UNIVERSITAT ROVIRA I VIRGILI

"NEW POLYURETHANES FROM VEGETABLE OIL-BASED POLYOLS"

Enrique del Rio Nieto

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Enrique del Río Nieto

New polyurethanes from vegetable oil-based polyols

PhD THESIS

Supervised by Dr. Marina Galià i Clua and Dr. Joan Carles Ronda i Bargalló

Departament de Química Analítica i Química Orgánica

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CERTIFICAMOS:

Que el presente trabajo, titulado “New polyurethanes from vegetable oil-based polyols”, que presenta Enrique del Río Nieto para la obtención del título de Doctor, ha sido realizado bajo nuestra dirección en el Departamento de Química Analítica y Química Orgánica de esta Universidad y que cumple los requisitos para poder optar a la Mención Europea.

Tarragona, 25 de enero de 2011

Dra. Marina Galià i Clua   Dr. Joan Carles Ronda i Bargalló

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A mi familia, que se lo debo todo, y todo se lo merecen.

Y a Mayra, mi apoyo incondicional.

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Introduction

SUSTAINABLE DEVELOPMENT

The sustainable development concept came out of the United Nations Commission on Environment and Development (Bruntland Commission) in 1987 and is defined as "the development that meets the needs of the present without compromising the ability of future generations to meet their own needs".[1] The availability of energy was admitted to be key for the future development; the necessity of a steady transition to a broader and more sustainable mix of energy sources was pointed out as a major objective.

With the same aims, Agenda 21, the comprehensive plan of action for a sustainable development in the 21st century which was adopted by more than 180 governments in Rio de Janeiro in 1992, is encouraging the environmentally sound and sustainable use of renewable natural resources.[2]

Regarding to the chemical science, the Environmental Protection Agency (EPA) coined a new term that collected the ideals of sustainability applied to chemistry: *Green Chemistry*. Based in a set of 12 principles and established by Anastas and Warner in 1998, the main challenges of Green Chemistry can be summarized as:[3]

- To promote innovative chemical technologies that reduce or eliminate the use and the generation of hazardous substances in the design, manufacture and use of chemical products.
- To develop engineering processes that minimize energy consumption.
- To minimize resources used as well as waste generated by using more efficient catalytic processes and maximizing the concept of atom economy.
- To use renewable resources and sub-products generated in other activities instead of limited ones.

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[1] World Commission on Environment and Development (WCED). Oxford University Press, 1987.

[2] Report of the United Nations Conference on Environment and Development, Rio de Janeiro, 1992; http//www.un.org/esa/sustdev.

[3] P. T. Anastas and J. C. Warner, Green Chemistry Theory and Practice, Oxford University Press, New York, 1998.

At this point, scientists have a new pathway to confront the current challenges of the society, which is the Green Chemistry. The priorities of this way should be the human health and the protection of the Earth, maintaining the equilibrium between society, economy and environment.

Some important advances have been made in the field of Green Chemistry in recent years. The Presidential Green Chemistry Challenge Awards provided by the EPA,[4] recognizes to those working in chemical technologies that incorporate the principles of Green Chemistry into chemical design, manufacture and use. Some of awards are good examples of Green Chemistry practices:

- The *Dow Chemical Company* and *BASF* were awarded in 2010 for the implementation of “Innovative, Environmentally Benign Production of Propylene Oxide via Hydrogen Peroxide”. This is a very efficient catalytic process with high conversions of propylene and high selectivity for propylene oxide, in which the only sub-product obtained is water.
- *Cargill, Incorporated* was awarded in 2007 for “BiOH^{TM} Polyols” for the development of vegetable oil based polyols that substitute petroleum-based polyols in the synthesis of polyurethane foams. Furthermore, this replacement reduces the total energy use by 23% and the carbon dioxide emissions by 36%.
- In 1997 Professor Barry M. Trost (Stanford University) received the award for “The Development of the Concept of Atom Economy”. Professor Trost's concept of atom economy includes reducing the use of nonrenewable resources, minimizing the amount of waste, and reducing the number of steps used to synthesize chemicals. Atom economy is one of the fundamental cornerstones of green chemistry.

The implementation of sustainability issues in Europe is also promoted. Thus, the European Environment Agency (EEA) has the task of provide sound, independent information on the environment. EEA is the major information source for those involved in developing, adopting, implementing and evaluating environmental policy, and also the general public. One of the clients of EEA is the European Commission, which has more than 40

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[4] U. S. Environmental Protection Agency, Office of Pollution Prevention and Toxics. htpp://www.epa.gov/gcc/pubs/pgcc/presgcc.html.

Directorates-General (DG), among them the Directorate-General for the Environment. The objective of DG Environment is to protect, preserve and improve the environment for present and future generations. To achieve this, it proposes policies that ensure a high level of environmental protection in the European Union and that preserve the quality of life of EU citizens.

Renewable resources in the chemical industry

Several advances have been made in the field of chemistry concerning the seventh principle of the Green Chemistry which says "A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable."

Plants are the most important renewable resource. It was estimated that around 120 billion tons carbon in biomass, equivalent to >80 billion tons of oil equivalents (toe), are generated globally year by year by photosynthesis.[5] The global primary energy supply in 2004 was 11.2 billion toe and was estimated to be 20.6 billion toe in 2030.[6] From a chemical point of view, about 75% of biomass is carbohydrates, 20% lignins and about 5% oils and others. In Figure 1 is shown the life cycle of the vegetable raw materials; after their transformation in products, which are used and then discarded, the sub-products produced should be assimilated for the biomass, closing de cycle, or recycled in order to minimize waste.

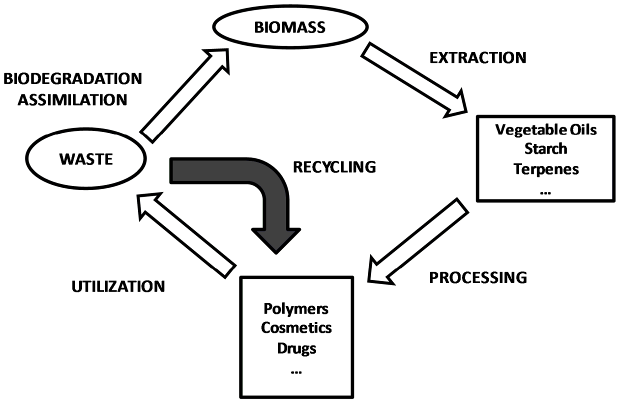

Figure 1. Life cycle of products derived from biomass.

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[5] IPCC: Climate change. In: Working Group I Report: The Phisycal Science Basis. Cambridge University Press, Cambridge (UK) and New York, NY, (USA) 2007, p. 512.

[6] International Energy Agency: World Energy Outlook 2006. OECD/IEA, Paris (France) 2006.

Obviously, the exhaustive knowledge of the chemistry of these biomolecules is absolutely necessary in order to reach a sustainable usage of biomass as renewable feedstock. Lignin, starch, terpenes and fats have been extensively studied for their possibilities as renewable resources in the chemical industry. Gandini et al. have extensively studied some biomass derivatives as renewable raw materials, and in 1997 published a review in which emphasize the furans importance as resource, its chemical transformations into reagents and monomers, and the possibilities that offer in polymer chemistry.[7] In 1998 they published another review focused in polymers derived from biomass components as lignins, furans, polysaccharides suberin and oils.[8] More recently, in 2008, they presented a review with the same topic but including the lasts contributions into the field; noteworthy is the especial mention to bacterial polymers.[9] The same year, Gandini and Belgacem published a book, which summarizes the synthesis of polymers from renewable resources.[10] Also in 2008 Hillmyer et al. published a review that depicts polylactide importance in polymer chemistry, vegetable oils as renewable resource and carbon dioxide as feedstock.[11] Corma et al., in 2007, reviewed in a comprehensive manner the routes to transform saccharides, vegetable oils and terpenes into chemicals.[12]

All these possibilities offered by the biomass should be profited for the scientists with the challenges to overcome the depletion of fossil resources in a greener way. Moreover, natural resources provide to chemists with new building blocks, which have interesting features as asymmetric centers in the molecules, more efficient processes when enzymes or bacteria are involved and so on.

Vegetable oils as renewable resources: polymer chemistry

The use of vegetable oils as raw materials in the chemical industry has become more important year by year. The global production of the most important oils in 2008/09 was 132 million tons, from which, about 15% are used in the non food industry. In 2005, 10% of all resources for the chemical

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[7] A. Gandini and M. N. Belgacem, Prog. Polym. Sci., 1997, 22, 1203-1379.
[8] A. Gandini and M. N. Belgacem, Polym. Int., 1998, 47, 267-276.
[9] A. Gandini, Macromolecules, 2008, 41, 9491-9504.
[10] M. N. Belgacem and A. Gandini; Monomers, Polymers and Composites from Renewable Resources; Elsevier: Oxford, 2008.
[11] C. K. Williams and M. A. Hillmyer, Polym. Rev., 2008, 48:1, 1-10.
[12] A. Corma, S. Iborra and A. Velty, Chem. Rev, 2007, 107, 2411-2502.

industry were renewable, and 30% of that, were plant oils.[13] This has been possible thanks to the development of chemical modifications on triglycerides and its derivatives.

In 1988 the application of the natural fats and oils as renewable raw materials in the chemical industry was extensively reviewed, dealing about economic aspects, their sources as well as their transformations.[14] Until that moment, more than 90% of oleochemical reactions have been those occurring at the fatty acid carboxy group, while less than 10% have involved transformations of the alkyl chain. In 2000, Metzger et al. published a review focused in the transformations of the fats and oils for the chemical industry with special emphasis on interdisciplinary collaboration involving chemistry, biochemistry, plant breeding, and agriculture to achieve a successful application of this technology.[15] In the last decade other important reviews have been published: K. Hill summarized the production situation and some examples of the applications of the fats and oils.[16] In 2003, F. D. Gunstone gave a personal view of the developments in the lipids chemistry in the last 60 years, reviewing the most important chemical transformations.[17] In 2006, the state of chemical and biotechnological conversion and diversification of lipids as renewable resources was revised.[18] Finally, in 2009 Metzger reviewed the fats and oils as renewable feedstock.[19]

Focused in polymer chemistry, some other reviews have covered the potential of fats and oils as renewable raw materials for polymer synthesis. In 2000, Nayak published a review about vegetable oils and the polymers derived from.[20] Later, Erciyes et. al. published a comprehensive article listing the most interesting transformations in the polymer chemistry obtained from

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[13] German Federal Ministry of Food, Agriculture and Consumer Protection, Agency of Renewable Resources, http://www.fnr.de.

[14] H. Baumann, M. Bühler, H. Fochem, F. Hirsinger, H. Zoebelein and J. Falbe, Angew. Chem., 1988, 100, 42-62; Angew. Chem. Int. Ed. Engl., 1988, 27, 41-62.

