 1). A decrease of the t-BuONa amount disfavoured the monomer deprotonation. As no tert-butoxide group is linked to the polymer chains, t-BuONa can still act as a non nucleophilic base thanks to the proposed equilibrium based on the intermediate 1 previously described (Scheme 1). Consequently, when decreasing t-BuONa amount, it is suggested that this equilibrium is less present and tend to limit the deprotonation reaction in favour of the branching one (Scheme 2).

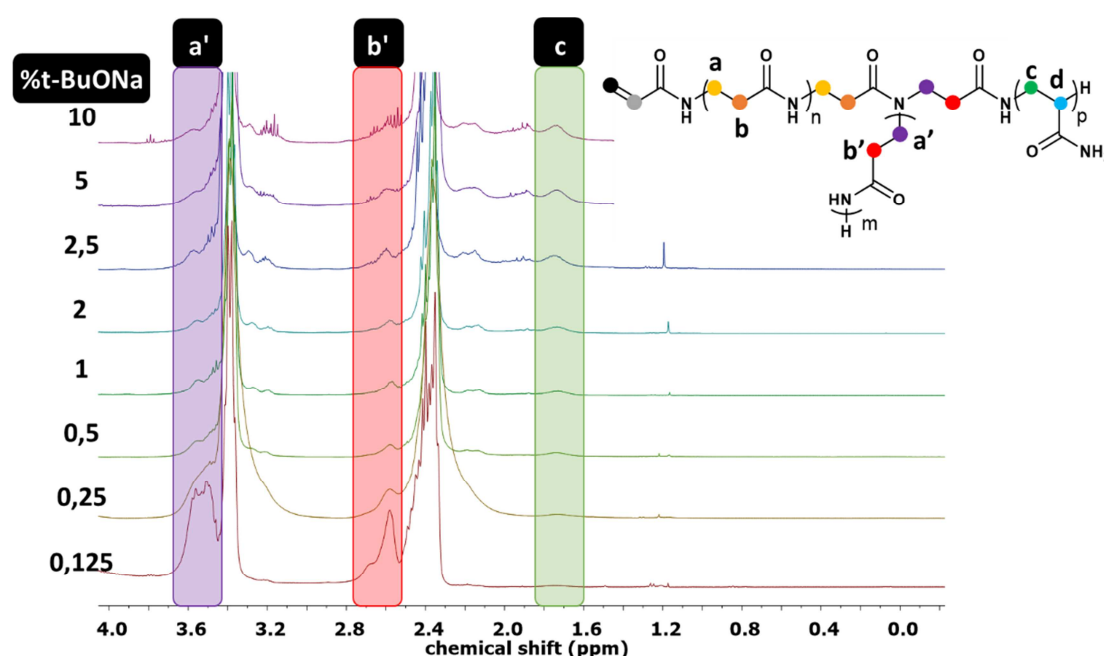
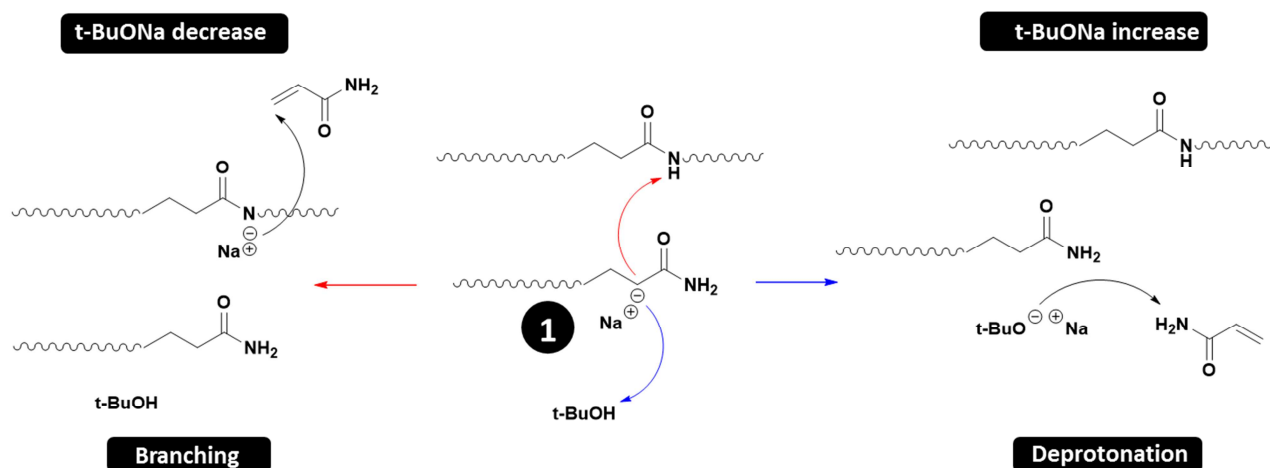


Figure 5: Superposition of ^1H NMR, zoom on the polymer signals, evidence of branching and acrylamide units. (top to bottom run 4 to 11, Table 1)



Scheme 2: Branching or deprotonation reaction depending on $t\text{-BuONa}$ amount

Thanks to the thermal probe directly dipped in the melted acrylamide, it was possible to record the exotherm of the polymerization reaction immediately triggered by the base addition. The Figure 6 represents the thermal evolution of the reaction medium in function of the polymerization time. Only appear the results for runs 7 to 11 (Table 1) corresponding to a $t\text{-BuONa}$ amount from 2 to 0.125 mol%. Traces obtained with higher base amounts are omitted for clarity as their profiles are similar to the one obtained with 2 mol% of base. One can note that the bulk anionic polymerization of acrylamide is highly exothermic with a maximal temperature of 275 °C which is reached in a few seconds. The amount of base affects clearly the exothermy and time of the reaction as the polymerization is slowing down when decreasing the $t\text{-BuONa}$ amount, and therefore the active species.