[15] U. Biermann, W. Friedt, S. Lang, W. Lühs, G. Machmüller, J. O. Metzger, M. Rüsch gen Klaas, H. J. Schäfer and M. P. Schneider, Angew. Chem., Int. Ed., 2000, 39, 2206–2224.

[16] K. Hill, Pure Appl. Chem., 2000, 72, 1255-1264.

[17] F. D. Gunstone, Biochim. Biophys. Acta, 2003, 1631, 207-217.

[18] J. O. Metzger and U. Bornscheuer, Appl. Microbiol. Biotechnol., 2006, 71, 13-22.

[19] J. O. Metzger, Eur. J. Lipid Sci. Technol., 2009, 111, 865–876.

[20] P. L. Nayak, Polym. Rev., 2000, 40, 1-21.

triglycerides.[21] In 2007, Schubert and coworkers published a review on polymers from plant oils.[22] Sharma and Kundu have published two reviews covering addition[23] and condensation[24] polymers from vegetable oils.

Plant oils are mainly constituted by triglycerides, which are the product of esterification between a molecule of glycerol and three molecules of fatty acids (Figure 2). Around 95% of the total weight of triglycerides is due to fatty acids, therefore, the properties and reactivity of triglycerides strongly depends on their composition.

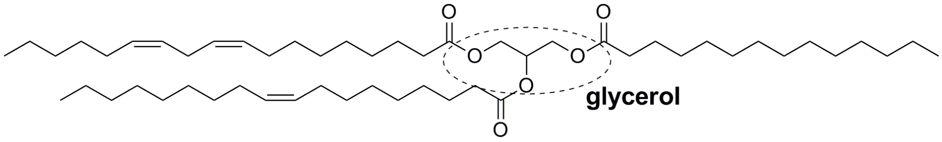

Figure 2. Structure of triglycerides

Fatty acids are aliphatic acids with 12 to 22 carbon atoms in a linear chain, some of them are totally saturated, however, more interesting for polymer chemistry are those with other functionalities in the chain. Most of the fatty acids present double bonds in the chain, others have functionalities as hydroxyl or epoxide groups. In Figure 3 are shown some of the most important fatty acids due to either their abundance or their functionality.

In Table 1 is summarized the fatty acid composition of some of the most important vegetable oils and the double bond content per triglyceride, which is one of the most important features together with the percentage of each fatty acid. Is noteworthy the high percentage of some fatty acids in some varieties of oils, as in high oleic sunflower and castor oils with up to 90% in oleic and ricinoleic acids respectively.

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[21] F. S. Güner, Y. Yagci and A. T. Erciyes, Prog. Polym. Sci., 2006, 31, 633‑670.
[22] M. A. R. Meier, J. O. Metzger and U. S. Schubert, Chem. Soc. Rev.,2007, 36, 1788-1802.
[23] V. Sharma and P. P. Kundu, Prog. Polym. Sci., 2006, 31, 983-1008.
[24] V. Sharma and P. P. Kundu, Prog. Polym. Sci., 2008, 33, 1199-1215.

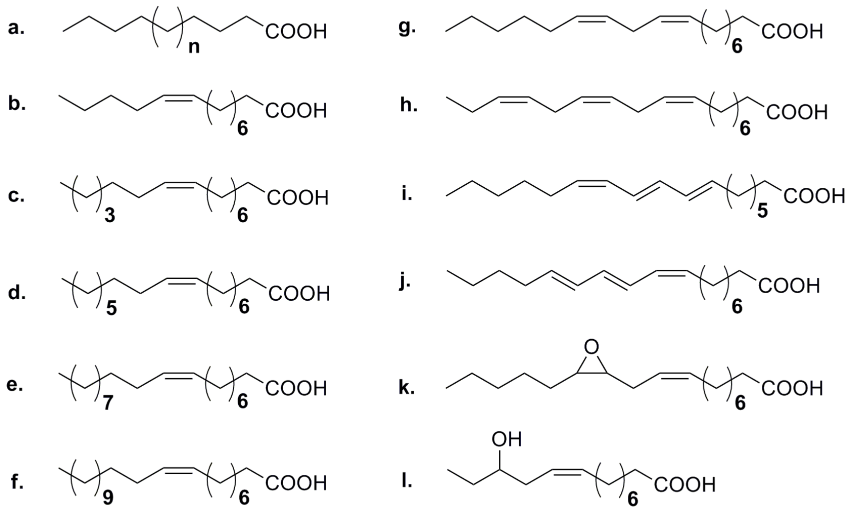


Figure 3. Structure of most important fatty acids: saturated fatty acids (a), myristoleic (b), palmitoleic (c), oleic (d), gadoleic (e), erucic (f), linoleic (g), linolenic (h), calendic (i), α-eleostearic (j), vernolic (k) and ricinoleic (l).

The high concentration of some fatty acids in a vegetable oil allows the development of technologies for their purification and transformation. Moreover, genetic is an important tool in the development of new improved vegetable oils for non food applications.

Table 1. Composition in % of some important plant oils.

R(x:y)	12:0	14:0	16:0	18:0	18:1	18:2	18:3
sunflower	-	-	6	4	28	61	-
palm kernel	50	15	7	2	15	1	-
linseed	-	-	5	4	22	15	52
soybeen	-	-	10	5	21	53	8
new rapeseed*	-	0.5	4	1	60	20	9
High Oleic Sunflower*	-	-	6.4	3.1	82.6	2.3	3.7

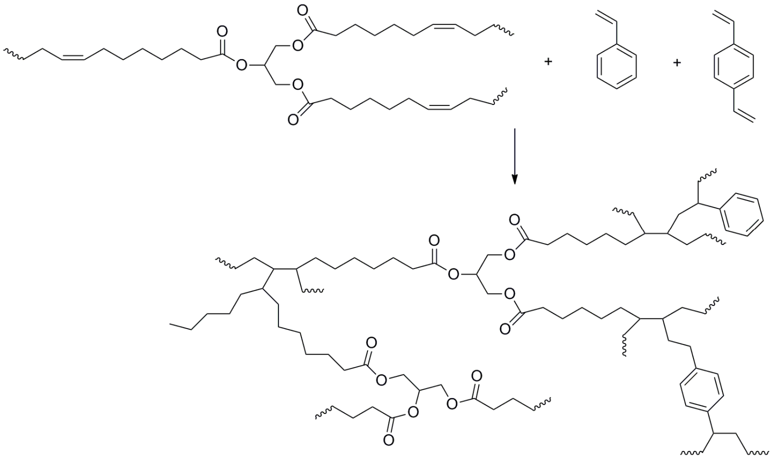
R(x:y)= number of carbon atoms (x), and number of double bonds (y).
* Obtained from genetically engineered seeds

Different strategies have been used in order to synthesize polymers from vegetable oils:

a) Direct polymerization of vegetable oils

There are some vegetable oils that due to their composition are capable to be polymerized directly. Vegetable oils such as linseed and tung oils have been classically exploited as drying oils. The drying power of these oils is directly related to their highly unsaturated nature. The reaction with atmospheric oxygen leads to the formation of a cross-linked network. This polymerization is used mostly in paints and coatings, but also in inks and resins.[25] Larock's group has intensively studied the cationic polymerization of the double bonds of some vegetable oils without any modification; however, other comonomers such as styrene, divinylbenzene and dicyclopentadiene must be added into the mixture to improve the polymer properties. Soybean, corn, tung oils among others have been studied in this polymerization.[26] In Scheme 1, the cross-linking reaction for these systems is shown.

Castor oil, with high content in ricinoleic acid, has been directly polymerized by reacting its hydroxyl groups with diisocyanates to yield polyurethanes, as well as by reacting with dicarboxylates to obtain thermosetting polyesters.[27]



Scheme 1. Direct copolymerization of a triglyceride with styrene and divinylbenzene.

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[25] a) W. L. Taylor, J. Am. Oil Chem. Soc., 1950, 472-476. b) J. Mallégol, J. Lemaire and J. L. Gardette, Prog. Org. Coat, 2000, 39, 107-113.
[26] a) D. Andjelkovic, M. Valverde, P. Henna, F. Li and R. C. Larock, Polymer, 2005, 46, 9674-9685. b) F. Li, M. W. Hanson and R. C. Larock, Polymer, 2001, 42, 1567-1579.
[27] Z. S. Petrovic, Polym. Rev., 2008, 48, 109-155.

b) *Modification of vegetable oils and polymerization*

Direct polymerization of oils normally yields materials with poor properties due to the low reactivity of both double bonds and secondary hydroxyl groups in castor oil. To improve the reactivity and to enhance the properties of the materials derived from vegetable oils, several chemical modifications have been investigated.

The most important modification of the fatty acid double bonds is the epoxidation. Epoxidation can be carried out on several ways in a very efficient manner, however, an enzymatic reaction, which involves H_2O_2 as oxidant, Novozym 435 and room temperature conditions can be presented as one the greenest procedures.[28] Epoxidized vegetable oils can be used directly in a wide range of polymer applications, such as, stabilizers of polyvinyl chloride or the direct photochemically initiated cationic polymerization and cross-linking with polyols, diamines or anhydrides.[29] However, the most interesting application of epoxidized vegetable oils is as intermediate in the synthesis of macromonomers. In Scheme 2 some of the most important derivatives obtained by ring opening reactions are shown. These modifications allow to introduce new functional groups; enhancing the properties of the vegetable oils in their utilization as macromonomers. The ring opening of the epoxide group yield an alcohol group and, depending on the procedure, other functionality as methoxy group, halogen, acrylate and so on can be obtained. Common uses of these derivatives are the synthesis of polyurethanes by reaction of the polyols with an isocyanate, or the radical polymerization in the case of the ring opening with acrylic acid. Also, the hydroxyl derivative can be functionalized to achieve other reactivities, for example, with acryloyl chloride to obtain acrylated monomers or with anhydrides to incorporate an acid functionality. Besides to the broad range of modifications that can be carried out with epoxides, we have to add the possibilities offered by polymer blends, partial modification, interpenetrating network, etc.

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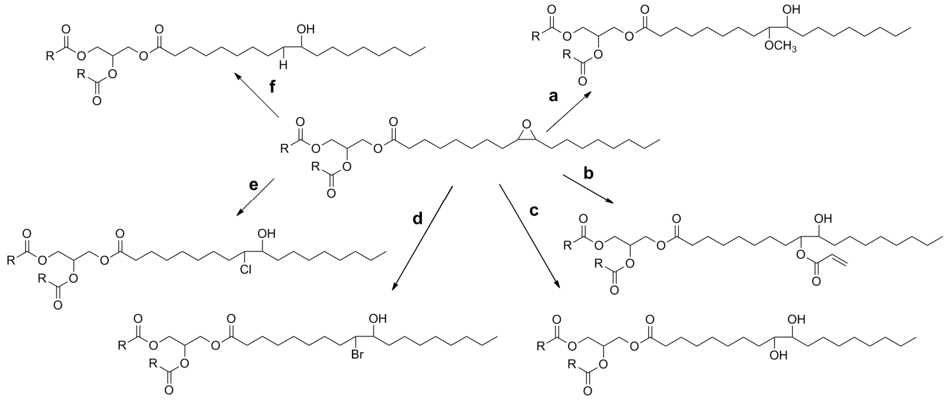
[28] a) M. Rüsch gen. Klaas and S. Warvel, J. Am. Oil Chem. Soc., 1996, 73, 1453-1457. b) M. Rüsch gen. Klaas and S. Warvel, Ind. Crops Prod., 1999, 9, 125-132.