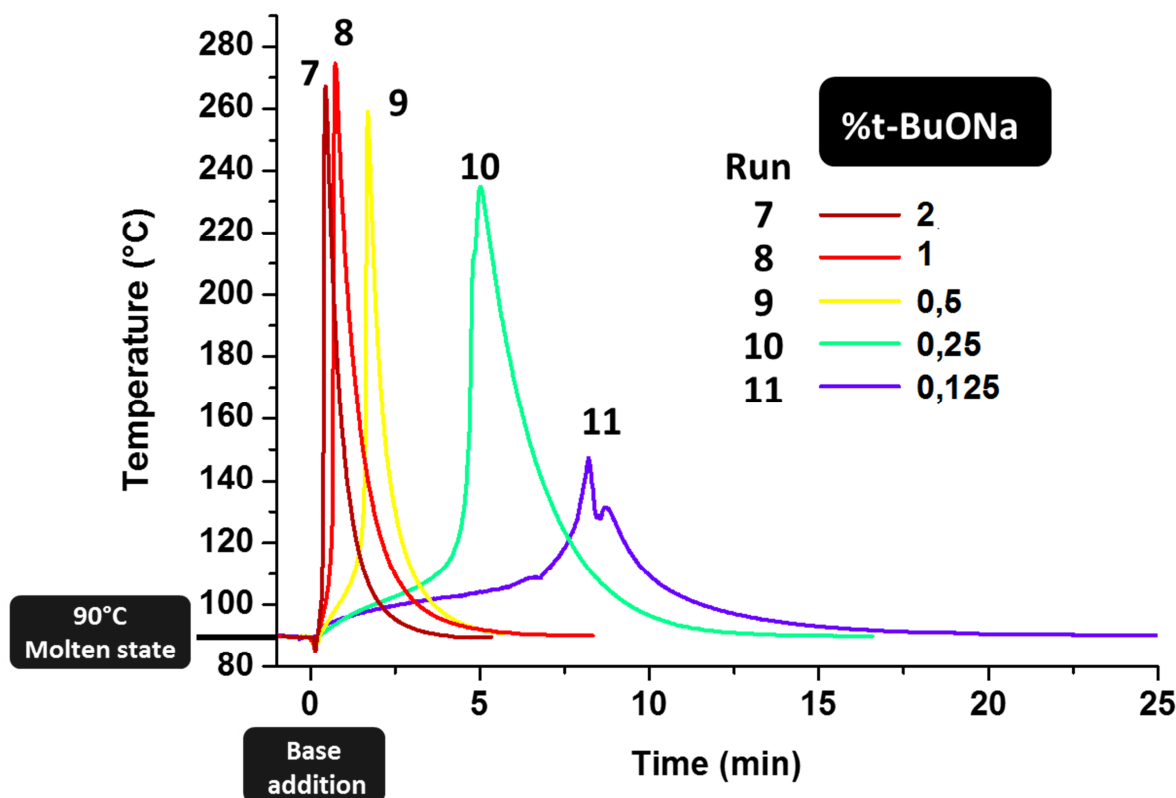
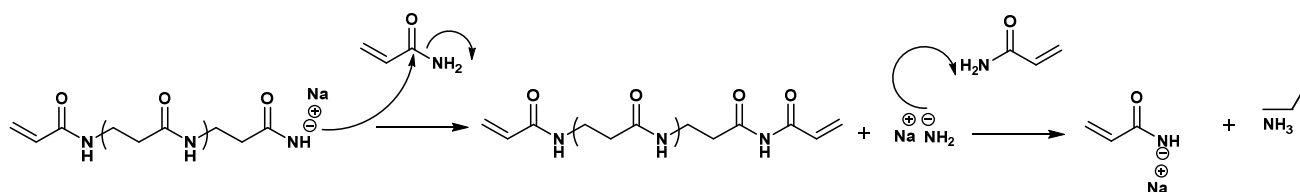


Figure 6: Temperature/time diagram of the bulk anionic polymerization of acrylamide initiated by t-BuONa

The formation of imide bond in the AROP of lactams is a common side reaction known to limit the concentration of active species and causing low conversions.[23] Such a reaction can also be expected here and resulting by ammonia emissions as a gaseous by-product (Scheme 3). Released under the form of sodium amide NaNH_2 , this reaction may not induce chain termination because of the formation of species still active in polymerization such as amide anion or terminal activated double bond. Sodium amide being a strong base it is therefore involved in a deprotonation reaction leading to the formation of gaseous ammonia. The evidence of such emissions was demonstrated by an acido-basic titration of the polymerization atmosphere. The pH measurements show two pH jumps in function of the NaOH volume (see supporting information Figure III-S2). This indicates the presence of two acid species. The first jump is attributed to the reaction between NaOH and the excess of HCl and the second one to the reaction between NaOH and the trapped ammonia under the form of ammonium chloride NH_4^+Cl^- . But it is difficult to assume that the amount of t-BuONa influences the imide formation. Indeed for 10%, 2.5% and 1% tBuONa the percentage

of NH_3 is very low and equal to 1.2mol%, 0.8mol% and 0.6mol% respectively. In addition, the formation of NH_3 may also come from a degradation reaction[92,93] of the produced polymer as high internal temperature is reached during the polymerization.



Scheme 3: Proposed mechanism for the formation of gaseous ammonia

The thermo-gravimetric analysis of all PA-3 samples gave thermograms which agree with a decrease of the PAAm content in the synthesized polyamide-3 when decreasing the t-BuONa amount as demonstrated earlier (Figure 7). With a high base content 2 degradations are observed (e.g. run 4) and tend to a unique one (e.g. run 11). This thermal behavior corroborates also mainly PA-3 structures. The main degradation temperature is so shifted from 300 °C to 357 °C and the minor signal disappears (see supporting information Figure III-S3 and III-S4). This main temperature is in agreement with the referenced degradation of PA-3[6]. DSC measurement indicate T_g values up to 88 °C with a slight shift depending on the t-BuONa amount (see supporting information Figure III-S5). These values contrast with the one obtained by Zhang and coll. [2] ($T_g = 126$ °C) where they gave evidences of a linear polyamide-3 structure obtained by anionic ring-opening polymerization of β -propiolactam. Despite a higher T_g for PAAm (178 °C[3]) the branching observed can explain the lower T_g values measured on the synthesized PA-3 materials. As also referenced, no melting of the polymer was observed as it is concomitant with the thermal decomposition[8].