[29] a) J. V. Crivello and R. Narayan, Chem. Mater., 1992, 4, 692-699. b) J. D. Earls, J. E. White, L. C. López, Z. Lysenko, M. L. Dettloff and M. J. Null, Polymer, 2007, 48, 712-719. c) V. Tanrattanakul and P. Saithai, J. Appl. Polym. Sci., 2009, 114, 3057-3067. d) J. Samuelsson, P. Sundell and M. Johansson, Prog. Org. Coat, 2004, 50, 193-198.



Scheme 2. Ring opening products of epoxidized triglycerides by reaction with methanol (a), acrylic acid (b), H_2O (c), HBr (d), HCl (e) and catalytic hydrogenation (f).

Other important modifications of vegetable oils are the reaction of the double bonds with maleic anhydride to attach maleates,[30] and the addition of acrylonitrile by the Ritter reaction to obtain acrylamide derivatives, which are, then radicalary polymerized.[31] Partial transesterification with glycerol yield mono and diglycerides with free hydroxyl groups that can be used in other reactions.[32] Guo et al. obtained primary alcohols for polyurethane synthesis by hydroformylation of Soybeen oil.[33] Montero de Espinosa et al. synthesized acrylated sunflower oil in three steps, a photo-peroxidation of the allylic position, reduction of the resulting hidroperoxide and esterification of the hydroxyl group with acryloyl chloride. The photo-peroxidated oil also can be converted into enones, which were used as Michael acceptors (Scheme 3).[34]

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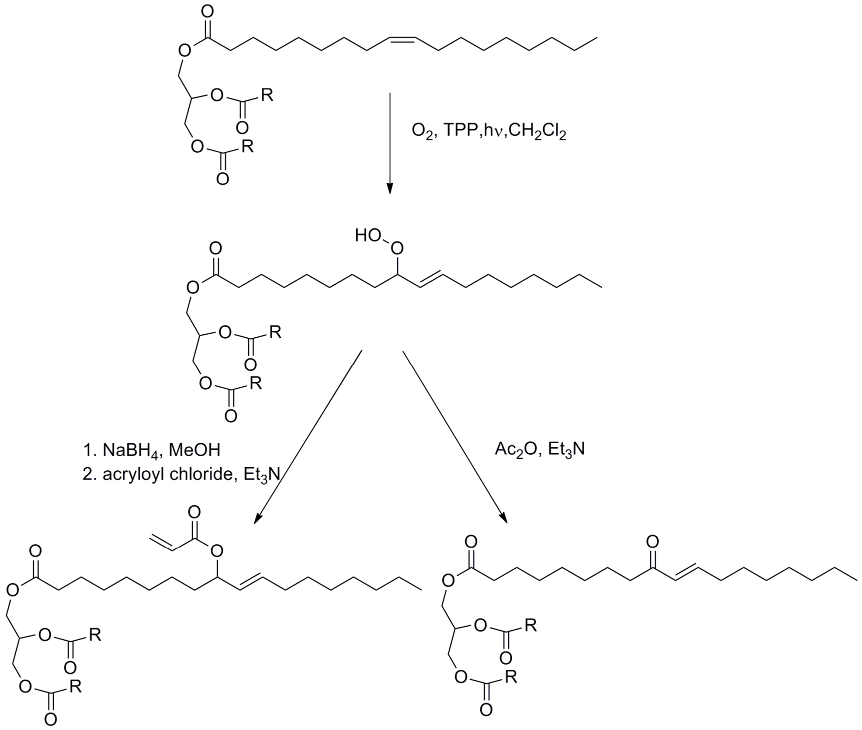
[30] T. Eren, S. H. Kusefoglu and R. Wool, J. Appl. Polym. Sci., 2003, 90, 197-202.

[31] T. Eren and S. H. Kusefoglu, J. Appl. Polym. Sci., 2005, 97, 2264-2272.

[32] N. O. V. Sonntag, J. Am. Oil Chem. Soc., 1984, 61, 229-232.

[33] A. Guo, D. Demydov, W. Zhang and S. Z. Petrovic, J. Polym. Environ., 2002, 10, 49-52.

[34] a) L. Montero de Espinosa, J. C. Ronda, M. Galià and V. Cádiz, J. Polym. Sci. Part. A Polym. Chem., 2009, 47, 1159-1167. b) L. Montero de Espinosa, J. C. Ronda, M. Galià and V. Cádiz, J. Polym. Sci. Part. A Polym. Chem., 2008, 46, 6843-6850.



Scheme 3. Photo-oxidation of a triglyceride and reactions to yield the enone and the acrylated derivatives.

c) *Polymerization of oil-derived platform chemicals*

Fatty acids and their esters as well as glycerol can be isolated from triglycerides trough hydrolysis or methanolysis in good purities. Although most of the chemical transformations of vegetable oils have been applied also to fatty acids derivatives, there are other transformations especially interesting when are applied on the fatty acid. In this way, monomers can be achieved for the synthesis of linear polymers. As an example, oleic acid can be converted in an α,ω-diacid via microbial oxidation and then by reaction with the diol obtained by reduction, it can yield a fully renewable polyester.[35] Fatty acids can be converted in oxazoline derivatives, and then, by ring opening

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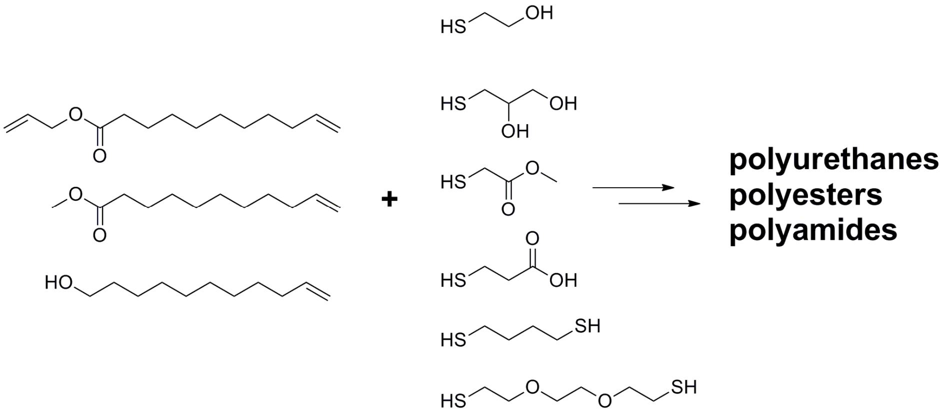
[35] a) D. Quinzler and S. Mecking, Angw. Chem. Int. Ed., 2010, 49, 4306-4308. b) Y. Yang, W. Lu, X. Zhang, W. Xie, M. Cai and R. A. Gross, Biomacromolecules, 2010, 11, 259-268.

polymerization it is possible to obtain polymers, copolymers or block-copolymers with low polydispersities and predefined molecular weights.[36]

Recently, thiol-ene coupling has been applied to the synthesis of monomers derived from vegetable oils, some of the structures are shown in Scheme 4. Diacids, diols and hydroxy-acids for the synthesis of linear polyesters and polyurethanes, as well as monomers for branched structures have been described.[37]



Scheme 4. Some reactions used in the synthesis of monomers via thiol-ene coupling for polyester, polyamide, and polyurethane synthesis.

One of the most important reactions applied recently to the transformation of fatty acids into monomers and polymers is the metathesis reaction. Self metathesis of fatty acid derivatives yields diacids and diols; in the same way; their cross metathesis with methyl acrylate yields also monomers for polymerization in conventional ways. Moreover, classic synthetic reactions can be applied to fatty acid derivatives in order to obtain α,ω-dienes. These dienes can be polymerized under acyclic diene metathesis conditions (Scheme 5). The development of new highly active catalysts which are tolerant to a wide range of functionalities opens new possibilities for this chemistry.[38]

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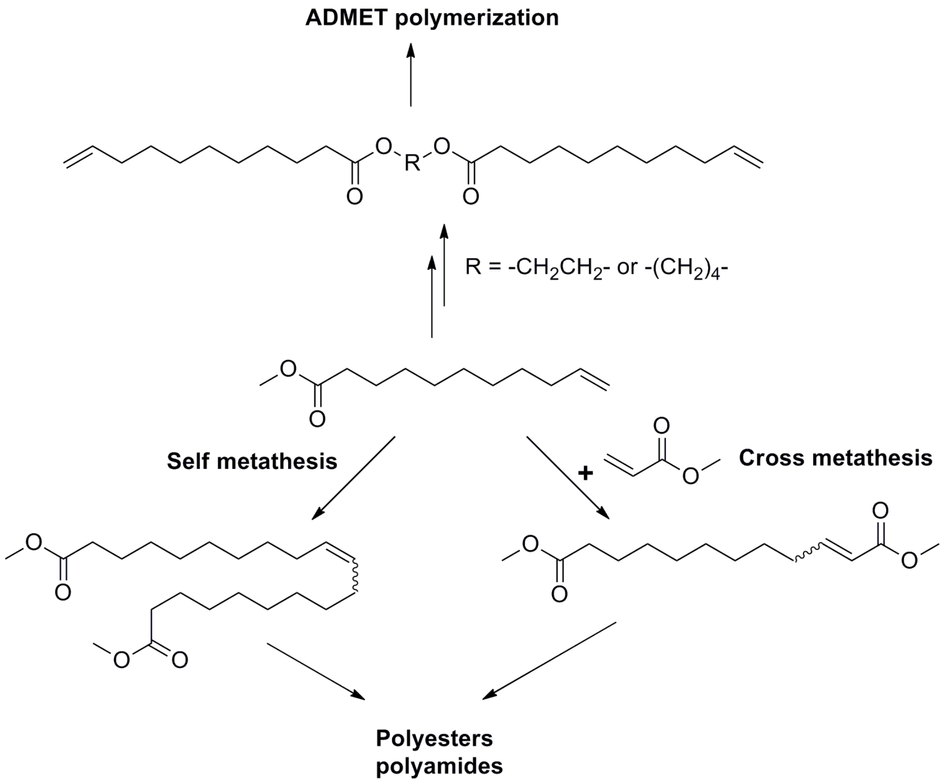
[36] a) G. Cai and M. H. Litt, J. Polym. Sci. Part A: Polym. Chem., 1996, 34, 2689-2699. b) R. Hoogenboom and U. Schubert, Green Chem., 2006, 8, 895-899.

[37] a) C. Lluch, J. C. Ronda, M. Galià, G. Lligadas and V. Cádiz, Biomacromolecules, 2010, 11, 1646-1653. b) O. Türünç and M. A. R. Meier, Macromol. Rapid Commun. 2010, 31, 1822-1826.

[38] a) H. M. Riepl, J. Pettrak, M. Faulstich and W. A. Herrmann, Macromol. Symp., 2010, 293, 39-42. b) M. A. R. Meier, Macromol. Chem. Phys., 2009, 210, 1073-1079.



Scheme 5. Synthesis of monomers by metathesis reaction, and synthesis of fatty acid derived monomers for ADMET polymerization.

POLYURETHANES FROM VEGETABLE OILS

Basic chemistry of polyurethanes

Polyurethanes were firstly described by Otto Bayer in 1937 as alternative materials to those already patented at that moment. With the Second World War, polyurethanes gained more importance and, later, with the commercialization of some isocyanates, the investigation was focused on the development of new polyols. The versatility of polyurethanes has allowed the synthesis of different materials such as foams, coatings, adhesives, sealants, and elastomers. These materials can be used in fields as automotive, footwear, in construction as insulators, and most recently in medical devices. Polyurethanes have become one of the most used polymers due to their wide range of applications, properties and versatility.

Polyurethanes are synthesized by reaction of a polyisocyanate with a polyol. Depending on the functionality of the reactants, one can obtain linear or cross-linked polymers. When the isocyanate reacts with the hydroxyl group a urethane linkage is obtained. In Figure 4 are shown some of the most important reactions involved in the synthesis of polyurethanes using isocyanates. Apart from the reaction with alcohol groups to form the urethane linkage, isocyanates can react with water generating CO_2 and an amine. Amines also react with isocyanates to obtain the urea linkage; this reaction has been exploited in the synthesis of polyureas. Isocyanates also react with carboxylic acids to yield an amide group and CO_2; with urethane moiety generating allophanates; and with other isocyanates to yield dimers and trimers (isocyanurates).

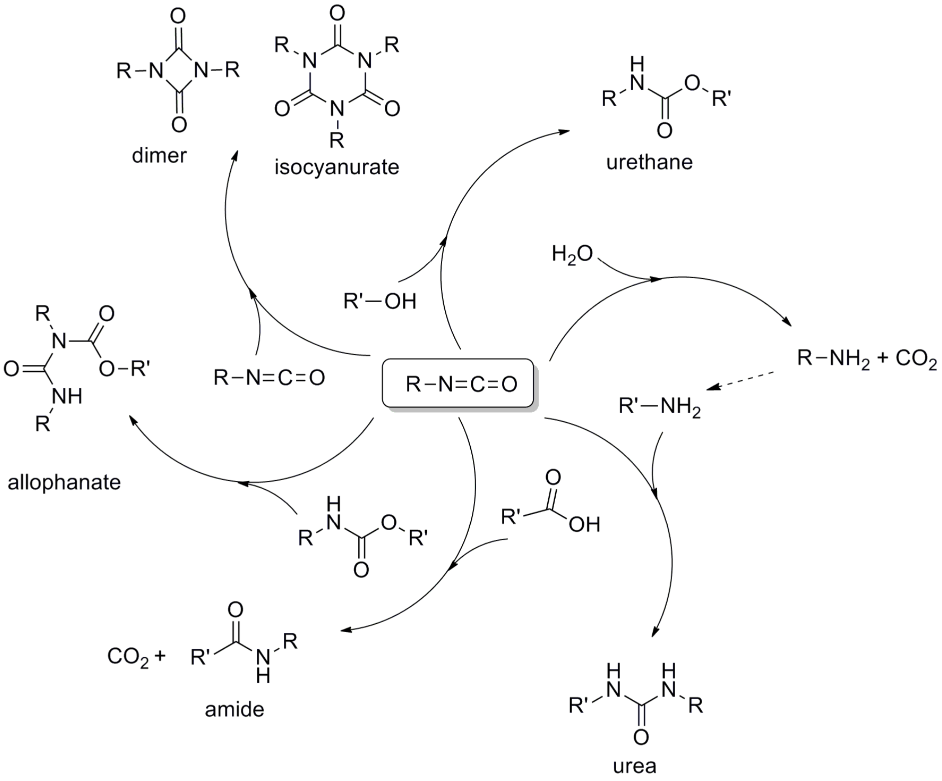


Figure 4. Typical reactions of isocyanates involved in the synthesis of PU.

As the synthesis of isocyanates is more complex than that of polyols, chemists tend to use commercially available isocyanates and design new polyols to tune the properties of the final material. In Figure 5 are represented the most common diisocyanates.

Whereas the diisocyanates used are usually commercial, polyols offer a wide range of possibilities; therefore, the properties of the final material strongly depend on the polyol. In general, high molecular weight polyols with low functionality yield flexible polyurethanes with lower glass transition temperatures than those synthesized with lower molecular weight and higher functionality polyols.

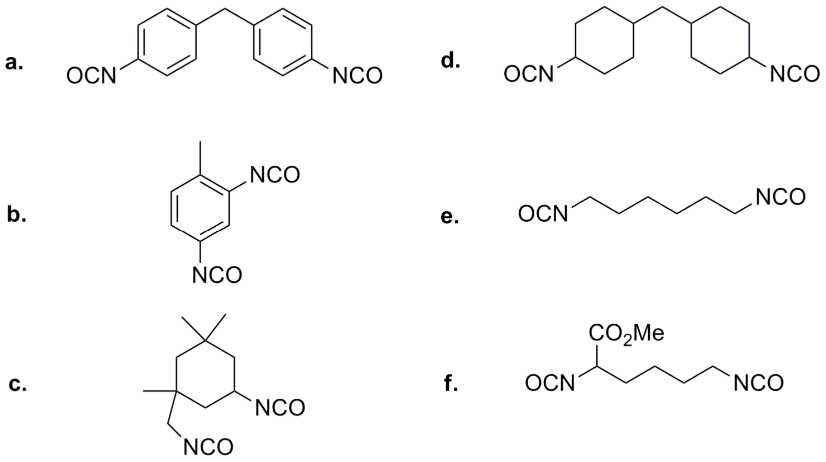
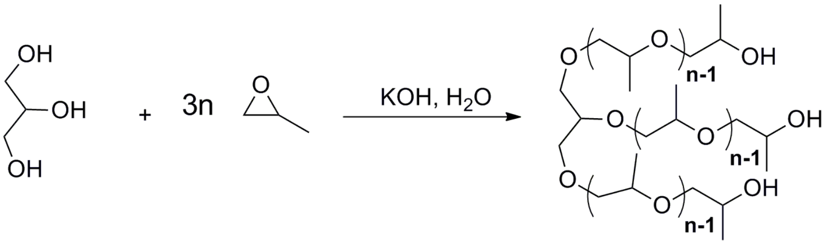


Figure 5. Common diisocyanates used in the synthesis of polyurethanes. 4,4'-methylene-bis(phenylisocyanate) (MDI) (a), 2,4-toluene diisocyanate (TDI) (b), isophorone diisocyanate (IPDI) (c), 4,4'-dicyclohexylmethane diisocyanate (d), hexamethylene diisocyanate (e), and lysine methylester diisocyanate (LDI) (f).

Traditionally, polyols have been synthesized by ring opening polymerization of oil-based cyclic ethers as ethylene oxide, propylene oxide or tetrahydrofuran, initiated by a polyol or polyamine as glycerol, sorbitol, trimethylolpropane, or diethylenetriamine; in the presence of a catalyst (Scheme 6). In the synthesis of segmented polyurethanes, a macrodiol combined with a low molecular weight diol as 1,6-hexanediol or 1,4-butanediol is used. Hard segments generated by reaction of small diols and diisocyanate usually show crystalline domains with high melting point, which act as physical cross-linking and improve the mechanical properties of the material. The macrodiol forms the soft domain as an amorphous network, and the hard domains are dispersed in. Soft segment gives flexibility and good elastic properties to the material. The macrodiol can be chosen to have melting point close to body temperature, which can be used in biomedical applications.



Scheme 6. Typical synthesis of petroleum-based polyols.

Vegetable oil-based polyurethanes

As commented above, most of the polyurethanes are synthesized from polyols based in petrochemicals. But, due to environmental concerns, big efforts have been focused on the development of polyols derived from renewable resources. Castor oil, which is rich in ricinoleic acid (see Figure 3), has been historically the first and almost the only vegetable oil used in the synthesis of polyurethanes and in interpenetrating polymer networks.[21] In general, the rest of vegetable oils have to be modified, introducing hydroxyl groups into their structure.

Transesterification of plants oils such as castor, palm and soybean oil with polyols such as pentaerythritol, trimethylol propane or glycerol has been used to obtain polyols.[39] However, the most used methodology to obtain polyols from vegetable oils is the combination of epoxidation of the double bonds and the subsequent ring opening of the epoxide group (Scheme 2). Vegetable oils such as sunflower, corn, soybean, linseed oils have been epoxidized, and reacted with boiling methanol with a catalyst to obtain polyols for polyurethane synthesis. Linseed oil derived polyurethane showed the higher glass transition and tensile strength, and the lowest elongation at break; which can be related with the high functionality of the obtained polyols.[40] It is noteworthy that the thermal stability of the polyurethanes obtained using this strategy was better than that for polypropylene oxide-based polyurethane both in nitrogen and air atmospheres.[41]

Other polyols based on the ring opening of epoxidized vegetable oils have been studied and characterized. The polyols obtained by opening with HBr, HCl or hydrogenation were compared to that opened with methanol. The physical and chemical properties of the polyols were different depending on the ring opening involved, and also the properties of the polyurethanes synthesized from them. Moreover, different characteristics can be introduced

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[39] a) Z. S. Petrovic, M. Ionescu and I. Javni, U. S. Patent Application 20090082483 (2009). b) S. Gryglewicz, W. Piechocki and G. Gryglewicz, Bior. Tech., 2003, 87, 35-39.

[40] A. Zlatanic, C. Lava, W. Zhang and Z. S. Petrovic., J. Polym. Sci. Part B: Polym. Phys., 2004, 42, 809-819.