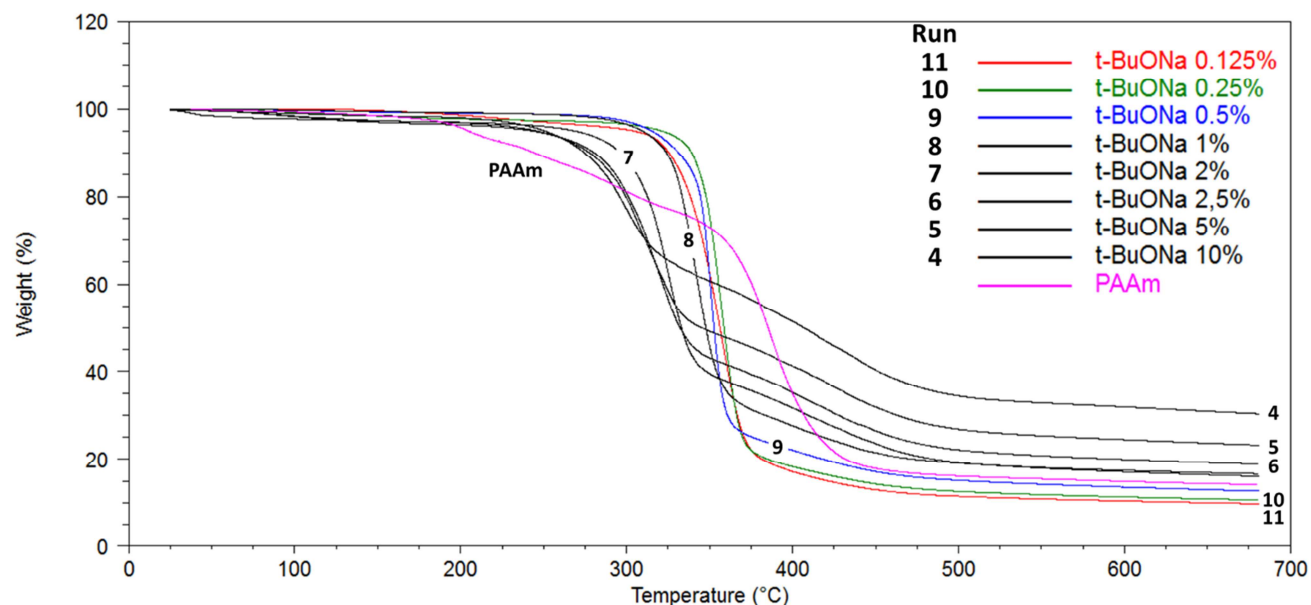
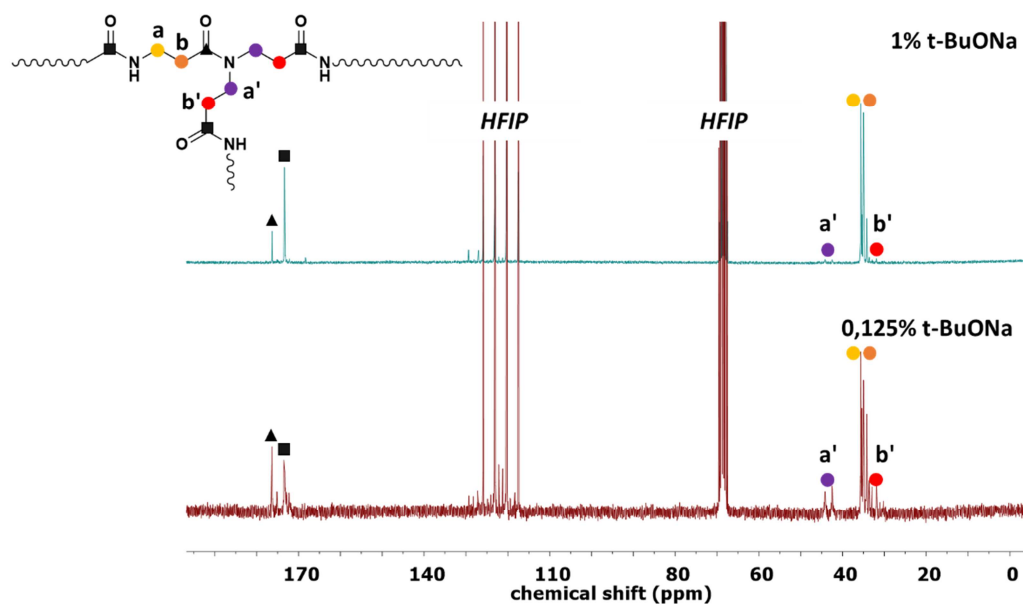
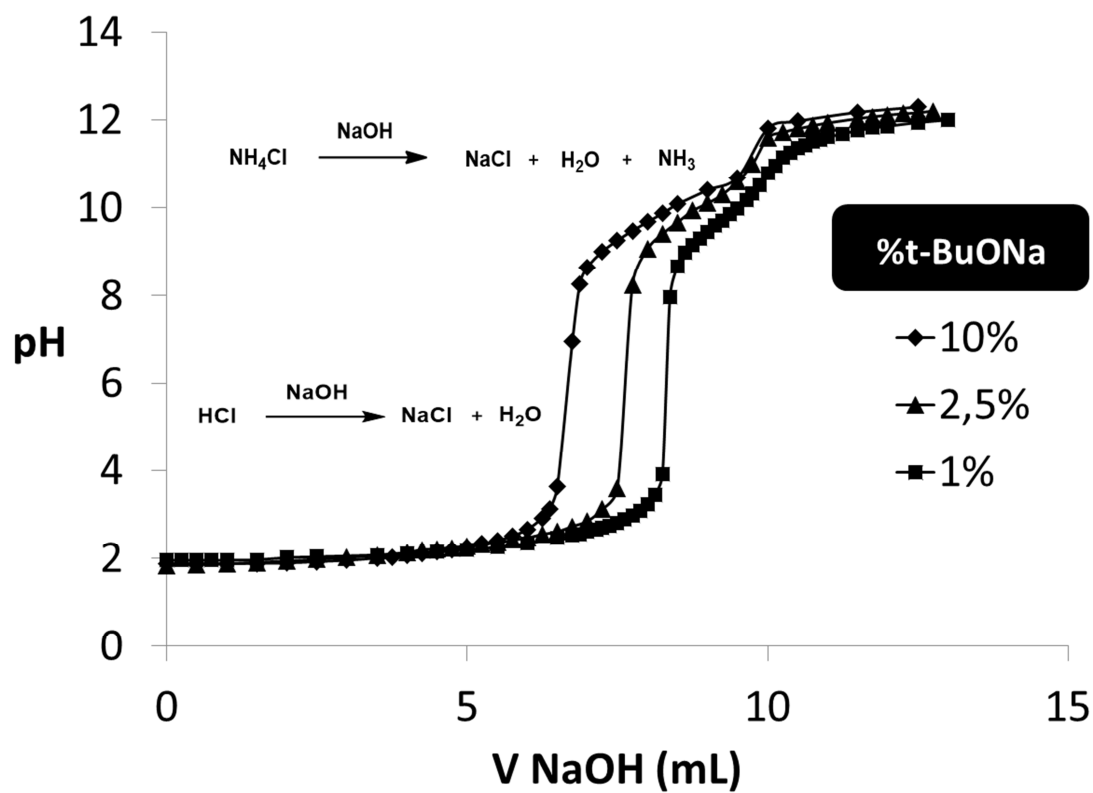


Figure 7: TGA thermograms of polyamide-3 in function of the t-BuONa amount (run 4 to 11, Table 1) compared to polyacrylamide

CONCLUSION

The anionic polymerization of acrylamide was carried out in bulk conditions with t-BuONa as initiator. Several polyamides-3 were synthesized in few minutes in this solvent free process. Despite all the possible reaction pathways presented, t-BuONa was shown to trigger the polymerization reaction but also to control the molar mass up to 23 000 g/mol. The so-formed polymers were shown to have different percentage of branching from 2.5 to 11 % and polyacrylamide content from 12 to 1 % depending on the base amount. This study therefore suggests that the propagation could either occurs by poly(Mikael addition) through the terminal amide or by nucleophilic attack on a terminal activated double bond with subsequent deprotonation reactions. The degradation temperature was shown to be more dependent on the polyacrylamide content than on the amount of branching. Those polyamides-3 exhibit glass transition temperatures in the range 80-90 °C higher than the polyamide-6 one.

SUPPORTING INFORMATION

Figure III-S1: Superposition of ^{13}C NMR spectra of polyamide-3 samples (run 8 and 11 Table 1)Figure III-S2: Evolution of the pH jumps in function of the $t\text{-BuONa}$ amount

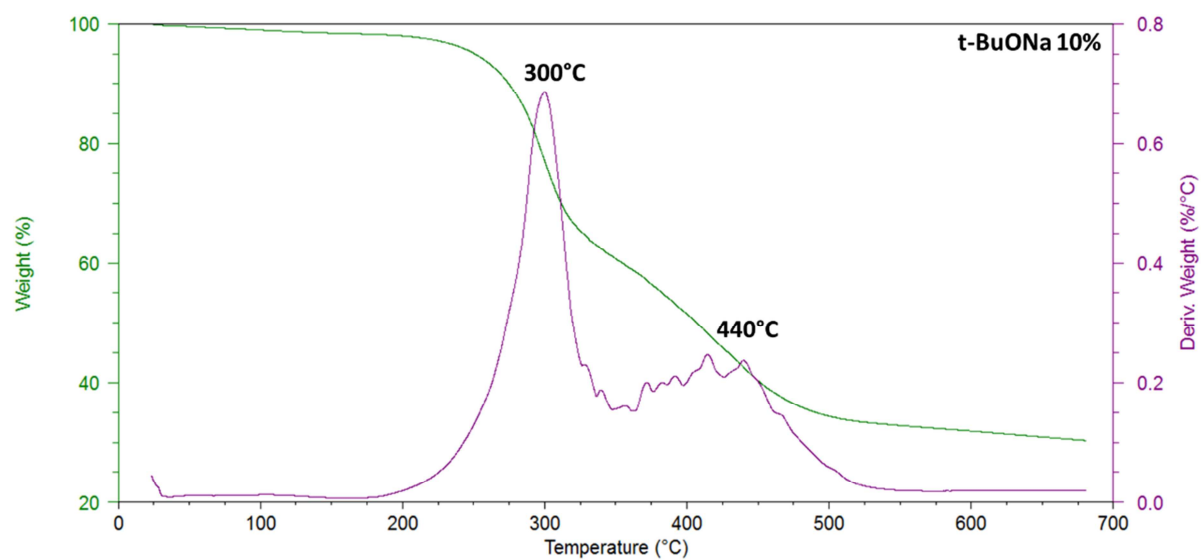


Figure III-S3: TGA thermogram of polyamide-3 run 4 Table 1

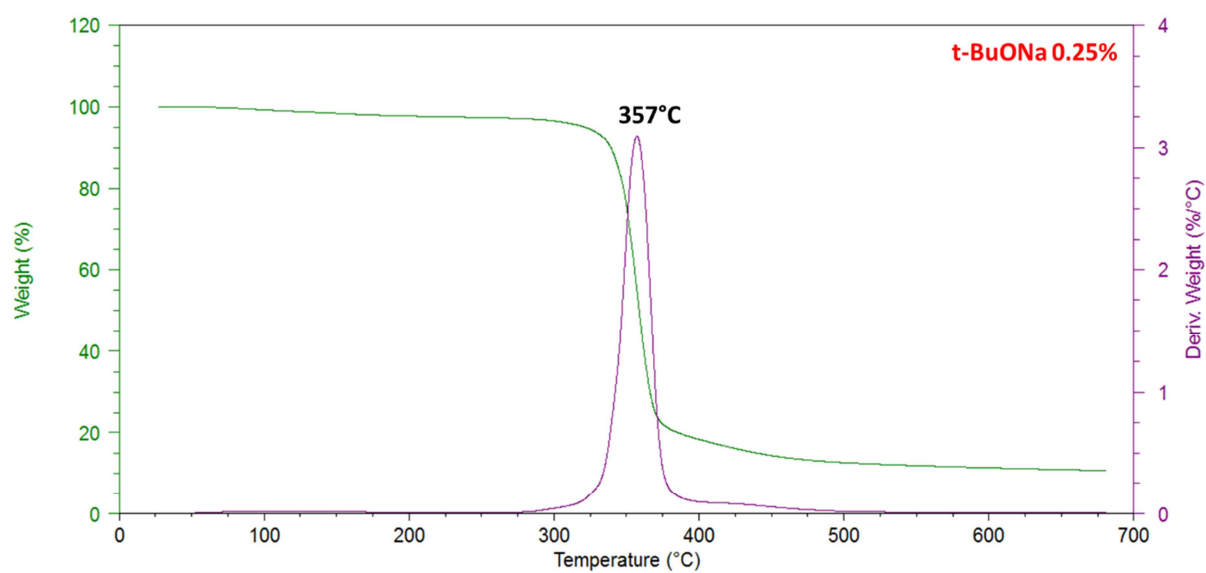


Figure III-S4: TGA thermogram of polyamide-3 run 10 Table 1

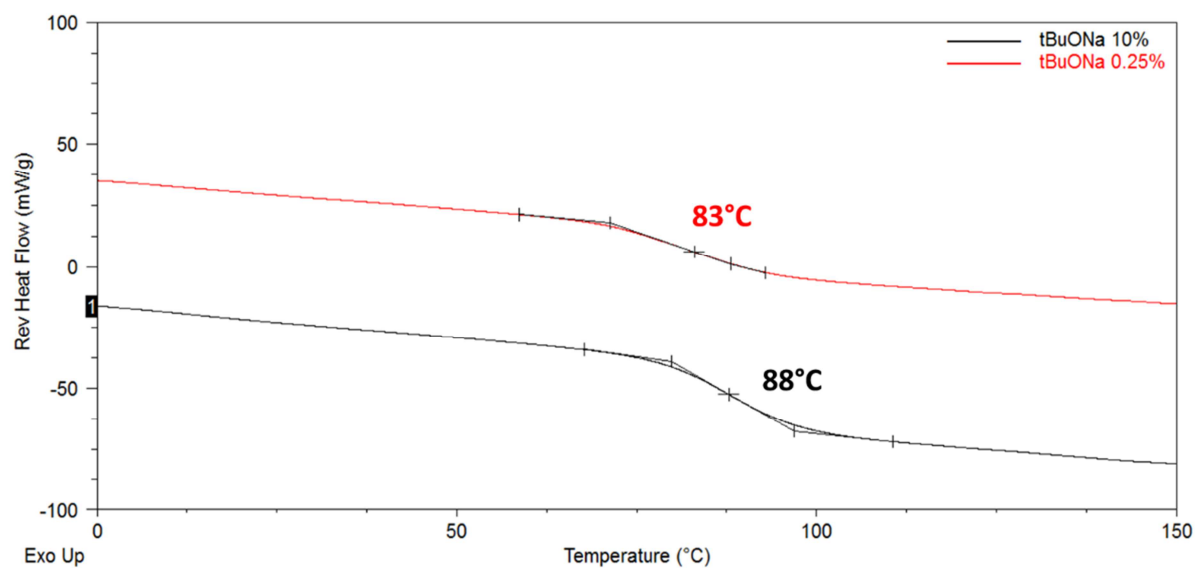


Figure III-S5: DSC thermograms of PA-3 (run 4 and 10, Table 1)