[41] I. Javni, Z. S. Petrovic, A. Guo and R. Fuller, J. Appl. Polym. Sci., 2000, 77, 1723-1734.

in the polyurethane depending on the reagent used in the ring opening. Thus, halogen containing polyurethanes show flame retardant properties.[42]

The influence of the isocyanate in the final properties of the polyurethane has been also studied for soy-polyol obtained by ring opening with methanol. The properties of the polyurethane strongly depend on cross-linking density and the structure of isocyanate. Thus, the highest density, glass transition, modulus and tensile strength were obtained for aromatic triisocyanate; while, aliphatic isocyanates gave rubbery materials with the highest elongation at break and swelling.[43]

The above mentioned vegetable oil-based polyurethanes have two main drawbacks, the first one is that the employed hydroxyl groups are secondary and their reactivity is three times lower than primary alcohols. The second one is the presence of dangling chains due to the internal position of the ethylene group in the fatty acid and the presence of a small proportion of saturated fatty acid. In order to obtain primary hydroxyl groups in the fatty acid chain, hydroformylation with a mixture of CO and H_2 gas in presence of either rhodium or cobalt as catalyst has been described. The obtained aldehyde derivative yields, with a subsequent reduction, the primary hydroxyl groups (Scheme 7).[44] By reaction of the secondary hydroxyl groups, obtained in the ring opening of epoxidized soybean oil with methanol, with ethylene oxide in presence of HBF_4 as catalyst, primary hydroxyl groups are also achieved.[45]

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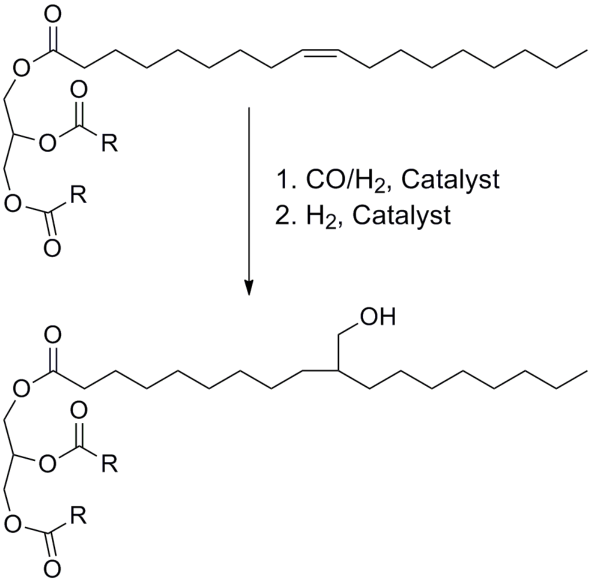
[42] A. Guo, Y. Cho and Z. S. Petrovic, J. Polym. Sci. Part A: Polym. Chem., 2000, 38, 3900-3910.

[43] I. Javni, W. Zhang and Z. S. Petrovic, J. Appl. Polym. Sci., 2003, 88, 2912-2916.

[44] a) A. Guo,D. Demydov, W. Zhang and Z. S. Petrovic, J. Polym. Environ., 2002, 10, 49-52. b) Z. S. Petrovic, A. Guo, I. Javni, I. Cvetkovic and D. P. Hong, Polym. Int., 2008, 57, 275-281.

[45] M. Ionescu, Z. S. Petrovic and X. Wan, J. Polym. Environ., 2007, 15, 237-243.



Scheme 7. Polyol synthesized by hydroformylation and reduction process.

Ozonolysis of vegetable oils produces aldehyde functionalities that by posterior reduction yield a polyol with almost three hydroxyl groups per molecule, except for saturated fatty acids in the oil (Scheme 8). This ozonolysis procedure has been successfully applied to soybean oil, castor oil, canola oil and triolein, and the polyurethanes derived from them displayed improved mechanical properties and higher glass transition temperature compared with those obtained by ring opening of the epoxidized oil. The improvement in the properties of these polyurethanes is not only due to the primary hydroxyl groups but also because dangling chains are almost avoided.[46] Triolein metathesis with ethylene and Grubbs catalyst produces a triglyceride with terminal double bonds, which can be epoxidized and the ring opening of oxiranes yield the polyols without dangling chains. Polyurethanes obtained in this way increase the glass transition temperature by about 6 °C, and improve the solvent resistance of the resulting materials.[47]

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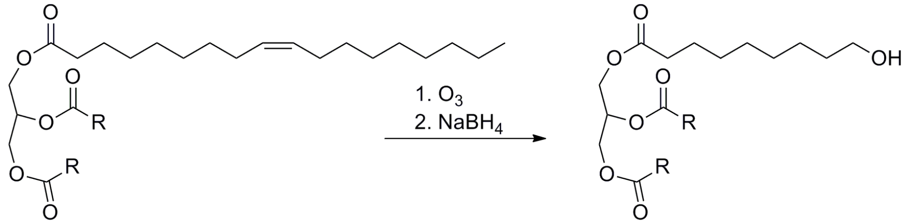
[46] a) Z. S. Petrovic, W. Zhang and I. Javni, Biomacromolecules, 2005, 6, 713-719. b) X. Kong and S. S. Narine, Biomacromolecules, 2007, 8, 2203-2209. c) X. Kong and S. S. Narine, Biomacromolecules, 2008, 9, 2221-2299.

[47] A. Zlatanic, Z. S. Petrovic and K. Dusek, Biomacromolecules, 2002, 3, 1048-1056.



Scheme 8. Synthesis of polyols by ozonolysis and reduction of triglycerides.

Other polyurethanes have been synthesized starting from fatty acid derivatives. The cationic ring opening polymerization of epoxidized methyl oleate and subsequent partial reduction of ester groups gave primary alcohols. Depending on the degree of reduction, polyols of different hydroxyl values were obtained. Those polyols were reacted with MDI and L-lysine diisocyanate to yield polyurethanes.[48] Methyl 10-undecynoate and methyl 9-octadecynoate, which were obtained from undecylenic acid and oleic acid by bromination and dehydrobromination were used to prepare aromatic triols. The triols were obtained by a transition-metal-catalyzed cyclotrimerization followed by the reduction of the ester groups (Scheme 9). To synthesize polyurethanes with these polyols, MDI was used as diisocyanate and butanediol as chain extender; and all of them presented glass transition temperatures above room temperature, increasing with the hard segment proportion.[49]

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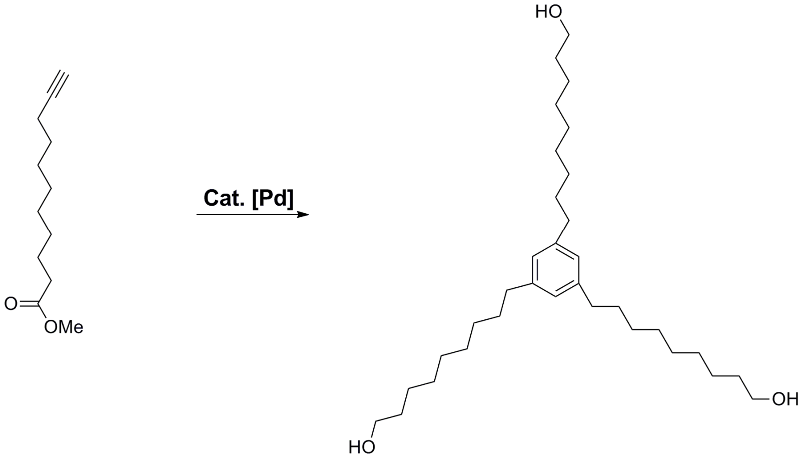
[48] a) G. Lligadas, J. C. Ronda, M. Galià, U. Biermann and J. O. Metzger, J. Polym. Sci. Part A: Polym. Chem., 2006, 44, 634-645. b) G. Lligadas, J. C. Ronda, M. Galià and V. Cádiz, Biomacromolecules, 2007, 8, 686-692.

[49] G. Lligadas, J. C. Ronda, M. Galià and V. Cádiz, Biomacromolecules, 2007, 8, 1858-1864.



Scheme 9. Polyol obtained by cyclotrimerization of methyl 10-undecinoate.

Thermoplastic polyurethanes have been synthesized entirely from fatty acid derivatives. Self metathesis of oleic acid with second generation Grubbs catalyst leads to an α,ω-diacid, which under reduction using $LiAlH_4$ yields 1,18-octadec-9-endiol. This diol was reacted with different diisocyanates to obtain thermoplastic polyurethanes. It is noteworthy, that the polyurethane synthesized with a diisocyanate based in fatty acid presented similar properties to those from commercial ones.[50] A polyester diol has been synthesized by reaction between methyl ricinoleate and diethylene glycol. This polyester was used as soft segment in the preparation of segmented polyurethanes (Figure 6).[51]

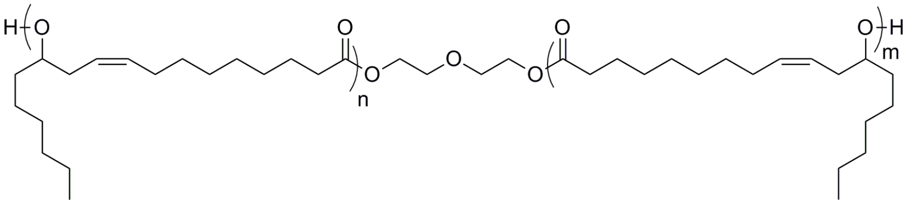


Figure 6. Polyesterdiol obtained by esterification of methyl ricinoleate and diethylene glycol.

Although most of polyurethanes synthesized from vegetable oils use petroleum-based isocyanates, there are some examples where the isocyanate

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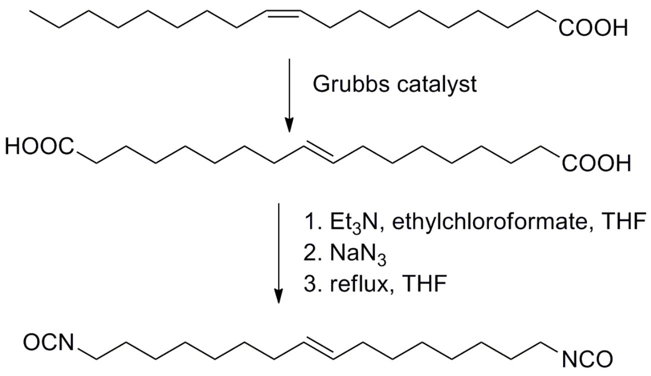
[50] L. Hojabri, X. Kong and S. S. Narine, Biomacromolecules, 2010, 11, 911-918.
[51] Y. Xu, Z. S. Petrovic, S. Das and G. L. Wilkes, Polymer, 2008, 49, 4248-4258.

is derived from vegetable oils. Küsefoglu et al. reported two synthetic routes to incorporate isocyanate moieties into soybean oil. In two steps, brominating the allylic position of the triglyceride, and then, reacting with AgNCO; in this manner the isocyanate groups per triglyceride were found to be 2.1.[52] The second way was treating soybean oil with iodine isocyanate, achieving 3.1 isocyanate groups per triglyceride.[53] Beside to these isocyanates, the synthesis of isothiocyanate derivatives has been also described.[54]

Diisocyanates derived from diacids obtained from oleic acid have been synthesized by Narine et al. via two-steps Curtius rearrangement. The self-metathesis of oleic acid with Grubbs catalyst yielded 1,18-octadec-9-enedioic acid that was converted into diisocyanate derivative by the above mentioned Curtius rearrangement (Scheme 10).[55]



Scheme 10. Synthesis of 1,18-octadec-9-enediisocyanate from oleic acid.

The high versatility offered by vegetable oil derivatives in the chemical industry, and specially, in the polymer chemistry has stimulated the development of a high number of works.

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[52] G. Çayll and S. Küsefoglu, J. Appl. Polym. Sci., 2008, 109, 2948-2955.
[53] G. Çayll and S. Küsefoglu, J. Appl. Polym. Sci., 2010, 116, 2433-2440.
[54] G. Çayll and S. Küsefoglu, J. Appl. Polym. Sci., 2010, 116, 125-131.
[55] a) L. Hojabri, X. Kong and S. S. Narine, Biomacromolecules, 2009, 10, 884-891. b) L. Hojabri, X. Kong and S. S. Narine, J. Polym. Sci. Part A: Polym. Chem., 2010, 48, 3302-3310.

Scope and Objectives

Scope and Objectives

As explained in the introduction, research into the industrial exploitation of products derived from renewable resources is of great importance from both environmental and economical aspects. In particular, the development of polymeric materials from renewable resources is receiving considerable attention since the availability of crude oil will become severely restricted within the foreseeable future. The replacement of crude oil by renewable raw materials is also consistent with the aim of global sustainability.

The main objective of this thesis was to develop new biobased polyurethanes from vegetable oil derivatives as renewable resources. To achieve this goal, the experimental work focused on exploiting the reactivity of unsaturated fatty acid compounds to prepare a set polyols for polyurethane synthesis by using different synthetic metodologies. The specific objectives were:

- To synthesize and characterize polyether polyols through the ionic-coordinative catalyzed ring opening polymerization of epoxidized methyl oleate and the subsequent partial reduction of the pendant ester groups

- To synthesize lineal polyols by ADMET polymerization of 1,3-di-10-undecenoxy-2-propanol

- To synthesize branched polyols by ATMET polymerization of glyceryl triundec-10-enoate

- To synthesize poly-2-oxazoline polyols by cationic ring opening polymerization of fatty acid derived 2-oxazolines and further tiol-ene click coupling of pendant double bonds with mercaptoethanol

- To apply these polyols to the synthesis of thermosetting segmented and non segmented polyurethanes by using 4-4'-methylene-bis(phenyl isocianate) or L-lysine diisocyanate as coupling agents and 1,3-propanediol as chain extender.

The thesis is organized in three chapters. The first describes the synthesis and characterization of polyether polyols and the obtention of the corresponding polyurethane derivatives. The experimental procedures and the results of the studies performed for this chapter have been published in Journal of Polymer Science PartA: Polymer Chemistry, 2010, 48, 4995-5008 and Journal of Polymer Science PartA: Polymer Chemistry, 2010, 48, 5009-5017.

The second chapter is focused on the ADMET and ATMET polymerizations of fatty acid-derived α,ω-dienes and trienes to obtain polyols. Polyurethanes with promising properties as shape memory materials have been obtained from these polyols. The results of this study have been published in Journal of Polymer Science PartA: Polymer Chemistry, 2011, 49, 518-525, and have been submitted to Macromolecular Chemistry and Physics.

The last chapter deals with the synthesis of polyoxazoline-polyols, which have also been applied to the synthesis of polyurethanes. The work corresponding to this part has been submitted for publication to Journal of Polymer Science PartA: Polymer Chemistry.

CHAPTER I

Polyurethanes from polyether-polyols synthesized by ring opening polymerization of epoxides

RING OPENING POLYMERIZATION OF EPOXIDES

Ring-opening polymerization of cyclic ethers is historically one of the oldest examples of the formation of macromolecules. The first synthesis of oligomers of ethylene oxide by Wurtz dates back to 1863.[56] Extensive and systematic investigation by Staudinger (1929)[57] on the polymerization of ethylene oxide was made in the very early stage of the establishment of polymer chemistry. Polymerizations of propylene oxide by Levene (1927)[58] and tetrahydrofuran by Meerwein (1937)[59] were also first reported at that time.

In pararell with the development of the petrochemical industry, which enabled the production of ethylene oxide and propylene oxide on a large scale, polymers and oligomers from these epoxides have become one of the most important products of the synthetic chemical industry. Polyethers have found important applications as surfactants, plasticizers, adhesives, coatings, and as raw materials for the manufacture of polyurethane elastomers, foams, etc. Polyepichlorohydrin and its copolymers are also produced industrially as a rubber. The polymer derived from the 4-membered cyclic ether, 3,3-bis(chloromethyl)oxetane, is also important as an engineering plastic. Hydroxyl terminated telechelic polymers and oligomers of tetrahydrofuran are now used in making polyurethanes.

Two main features are responsible of the reactivity of cyclic ethers in ring opening polymerization (ROP), the presence of an oxygen atom in the ring and the tension resulting from the requirements imposed by the ring size. In Table 1 are shown the ring strain values for some typical cyclic ethers. Three member cyclic ethers or epoxides are the most tensioned and therefore, the most reactive. As the ring size increases the cyclic ethers become more stable and less reactive.

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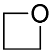
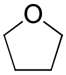
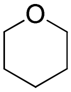
[56] A. Wurtz, Ann. Chim, Phys., 1863, 69, 330-334.

[57] a) H. Staudinger and O. Schweitzer, Ber. Deutsch Chem. Ges., 1929, 62, 2395-2405. b) H. Staudinger and H. Lohmann, Justus Liebigs Ann.Chem., 1933, 505, 41-51.

[58] P. A. Levene and A. Walti, J. Biol. Chem., 1927, 75, 325-336.

[59] H. Meerwein, German Patent, 741478 (1937).

Table 1. The ring strain of typical cyclic ethers.

Cyclic ether	Structure	Ring strain (kJ mol^{-1})
Oxirane (ethylene oxide)		114
Oxetane (trimethylene oxide)		107
Oxolane (tetrahydrofuran)		23
Oxane (tetrahydropyran)		5

The angle of the unperturbed C-O-C bond is close to 110°, whereas in ethylene oxide it is equal to 60°. Moreover, the reaction of the oxyranic oxygen with electrophylic reagents or Lewis acids leds to a tricoordinated oxygen in which the C-O-C angle is close to 120°, thus protonation (as well as alkylation) of oxirane rings leads to an even increased ring strain.

In the cyclic ethers polymerization process the ring tension is liberated shifting the equilibrium to the formation of the polyether. As the ring strain is the driving force in the polymerization reaction, epoxide groups are the most reactive monomers, and the only ones that, with some exceptions, can be polymerized by the three different existing ionic mechanisms, cationic, anionic and ionic-coordinative, which is not true for higher cycles.

In the three ionic mechanisms, which are produced using different catalysts, the ring opening involves a S_N2 substitution by attack over the oxyranic carbons but differs basically in the species that promotes this attack.

a) Cationic ring opening polymerization

The cationic ring opening polymerization is promoted by protic or Lewis acids or alkylating agents alone or in presence of water or alcohol.[60] The main reaction is the formation of a cyclic oxonium ion that enhances the reactivity towards weak nucleophyles like the oxyranic oxygen which is the actual nucleophyle that starts the propagation. This process is usually

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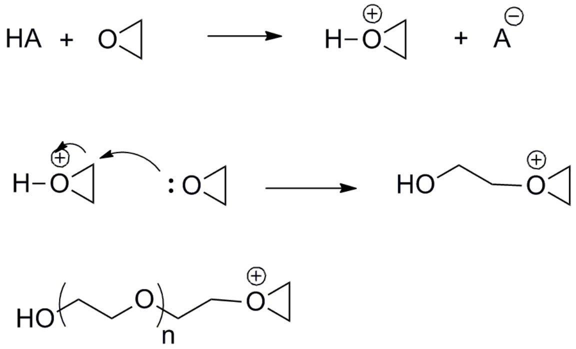
[60] a) S. Penczek, P. Kubisa and K. Matyjaszewski, Adv. Polym. Sci., 1980, 37, 1. b) S. Penczek, P. Kubisa, and K. Matyjaszewski: Cationic Ring-Opening Polymerization. Springer Verlag; Berlin 1980; ISBN: 3-540-10209-4.

complicated by the existence of various by-side reactions such as depolymerization and back-biting reactions that generally limits the polymer molecular weight and produces variable amounts of cyclic structures. Moreover, in cationic polymerization the ring opening can succeed indistinctly by attack to both oxiranic carbons leading to regioirregular structures.

Depending of the initiator system used the propagation step can proceed following two different mechanisms, known as "activated chain end" mechanism (ACE) and "activated monomer mechanism" (AM).

Activated chain end mechanism (ACE)

The ACE mechanism (Scheme 1) is characteristic for protic and Lewis acid initiators. In the initiation step the monomer is activated by reaction with the acid leading to an oxonium ion that is attacked by the oxygen of other monomeric unit.[61] The new resulting oxonium ion follows the chain propagation by successive reaction with other monomeric units. In this way, the active specie remains always in the propagating extreme of the polymeric chain.



Scheme 1. Activated chain end mechanism in cationic ROP.

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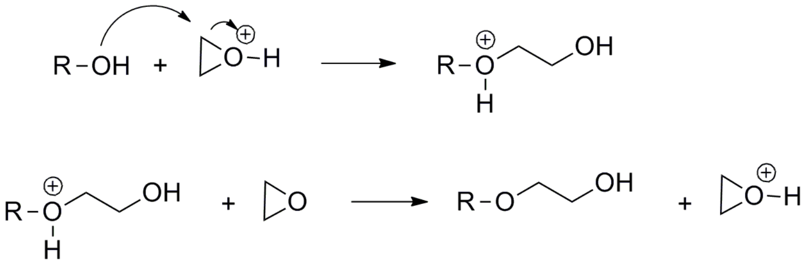
[61] H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willfang, J. Prakt. Chem., 1939, 154, 83-156.

Activated monomer mechanism (AM)

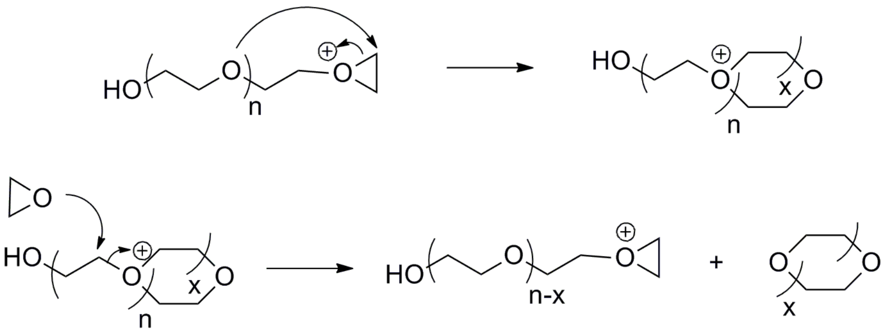
The AM mechanism (Scheme 2) is characteristic for acids in presence of water or alcohols.[62] In the AM mechanism, after the initial protonation of the monomer, a hydroxyl group instead of the oxyranic oxygen, attacks the oxoniun ion producing a protonated alcoholic specie which transfers the proton to a new monomeric molecule leading a new activated monomer which starts again the process.