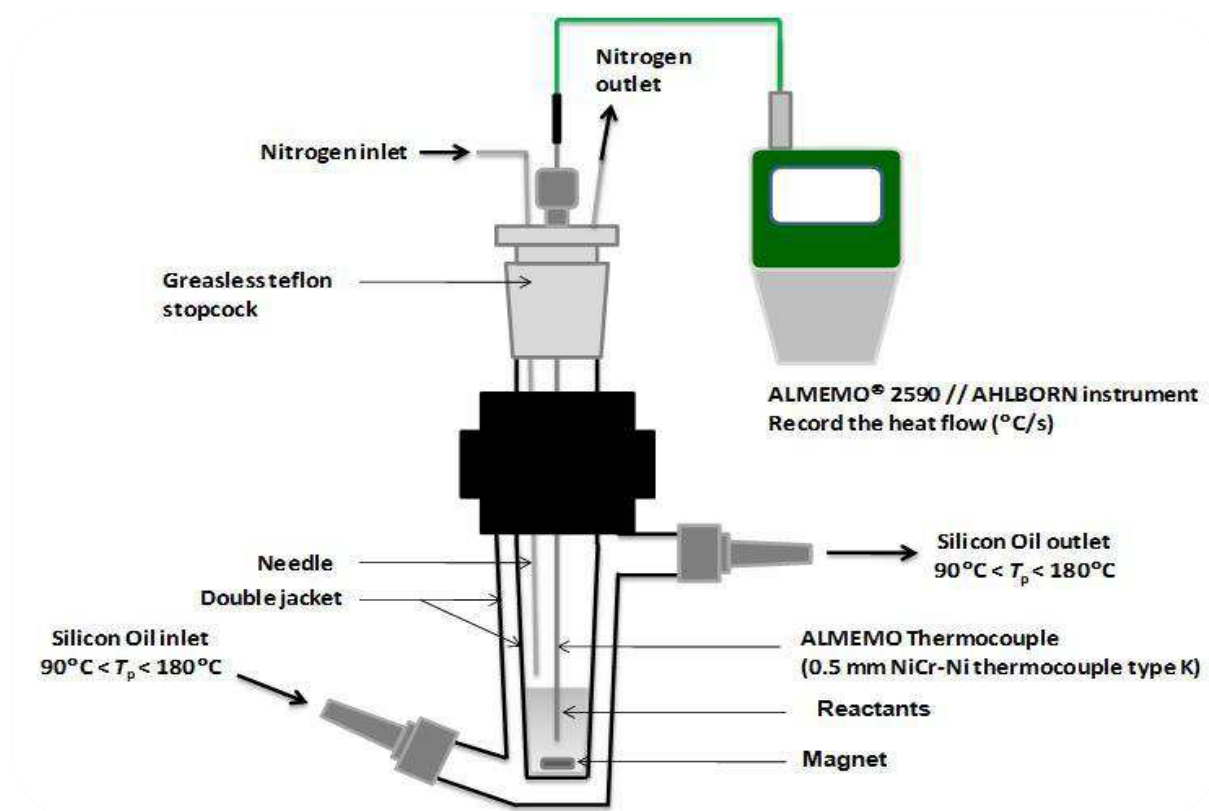


Figure III-S6: Reactor used for the anionic bulk polymerization of acrylamide equipped with a thermal probe.

REFERENCES

1. Wexler, H. Migrational polymerization of methacrylamide. *Die Makromol. Chemie* **1968**, *115*, 262–267.
2. Yang, H.; Zhao, J.; Yan, M.; Pispas, S.; Zhang, G. Nylon 3 synthesized by ring opening polymerization with a metal-free catalyst. *Polym. Chem.* **2011**, *2*, 2888–2892.
3. Morgenstern, U.; Berger, W. Studies on polyamide 3 — synthesis, characterization and properties. *Die Makromol. Chemie* **1992**, *193*, 2561–2569.
4. Masamoto, J.; Sasaguri, K.; Ohizumi, C.; Yamaguchi, K.; Kobayashi, H. A new synthetic fiber made of nylon 3. *J. Appl. Polym. Sci.* **1970**, *14*, 667–680.
5. Masamoto, J.; Sasaguri, K.; Ohizumi, C.; Kobayashi, H. Polymorphic forms of nylon 3. *J. Polym. Sci. Part A-2 Polym. Phys.* **1970**, *8*, 1703–1711.
6. Masamoto, J. Nylon 3. *Mem. Fukui Univ. Technol.* **2003**, *33*, 291–296.
7. Muñoz-Guerra, S.; Fernandez-Santin, J. M.; Rodriguez-Galan, A.; Subirana, J. a Structural studies on the polymorphism of nylon 3. *J. Polym. Sci. Polym. Phys. Ed.* **1985**, *23*, 733–742.
8. Glickson, J. D.; Applequist, J. Chain Branching in Poly- β -alanine. *Macromolecules* **1969**, *2*, 628–634.
9. Itagaki, T.; Komori, Y.; Sugahara, Y.; Kuroda, K. Synthesis of a kaolinite–poly(β -alanine) intercalation compound. *J. Mater. Chem.* **2001**, *11*, 3291–3295.
10. Lee, M. W.; Chakraborty, S.; Schmidt, N. W.; Murgai, R.; Gellman, S. H.; Wong, G. C. L. Two interdependent mechanisms of antimicrobial activity allow for efficient killing in nylon-3-based polymeric mimics of innate immunity peptides. *Biochim. Biophys. Acta* **2014**, *1838*, 2269–2279.
11. Deshayes, G.; Delcourt, C.; Verbruggen, I.; Trouillet-Fonti, L.; Touraud, F.; Fleury, E.; Degée, P.; Destarac, M.; Willem, R.; Dubois, P. Activation of the hydrolytic polymerization of ϵ -caprolactam by ester functions: Straightforward route to aliphatic polyesteramides. *React. Funct. Polym.* **2008**, *68*, 1392–1407.
12. Zhang, S.; Dias Goncalves, L.; Lefebvre, H.; Tessier, M.; Rousseau, B.; Fradet, A. Direct Poly(β -alanine) Synthesis via Polycondensation in Ionic Liquids. *ACS Macro Lett.* **2012**, *1*, 1079–1082.
13. Vygodskii, Y. S.; Lozinskaya, E. I.; Shaplov, A. S. Ionic Liquids as Novel Reaction Media for the Synthesis of Condensation Polymers. *Macromol. Rapid Commun.* **2002**, *23*, 676–680.
14. Mallakpour, S.; Taghavi, M. Direct polyamidation in green media: Studies on thermal degradation of novel organosoluble and optically active flame retardant polyamides. *React.*

Funct. Polym. **2009**, 69, 206–215.

15. Mallakpour, S.; Kowsari, E. Ionic liquids as novel solvents and catalysts for the direct polycondensation of N,N'-(4,4'-oxydipthaloyl)-bis-L-phenylalanine diacid with various aromatic diamines. *J. Polym. Sci. Part A Polym. Chem.* **2005**, 43, 6545–6553.

16. Lozinskaya, E. I.; Shaplov, A. S.; Vygodskii, Y. S. Direct polycondensation in ionic liquids. *Eur. Polym. J.* **2004**, 40, 2065–2075.

17. Ali Mohamed, A.; Salhi, S.; Abid, S.; El Gharbi, R.; Fradet, A. Random and quasi-alternating polyesteramides deriving from ϵ -caprolactone and β -alanine. *Eur. Polym. J.* **2014**, 53, 160–170.

18. Steunenbergh, P.; Könst, P. M.; Scott, E. L.; Franssen, M. C. R.; Zuilhof, H.; Sanders, J. P. M. Polymerisation of β -alanine through catalytic ester–amide exchange. *Eur. Polym. J.* **2013**, 49, 1773–1781.

19. Puffr, R.; Kubanek, V. Lactam-based polyamides, vol 1. *CRC Press* **1991**.

20. Reimschuessel, H. K. Nylon 6. Chemistry and mechanisms. *J. Polym. Sci. Macromol. Rev.* **1977**, 12, 65–139.

21. Sebenda, J. Comprehensive Chemical Kinetics Elsevier, Amsterdam. Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier **1976**, 15, 379.

22. Sekiguchi, H. Ring-Opening Polymerization. *J., Saegusa, T., Eds.; Elsevier London UK* **1984**, Vol 2, 809.

23. Hashimoto, K. Ring-opening polymerization of lactams. Living anionic polymerization and its applications. *Prog. Polym. Sci.* **2000**, 25, 1411–1462.

24. Bernášková, A.; Chromcová, D.; Brožek, J.; Roda, J. Polymerization of lactams, 95 Preparation of polyesteramides by the anionic polymerization of ϵ -caprolactam in the presence of poly(ϵ -caprolactone). *Polymer (Guildf)*. **2004**, 45, 2141–2148.

25. Russo, S.; Casazza, E. Polymer Science: A Comprehensive Reference. *Matyjaszewski, K., Möller, M., Eds.; Elsevier Amsterdam* **2012**, 331–396.

26. Carlotti, S.; Peruch, F. Cyclic Monomers: Epoxides, Lactide, Lactones, Lactams, Cyclic Silicon containing monomers, Cyclic Carbonates and others in Anionic Polymerization - Principles, Practice, Strength, Consequences and Applications. *Hadjichristidis, N., Hirao, A., Eds Springer* **2015**.