Scheme 2. Activated monomer mechanism in cationic ROP.

Back-biting processes

The back-biting is produced when, in the ACE mechanism, an oxygen from the polymeric chain acts as the nucleophile atom (Scheme 3). The intramolecular oxygen attack to the electrophile produces a cyclic oxonium ion which is attacked by another monomer to generate new active chain end species and liberating a cyclic structure. Therefore, back-biting processes originate cyclic structures which are normally not desired.



Scheme 3. Cycle formation by back-biting in cationic ROP.

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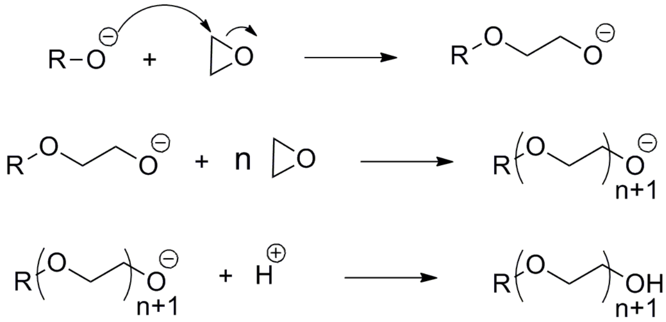
[62] S. Penczek, P. Kubisa K. Matyjaszewski and R. Szymansky, Pure Appl. Chem., 1984, 140.

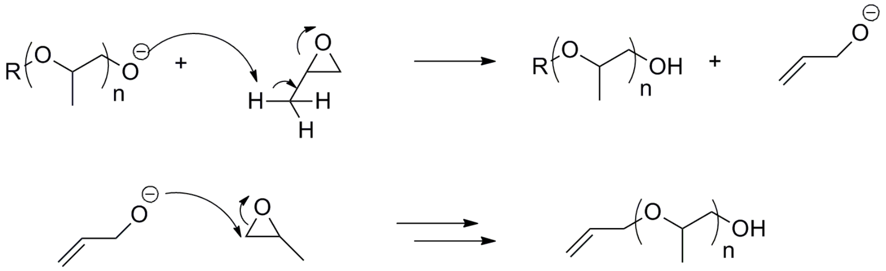
b) Anionic ring opening polymerization

The anionic polymerization is promoted by compound with strong basic and nucleophylic character like alkaline oxides, hydroxides, alkoxides and some organometallic compounds.[63] In this case the initiation is produced by direct attack of the nucleophilic initiator directly over the oxirane ring (Scheme 4). This initiation process results in an alcoholate that can act as nucleophile in the next ring opening step resulting in the propagation of the chain.



Scheme 4. Anionic mechanism in ROP.

In the case of ethylene oxide this polymerization has living character allowing the control of the molecular weight by tuning the initiator/epoxide ratio. However, for higher monomers the relative acidity of the protons in α-position to the epoxide lead to chain transfer side reactions by reaction with the initiator or with the growing chain ends (Scheme 5), leading to a decrease in the molecular weight and the formation of unsaturated ends.



Scheme 5. Chain transfer to monomer in anionic ROP.

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[63] D. J. Brunelle. Ring Opening Polymerization/Mechanisms, Catalysis, Structure, Utility. Ed; Carl Hanser Verlag: Munich, 1993.

As the anionic polymerization proceeds following a S_N2 process, the ring opening succeeds almost exclusivelly by attack to the less hindered position of the oxiranic ring leading to highly regioregular polymers and in some specific cases to stereoregular polymers.

c) Ionic-coordinative ring opening polymerization

The mechanism of coordinative ring opening polymerization has been described in the literature as a coordination insertion process and is considered by some authors as a specific case of the anionic polymerization. This polymerization is produced mostly by complex oxoalcoxide species produced by combination of metal alkyls or salts with water, alcohols, porphirins and some chelating compounds. The monomer is coordinated to a metallic centre enhancing the electrophility of the epoxide group, then, a nucleophile group initiates the polymerization. The polymeric chain remains bonded to the metallic center by the oxygen, and is this atom which attacks to a new monomer molecule coordinated to another metallic center. The polymeric chain gets anchored to a new metallic center, and the other center reamains free for the coordination a new monomer molecule.

This mechanism was proposed by Vandenberg explaining the formation of a stereospecific polymer.[64] Ideally, the growing chain moves alternatively between two vicinal metallic active sites in a known as “flip-flap” mechanism (Scheme 6).

The ionic coordinative polymerization shares characteristics of the anionic and the cationic polymerization and produces high molecular weight regioregular polymers with variable percentages of stereoregularity.

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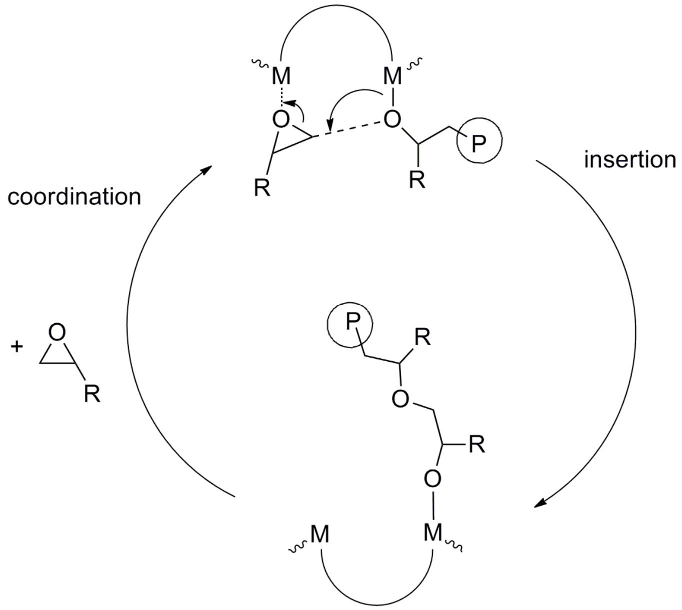
[64] E. J. Vandenberg, J. Polym. Sci., 1960, 47, 486-489.



Scheme 6. Proposed mechanism of the coordinative ROP.

Ring Opening Polymerization of vegetable oil-based epoxides

Epoxide polymerization has been traditionally focused in petroleum-based epoxides, as ethylene oxide and propylene oxide for the synthesis of polyetherpolyols, which are especially used for the production of polyurethane foams. However, due to environmental concerns, the polymerization of renewable epoxides has become a topic of study for some chemists. Vegetable oil-based epoxides are one of the most used renewable monomers because of its easy synthesis and the availability of the starting unsaturated triglycerides. The double bonds are easily converted into an epoxide group in several ways such as using m-chloroperbenzoic acid, Prilezhaev epoxidation or, more environmentally friendly, chemo-enzymatic epoxidation. However, polyethers from long chain or functionalized epoxides are rare because of the lack of reactivity regarding their high sterical hindrance that prevents the interaction with the catalyst sites.

In 1992 Crivello and Narayan published a study of ring opening polymerization of various epoxidized triglycerides.[65] The commercially available triglycerides were epoxidized in two different ways, with acetic acid and H_2O_2 in presence of Amberlite IR 120 resin, and with H_2O_2 and methyltrioctylammonium (diperoxotungsto) phosphate as phase-transfer catalyst. The epoxidized triglycerides were cationically photopolymerized using diaryliodonium and triarylsulfonium salt photoinitiators. The polymers obtained as thin films presented good adhesion and mechanical properties.

Vogl et al. have reported the epoxidation and subsequent polymerization of methyl 10-undecenoate.[66] The polymerization was carried out using the Vandenberg catalyst. This coordinative initiating system is composed by $Al(C_2H_5)_3/H_2O/AcAc$ (1.0/0.5/1.0). The polyether obtained, which have pendant methyl ester groups, were hydrolyzed with the aim to obtain (polyalkylene oxide) ionomers.

Using a similar ionic-coordinative initiator system Warwel et al. have studied the ROP of different monomers derived from 10-undecenoic acid.[67] Initiator systems used were a combination of commercially available aluminoxanes and acetyl acetone. Methylaluminoxane (MAO) and tetraisobutylaluminoxane (TIBAO) were chosen as aluminoxane to polymerize the epoxide monomers shown in Scheme 7. The comb-like polyethers and copolyethers obtained had high molecular weight (M_w = 1.5-2.9 x 10^5), which was dependent of the initiator system and of the functionality of the monomers.

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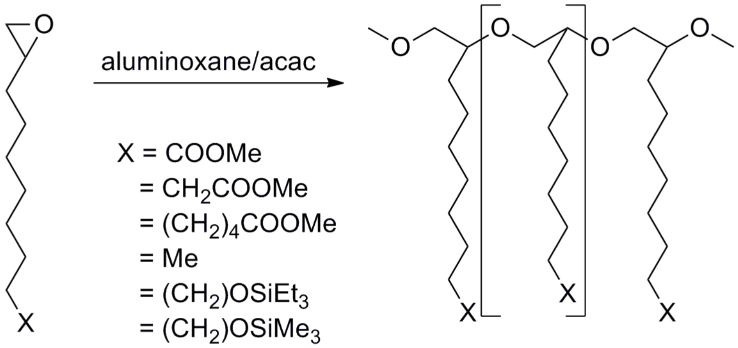
[65] J. V. Crivello and R. Narayan, Chem. Mater., 1992, 4, 692-699.

[66] a) J. Muggee and O. Vogl, J. Polym. Sci., Polym. Chem. Ed., 1984, 22, 2501-2521. b) J. Muggee and O. Vogl, J. Polym. Sci., Polym. Chem. Ed., 1985, 23, 649-671. c) D. A. Bansleben and O. Vogl, J. Polym. Sci., Polym. Chem. Ed., 1985, 23, 673-701.

[67] S. Warwel, B. wiege, E. Fehling and M. Kunz, Eur. Polym. J., 2000, 36, 2655-2663.



Scheme 7. Coordinative ROP of long chain monomers with terminal epoxides

Although terminal epoxides have demonstrated to be very reactive in ROP, only few less reactive internal epoxides have been polymerized in order to obtain vegetable oil-based polyethers. Warwel et al. have published the study of the polymerization of epoxidized methyl oleate with a iodonium salt based photoinitiator (Scheme 8).[68] The polymer obtained presented a high proportion of cyclic oligomers via back-biting reactions; this macrocyclization was suppressed by addition of water or ethylene glycol, yielding diol-oligoethers with molecular weights of approximately 1.300 g/mol. Lligadas et al. obtained the polyethers by cationic ROP of epoxidized methyl oleate using $HSbF_6$ as initiator; the methyl ester groups of the polyether were partially reduced to be applied in polyurethane synthesis.[69]

In recent years there has been a considerable focus on the preparation of polyols and polyurethanes from fatty acids and oils, but limited attention has been paid to the preparation of polyether polyols from these compounds, particularly to higher molecular weight polyols. The purpose of the work described in this chapter was to develop and apply a new family of polyether polyols derived from epoxidized methyl oleate in the synthesis of polyurethanes for use in specific applications. The molecular structure has been elucidated using NMR spectroscopy and MALDI-TOF-MS analysis.