27. Šebenda, J. Lactam Polymerization. *J. Macromol. Sci. Part A - Chem.* **1972**, 6, 1145–1199.

28. Šittler, E.; Šebenda, J. Alkaline polymerization of 6-caprolactam. XXXII. The kinetics of polymerization activated by N,N,N',N'-tetraacetylhexamethylenediamine. *Collect.*

Czechoslov. Chem. Commun. **1968**, *33*, 270–277.

29. Russo, S.; Biagini, E.; Bonta, G. Novel synthetic approaches to poly(ϵ -caprolactam)-based materials. *Makromol. Chemie. Macromol. Symp.* **1991**, *48-49*, 31–46.

30. Sekiguchi, H.; Tsourkas, P. R.; Coutin, B. Anionic polymerization of α -pyrrolidone and α -piperidone using their quaternary ammonium salts as catalysts. *J. Polym. Sci. Polym. Symp.* **1973**, *42*, 51–61.

31. Huisgen, R.; Brade, H.; Walz, H.; Glogger, I. Mittlere Ringe, VII. Die Eigenschaften Aliphatischer Lactame und Diecis-trans-Isomerie der Säureamidgruppe. *Chem. Ber.* **1957**, *90*, 1437–1447.

32. Mougin, N.; Rempp, P.; Gnanou, Y. New activating agents for the anionic polymerization of lactams. *Macromolecules* **1992**, *25*, 6739–6743.

33. Mougin, N.; Rempp, P.; Gnanou, Y. Synthesis and characterization of polysiloxane–polyamide block and graft copolymers. *J. Polym. Sci. Part A Polym. Chem.* **1993**, *31*, 1253–1260.

34. Daniel, L.; Brožek, J.; Roda, J.; Křilíček, J. Polymerization of lactams, 52. Anionic polymerization of 2-pyrrolidone accelerated with CO₂, part 1. *Die Makromol. Chemie* **1982**, *183*, 2719–2729.

35. Hu, G.-H.; Li, H.; Feng, L.-F. Follow-up of the course of the anionic ring-opening polymerization of lactams onto an isocyanate-bearing polymer backbone in the melt. *J. Appl. Polym. Sci.* **2006**, *102*, 4394–4403.

36. Petit, D.; Jerome, R.; Teyssie, P. Anionic block copolymerization of ϵ -caprolactam. *J. Polym. Sci. Polym. Chem. Ed.* **1979**, *17*, 2903–2916.

37. Merna, J.; Chromcová, D.; Brožek, J.; Roda, J. Polymerization of lactams: 97. Anionic polymerization of ϵ -caprolactam activated by esters. *Eur. Polym. J.* **2006**, *42*, 1569–1580.

38. Roda, J.; Brožek, J.; Křilíček, J. Polymerization of lactams, 37. Isolation and characterization of alkali carboxylates of 2-pyrrolidone. *Die Makromol. Chemie, Rapid Commun.* **1980**, *1*, 165–169.

39. Dybal, J.; Schneider, B.; Doskočilová, D.; Baldrian, J.; Pavlíková, H.; Kvarda, J.; Prokopová, I. Spectral and structural characterization of a cyclic trimeric model of poly(6-hexanelactam). *Polymer (Guildf)*. **1997**, *38*, 2483–2491.

40. Carlo Alfonso, G.; Cirillo, G.; Russo, S.; Turturro, A. Adiabatic polymerisation of ϵ -caprolactam in presence of calcium chloride. Thermodynamic and kinetic aspects. *Eur. Polym. J.* **1983**, *19*, 949–953.

41. Greenberg, A.; Hsing, H.-J.; Liebman, J. F. Aziridinone and 2-azetidinone and their

protonated structures. An ab initio molecular orbital study making comparisons with bridgehead bicyclic lactams and acetamide. *J. Mol. Struct. THEOCHEM* **1995**, 338, 83–100.

42. Šebenda, J.; Hauer, J. Living polymerization of lactams and synthesis of monodisperse polyamides. *Polym. Bull.* **1981**, 5-5, 529–534.

43. Šebenda, J.; Hauer, J.; Svetlik, J. An unusual kinetics of anionic polymerization of four-membered lactams. *J. Polym. Sci. Polym. Symp.* **1986**, 74, 303–310.

44. Hashimoto, K.; Hotta, K.; Okada, M.; Nagata, S. Synthesis of Monodisperse Polyamides by living Anionic Polymerization of β -Lactams in the Mixture of N, N-Dimethylacetamide and Lithium Chloride. *J. Polym. Sci. Part A Polym. Chem.* **1995**, 33, 1995–1999.

45. Hashimoto, K.; Oi, T.; Yasuda, J.; Hotta, K.; Okada, M. Molecular weight distribution of polyamides obtained in anionic polymerization of methyl-substituted β -lactams and aminolysis of their N-benzoyl lactams. *J. Polym. Sci. Part A Polym. Chem.* **1997**, 35, 1831–1838.

46. Hashimoto, K.; Yasuda, J.; Kobayashi, M. Proton transfer-controlled anionic polymerization of methyl-substituted β -lactams with potassium t-butoxide and subsequent coupling reaction with saccharides. *J. Polym. Sci. Part A Polym. Chem.* **1999**, 37, 909–915.

47. Zhang, J.; Gellman, S. H.; Stahl, S. S. Kinetics of Anionic Ring-Opening Polymerization of Variously Substituted β -Lactams: Homopolymerization and Copolymerization. *Macromolecules* **2010**, 43, 5618–5626.

48. Zhang, J.; Markiewicz, M. J.; Weisblum, B.; Stahl, S. S.; Gellman, S. H. Functionally Diverse Nylon-3 Copolymers from Readily Accessible β -Lactams. *ACS Macro Lett.* **2012**, 1, 714–717.

49. Zhang, J.; Markiewicz, M. J.; Mowery, B. P.; Weisblum, B.; Stahl, S. S.; Gellman, S. H. C-terminal functionalization of nylon-3 polymers: effects of C-terminal groups on antibacterial and hemolytic activities. *Biomacromolecules* **2012**, 13, 323–331.

50. Liu, R.; Chen, X.; Hayouka, Z.; Chakraborty, S.; Falk, S. P.; Weisblum, B.; Masters, K. S.; Gellman, S. H. Nylon-3 polymers with selective antifungal activity. *J. Am. Chem. Soc.* **2013**, 135, 5270–5273.

51. Nadithe, V.; Liu, R.; Killinger, B. A.; Movassaghian, S.; Kim, N. H.; Moszczynska, A. B.; Masters, K. S.; Gellman, S. H.; Merkel, O. M. Screening nylon-3 polymers, a new class of cationic amphiphiles, for siRNA delivery. *Mol. Pharm.* **2015**, 12, 362–374.

52. Schwab, L. W.; Kroon, R.; Schouten, A. J.; Loos, K. Enzyme-Catalyzed Ring-Opening Polymerization of Unsubstituted β -Lactam. *Macromol. Rapid Commun.* **2008**, 29, 794–797.

53. Park, S.; Forró, E.; Grewal, H.; Fülöp, F.; Kazlauskas, R. J. Molecular Basis for the

Enantioselective Ring Opening of β -Lactams Catalyzed by *Candida antarctica* Lipase B. *Adv. Synth. Catal.* **2003**, *345*, 986–995.

54. Matlack, A. S. Preparation of beta-alanine. **1954**, US patent 2,672,480.

55. Breslow, D. S.; Hulse, G. E.; Matlack, A. S. Synthesis of Poly- β -alanine from Acrylamide. A Novel Synthesis of β -Alanine. *J. Am. Chem. Soc.* **1957**, *79*, 3760–3763.

56. Bush, L. W.; Breslow, D. S. The Mechanism of Hydrogen-Transfer Polymerization. *Macromolecules* **1968**, *1*, 189–190.

57. Ogata, N. The Transition Polymerization of Acrylamide. I. On the Polymerization Condition and the Property of Polymer. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 906–912.

58. Ogata, N. The transition polymerization of acrylamide. Part II.1. On the reaction mechanism. *Die Makromol. Chemie* **1960**, *40*, 55–63.

59. Tani, H.; Oguni, N.; Araki, T. Initiation reaction in the strong base catalyzed polymerization of acrylamide. *Die Makromol. Chemie* **1964**, *76*, 82–88.

60. Ogata, N. The transition polymerization of acrylamide in the presence of Grignard reagents. *J. Polym. Sci.* **1960**, *46*, 271–272.

61. Carraher, C. E. Synthesis of poly(β -alanine) and β -alanine. *J. Chem. Educ.* **1978**, *55*, 668–669.

62. Nakayama, H.; Higashimura, T.; Okamura, S. The Transition Polymerization of Acrylamide by Anionic Mechanism. *Kobunshi Kagaku* **1966**, *23*, 433–439.

63. Trossarelli, L.; Guaita, M.; Camino, G. On the initiation mechanism of the sodium tert-butoxide catalyzed hydrogen transfer polymerization of acrylamide in aprotic solvents. *Die Makromol. Chemie* **1967**, *105*, 285–288.

64. Camino, G.; Guaita, M.; Trossarelli, L. Chain growth in the base catalyzed hydrogen transfer polymerization of acrylamide to poly(β -alanine). *Die Makromol. Chemie* **1970**, *136*, 155–159.

65. Iwamura, T.; Ashizawa, K.; Sakaguchi, M. Efficient and eco-friendly anionic polymerization of acrylamide under microwave irradiation and hydrolysis of the obtained polymers by microwave irradiation. *Macromolecules* **2009**, *42*, 5001–5006.

66. Murakami, Y.; Suzuki, T.; Takegami, Y. Anionic Polymerization of Acrylamide Initiated with the Disodium Salt of Poly(ethylene oxide). *Polym. J.* **1985**, *17*, 855–861.

67. Kumar, K.; Adhikary, P.; Tungala, K.; Azmeera, V.; Krishnamoorthi, S. Synthesis, characterization, and in vitro drug release study of 3-arm poly- β -alanine. *J. Appl. Polym. Sci.* **2015**, *132*, DOI: 10.1002/APP.42124.

68. Camino, G.; Lim, S. L.; Trossarelli, L. Branching in the base catalyzed hydrogen transfer polymerization of acrylamide in n-methyl-2-pyrrolidone at 100°C. *Eur. Polym. J.* **1977**, *13*, 479–481.
69. Gur'eva, L. L.; Tkachuk, a. I.; Dzhavadyan, E. a.; Estrina, G. a.; Surkov, N. F.; Sulimenkov, I. V.; Rozenberg, B. a. Kinetics and mechanism of the anionic polymerization of acrylamide monomers. *Polym. Sci. Ser. A* **2007**, *49*, 987–999.
70. Otsu, T.; Yamada, B.; Itahashi, M.; Mori, T. Hydrogen-transfer polymerization of methyl-substituted acrylamides. *J. Polym. Sci. Polym. Chem. Ed.* **1976**, *14*, 1347–1361.
71. Iwamura, T.; Tomita, I.; Suzuki, M.; Endo, T. Hydrogen-transfer polymerization behavior of N-acylacrylamide. *J. Polym. Sci. Part A Polym. Chem.* **2000**, *38*, 430–435.
72. Iwamura, T.; Tomita, I.; Suzuki, M.; Endo, T. Hydrogen-transfer polymerization of vinyl monomers derived from 4-methylbenzoyl isocyanate and acrylamide derivatives. *J. Polym. Sci. Part A Polym. Chem.* **1999**, *37*, 465–472.
73. Iwamura, T.; Tomita, I.; Suzuki, M.; Endo, T. Hydrogen-transfer polymerization of vinyl monomers derived from p-tolyl isocyanate and acrylamide derivatives. *React. Funct. Polym.* **1999**, *40*, 115–122.
74. Kondo, K.; Tanioku, S.; Takemoto, K. Functional Monomers and Polymers. LI. On the Synthesis and Polymerization of Acryloylaminomethyl Derivatives of Nucleic Acid Bases. *Polym. J.* **1979**, *11*, 81–82.
75. Iwamura, T.; Tomita, I.; Suzuki, M.; Endo, T. Novel hydrogen-transfer polymerization of vinyl monomer derived from p-toluenesulfonyl isocyanate and acrylamide. *J. Polym. Sci. Part A Polym. Chem.* **1998**, *36*, 1491–1494.
76. Kobuke, Y.; Hanji, K.; Furukawa, J.; Fueno, T. Hydrogen-transfer polymerization of cis- and trans-crotonamides. *J. Polym. Sci. Part A-1 Polym. Chem.* **1971**, *9*, 431–440.
77. Kojima, K.; Yoda, N.; Marvel, C. S. Base-catalyzed polymerization of maleimide and some derivatives and related unsaturated carbonamides. *J. Polym. Sci. Part A-1 Polym. Chem.* **1966**, *4*, 1121–1134.
78. Iwakura, Y.; Nakabayashi, N.; Sagara, K.; Ichikura, Y. Hydrogen-transfer polymerization of cinnamide. *J. Polym. Sci. Part A-1 Polym. Chem.* **1967**, *5*, 675–676.
79. Imanishi, Y.; Andoh, T.; Okamura, S. α -Polypeptide synthesis by the hydrogen-migration polymerization of trans-p-nitrocinnamide. *J. Polym. Sci. Part A-1 Polym. Chem.* **1969**, *7*, 773–778.
80. Konishi, A.; Yoda, N.; Marvel, C. S. Base-catalyzed polymerization of p-styrenesulfonamides. II. N-methyl and N-phenyl derivatives. *J. Polym. Sci. Part A Gen. Pap.*

1965, 3, 3833–3842.

81. Iwatsuki, S.; Yamashita, Y.; Ishii, Y. An evidence of the hydrogen transfer polymerization of methyl vinyl ketone. *J. Polym. Sci. Part B Polym. Lett.* **1963**, 1, 545–549.

82. Saegusa, T.; Kobayashi, S.; Kimura, Y. Hydrogen-Transfer Polymerization of Acrylic Acid to Poly(β -propiolactone). *Macromolecules* **1974**, 7, 256–258.

83. Hong, M.; Chen, E. Y.-X. Proton-transfer polymerization (HTP): converting methacrylates to polyesters by an N-heterocyclic carbene. *Angew. Chem. Int. Ed. Engl.* **2014**, 53, 11900–11906.

84. Gadwal, I.; Binder, S.; Stuparu, M. C.; Khan, A. Dual-Reactive Hyperbranched Polymer Synthesis through Proton Transfer Polymerization of Thiol and Epoxide Groups. *Macromolecules* **2014**, 47, 5070–5080.

85. Iwamura, T.; Tomita, I.; Suzuki, M.; Endo, T. Hydrogen-transfer polymerization behavior of N-acylacrylamide. *J. Polym. Sci. Part A Polym. Chem.* **2000**, 38, 430–435.

86. Yoda, N.; Marvel, C. S. Base-Catalyzed Polymerization of Maleimide and LCH-CO₂. **1983**, 4, 1121–1134.

87. Mather, B. D.; Viswanathan, K.; Miller, K. M.; Long, T. E. Michael addition reactions in macromolecular design for emerging technologies. *Prog. Polym. Sci.* **2006**, 31, 487–531.

88. Zhang, S.; Goncalves, L. D.; Lefebvre, H.; Tessier, M.; Rousseau, B.; Fradet, A. Direct Poly(β -alanine) Synthesis via Polycondensation in Ionic Liquids. *ACS Macro Lett.* **2012**, 31–34.

89. Eisenbach, C. D.; Lenz, R. W. Synthesis and Polymerization of Substituted β -Propiolactams. *Macromolecules* **1976**, 9, 227–230.

90. Fournier, M.; Prud'homme, R. E. Synthesis and characterization of poly(4-alkyl-4-methyl-2-azetidinone)s. *J. Polym. Sci. Part A Polym. Chem.* **1999**, 37, 761–769.

91. Bestian, H. Poly- β -amides. *Angew. Chemie Int. Ed. English* **1968**, 7, 278–285.

92. Leung, W. M.; Axelson, D. E.; Van Dyke, J. D. Thermal degradation of polyacrylamide and poly(acrylamide-co-acrylate). *J. Polym. Sci. Part A Polym. Chem.* **1987**, 25, 1825–1846.

93. Herrera, M.; Matuschek, G.; Kettrup, a. Main products and kinetics of the thermal degradation of polyamides. *Chemosphere* **2001**, 42, 601–607.

General Conclusion & Perspectives

The polymerization control is a determining factor regarding the polymer synthesis. Initiation, propagation, and termination steps are all of importance as they individually govern a part of the final polymer. Anionic polymerization is considered to be one of the most powerful tool to control each step enabling to get well-defined polymers. However, it would be utopian to ignore transfer reactions which can occur and many works, up to now, as well as this thesis would not have any interest to exist.

Taking into account the versatility of the initiators, or of the monomers, but also of the reaction conditions, it appears evident that many parameters can influence the structure of the final material. On this basis, the control of the reactivity is thus the key feature of each polymerization process and here, by anionic polymerization, this was investigated through the monomer activation methodology.

In this context, this work was focused on the synthesis of two types of polymer such as polyethers – flexible materials with an oxygen-rich structure – and polyamides – stiff materials known for their inter- and intramolecular hydrogen bondings.

The first part was dedicated to the development of simple Mg/Al systems able to perform the anionic ring-opening polymerization (AROP) of substituted epoxides. Magnesium compounds such as Grignard reagents or dialkylmagnesium were shown to be sustainable deprotonating agents for the generation of active initiators. Combined with a simple trialkylaluminum like triisobutylaluminum, they were also sustainable initiating and growing species in the AROP of substituted epoxides. A molar mass control was achieved, as well as an α -functionalization. As the Mg-compounds played a crucial role in the formation of the initiators (deprotonation of protic molecules), the Al-compound was equally crucial as it activated the epoxides but also complexed the Mg-initiator unable to polymerize epoxides when used alone. These Mg/Al systems still suffered from transfer reactions but may be envisaged as an alternative to the expensive phosphazene bases.

The second part was focused on the synthesis of cross-linkable polyethers through two distinct approaches which determined our synthesis methodology.

Reversibly cross-linkable polyethers were synthesized according to a side-chain approach. Activated anionic ring-opening copolymerization of propylene oxide with furfuryl glycidyl ether was performed using tetraoctylammonium bromide and triisobutylaluminum. The obtained polyethers were thus bearing pendant furan groups able to react with bis-maleimide compounds via Diels-Alder chemistry, and more precisely by a [4+2] cycloaddition under thermal treatment. The combination of such chemistries was shown to be sustainable for the preparation of reversibly cross-linkable polyether-based materials having an elastomeric behaviour. Other various substituted epoxides could be employed to enlarge the diversity of such thermo-reversible materials.

An in-chain approach was also studied. By activated anionic ring-opening copolymerization of propylene oxide with maleic anhydride using tetraoctylammonium bromide and triisobutylaluminum, we were able to introduce double bonds inside the polyether backbone. This latter was permanently cross-linked by a vulcanization process. Low proportions of maleic anhydride should be involved to get flexible materials.

Finally, the last part was dedicated to the synthesis of polyamide-3 by hydrogen transfer polymerization (HTP) of acrylamide in bulk conditions. The polymerization occurring in a few minutes by an activated monomer (AM) mechanism was shown to be controlled regarding the increasing of the molar masses with the decreasing of the base amount. This solvent free process was shown to be a sustainable method to obtain branched PA-3 of different lengths. The understanding of the polymerization mechanism in such conditions provided an open-window for the copolymerization of reactive molecules via HTP.

Titre : Polymérisation anionique par activation du monomère pour la synthèse de polyéthers et de polyamide-3

Résumé : Ces travaux de thèse traitent de la polymérisation anionique combinée à deux méthodologies différentes d'activation du monomère visant à contrôler les réactivités des monomères et/ou des espèces actives lors de la propagation pour la synthèse de polyéthers et de polyamide-3. L'étude de nouveaux systèmes efficaces d'amorçage/propagation à base de magnésium et d'aluminium pour la polymérisation anionique par ouverture de cycles des époxydes substitués est présentée. Deux types de polyéthers réticulables ont également été synthétisés par l'utilisation de bromure de tétraoctylammonium et de triisobutyl-aluminium. Dans le premier cas, l'objectif est d'incorporer des fonctions furane pendantes le long des chaînes polyéthers. Dans le second cas il s'agit d'introduire des doubles liaisons au sein même du squelette polyéther. Les réticulations ont ensuite été effectuées thermiquement par le biais d'une chimie réversible de type Diels-Alder entre groupement furane et maléimide pour le premier cas et par vulcanisation pour le deuxième. Enfin, une étude menant à une compréhension mécanistique a été conduite sur la synthèse de polyamide-3 en masse par polymérisation par transfert d'hydrogène à partir de l'acrylamide.

Mots clés : polymérisation anionique par ouverture de cycle, activation du monomère, polyéther, réticulation, polymérisation par transfert d'hydrogène, acrylamide, polyamide-3

Title : Polyethers and polyamide-3 synthesis by monomer activated anionic polymerization

Abstract : The studies presented in this thesis report on the use of the anionic polymerization with two different methodologies of monomer activation aiming to control the reactivity of monomers and/or growing species for the synthesis of polyethers and polyamide-3. New magnesium/aluminium active systems efficient for the anionic ring-opening polymerization of substituted epoxides are proposed and developed. Cross-linkable polyethers were also synthesized by using the combination of tetraoctylammonium bromide with triisobutylaluminum. Furan groups or double bonds were introduced as pendant or in-chain functions respectively in polyether-based materials. The so-formed polymers were cross-linked using reversible Diels-Alder reaction between furan and maleimide, and vulcanization for the double bonds. Finally, we investigated the mechanism of the hydrogen-transfer polymerization of acrylamide in bulk conditions as a sustainable route to get polyamide-3.

Keywords : anionic ring-opening polymerization, monomer activation, polyether, cross-linking, hydrogen-transfer polymerization, acrylamide, polyamide-3