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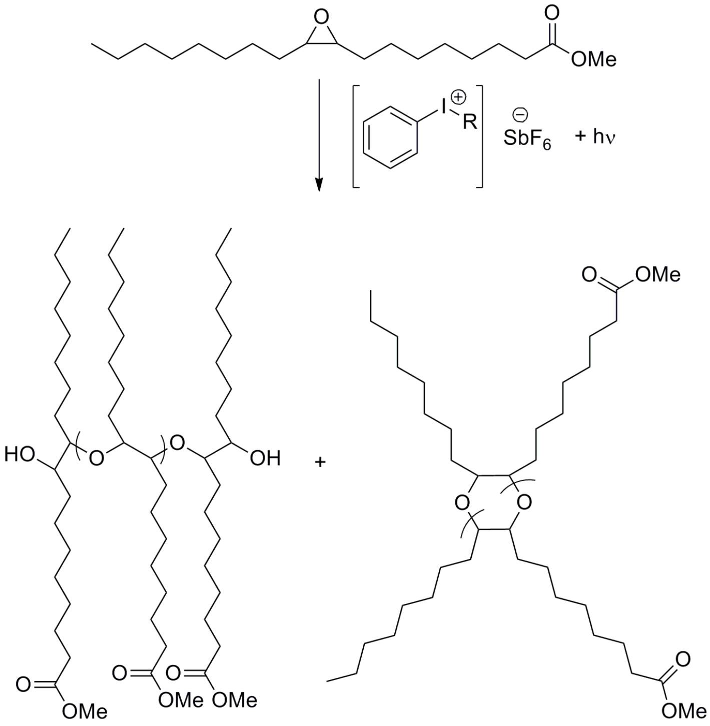
[68] S. Warwel, E. Fehling and M. Kunz, Eur. J. Lipid Sci. Technol., 2001, 103, 133-140.

[69] G. Lligadas, J. C. Ronda, M. Galià, U. Biermann and J. O. Metzger, J Polym. Sci. Part A: Polym. Chem., 2006, 44, 634-645.



Scheme 8. Photoinitiated cationic ROP of epoxidized methyl oleate.

The partial reduction of the methyl ester groups led to a family of polyether-polyols, which was reacted with MDI and LDI in order to obtain polyurethane networks with different T_g values and mechanical properties. Adding 1,3-propanediol as chain extender to the reaction mixture, two different families of segmented polyurethanes were achieved.

Polymerization of epoxidized vegetable oil derivatives: Ionic-coordinative polymerization of methylepoxyoleate

Polymerization of epoxidized vegetable oil derivatives: ionic-coordinative polymerization of methylepoxyoleate

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Summary

Ring opening polymerization of epoxidized methyloleate (EMO) with various ionic-coordinative initiators have been studied and compared to other internal epoxy monomers: benzyl 9,10-epoxyoleoylether (BEO) and cis-4,5-epoxyoctane (EO). The structure and molecular weight of the resulting polymers have been studied by ^{1}H and ^{13}C NMR, MALDI-TOF-MS and SEC analysis. Polymers with higher molecular weight than those obtained with conventional cationic catalyst are obtained. These materials have been found to consist of a complex mixture of cyclic and linear polymer chains with different chain ends that can be related to the catalyst nature and the occurrence of two main polymerization mechanisms, the cationic and the ionic-coordinative. In the polymerization of EMO, transesterification by side-reactions leading to ester linkages in the main chain have been identified. These undesired reactions have been suppressed by copolymerization with small amounts of THF with no substantial decrease in the polymer yield and molecular weight. Finally, the polymerization of EMO has been tested in a larger scale in order to prepare a renewable resource-based polyether as starting material to produce polyether-polyols for polyurethane applications.

Introduction

Sustainable development has become the key ideal of the 21st century. In the search for sustainable chemistry, considerable importance is being attached to renewable raw materials, which exploit the synthetic capabilities of nature and may eventually substitute fossil and depleting feedstocks.[1] Oils and fats of vegetable and animal origin make up the greatest proportion of the current consumption of renewable raw materials in the chemical industry because of their availability, structural variety and chemical

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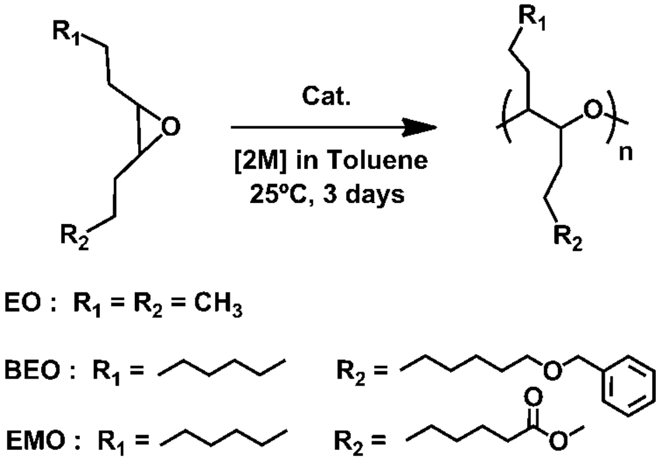
versatility. Vegetable oils containing unsaturated fatty acids can be used in polymerizations to make biobased polymers.[2-5] Moreover, numerous fatty acids are now available in a purity that makes them attractive for synthesis and as raw materials for the chemical industry.[6] Although they possess double bonds, which are used as reactive sites in coatings, they cannot be converted easily to high-molecular-weight products without the introduction of more reactive functional groups, such as hydroxyl, epoxy, or carboxyl groups. Epoxidation is one of the most important functionalization reactions of the C=C double bond. The chemistry of the Prileshajev epoxidation of unsaturated fatty compounds is well known,[7,8] but many other epoxidation methods have been described.[9-13] Epoxidized fatty acids are suitable monomers for ring-opening polymerizations.[14] The preparation of polyols from fatty acids and oils for general polyurethane use has been the subject of many studies[15-17] however, limited attention has been paid to the preparation of polyether polyols. Polyether polyols with molecular weights of 200–10000 g/mol[18] are important building blocks for polyurethane applications. Polyether polyols are usually produced by the anionic ring-opening polymerization of alkylene oxides, such as ethylene oxide or propylene oxide. In contrast, polyether polyols from longer chain or functionalized epoxides are rare because of their lower reactivity due to a higher sterical hindrance, interaction with the catalyst sites and the occurrence of side reactions. The cationic ring-opening polymerization of higher epoxides usually leads to low-molecular-weight polyethers due to the occurrence of backbiting processes but has been applied in the case of terminal epoxidized fatty compounds.[19-21] The polymerization of internal epoxidized fatty acid derivatives such as epoxidized methyloleate (EMO) is expected to proceed in a more difficult way due to the higher steric demand of the epoxy groups. However, the resulting comb-like polyethers having side chain ester groups can be used to produce fully renewable polyethers with varying amounts of primary hydroxyl groups by controlled reduction of the ester groups. We have already used this methodology to synthesize low molecular weight polyols from methyl epoxy oleate that were used to prepare rigid polyurethanes.[22] The cationic polymerization of EMO led to polyethers with maximum molecular weight of 1200 Da hence, achieving high molecular weight renewable polyether-polyols suitable for the preparation of flexible polyurethanes is still a challenge that excludes the use of either cationic or anionic catalysts.

Coordinative ring-opening polymerization of epoxides has been intensively studied since the late 1950s and various coordinative catalysts mainly based on aluminum and zinc alkyls have been developed.[23-25] Some of these initiating systems also allow the polymerization of epoxides having additional functional groups in the molecule. Polymers from phenylglycidylethers, which contain methyl ester groups of different chain lengths in the para position, were synthesized by Ronda et al.[26] Shih et al.[27] studied the polymerization of 4,5-epoxypentanol esters whereas Vogl and coworkers described the polymerization of ω-epoxy alkanoates using the so-called “Vandenberg'' catalyst.[28-30]

Hydrolysis or solvolysis of organoaluminum compounds generally leads to complex product mixtures, which are highly dependent on the reaction conditions. To avoid uncertainty concerning the catalyst preparation, similar catalyst systems based on commercially available aluminoxanes have also been described.[31] In this way, catalyst systems based on methyl aluminoxane (MAO) and tetraisobutyldialuminoxane (TIBAO) have been used to polymerize ω-C10, C11 and C14 epoxy carboxylic acid methyl esters, 1,2-decene oxide, silylated 10,11-epoxyundecanol, 9-decenoic and 13-tetradecenoic methyl esters monomers.[32]

Until now, the ionic-coordinative ring-opening polymerization of internal epoxidized fatty acid has not received much attention, so, in this article, we report the synthesis and characterization of polyethers from methyl 9,10-epoxyoctadecenoate (epoxidized methyloleate, EMO), as precursors for high molecular weight renewable polyether polyols. The polymerization of benzyl 9,10-epoxyoctadecenylether (BEO) and 4,5-epoxyoctane (EO) as model monomers has been also considered. (Scheme 1)



Scheme 1. Chemical structures of monomers and polyethers.

Experimental

Materials

Benzyl chloride 99%, tetrabutylammonium hydrogen sulfate (TBAH) and triflouroacetic anhydride (TFAA) were purchased from Fluka. Methyl oleate 99%, oleoil alcohol (85%), 3-chloroperbenzoic acid (MCPBA), H_2O_2 30%, triethylaluminum 25 wt.% (1.9 M) solution in toluene, tetraisobutyldialumin-oxane (TIBAO), 10 wt.% solution in toluene and triisobutylaluminium 25 wt. % (1.0 M) solution in toluene were purchased from Aldrich and used as received. Methyl oleate 90plus® was kindly supplied by T+T Oleochemie, cis-4-octene 97% were purchased from Alfa Aesar. Anhydrous sulfur free toluene, diethyl ether and THF were prepared by refluxing with sodium/benzophenone.

Synthesis of benzyl-9-octadecenylether

In a 500 ml round bottom flask 97 g (0.36 mol) of oleyl alcohol, 57 g (0.45 moles) of benzyl chloride, toluene (100 ml), 6.1 g (0.018 moles, 5 mol %) of TBAH and 40 ml (0.5 mol) of 50% (w/w) aqueous solution of NaOH were introduced. The mixture was stirred vigorously at rt. and the reaction was followed by TLC until completion (24 h). The organic layer was decanted and washed several times with water, 5% HCl, 5% $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give a yellow liquid that was fractionated under vacuum. The fraction between 160-162 °C (0.1 mmHg) was collected as a colorless oil (92 g , yield 71%)

^{1}H NMR ($CDCl_3$, TMS, δ in ppm): 7.45-7.35 (2 H, m, *o*-ArH), 7.35-7.25 (3 H, m, *m,p*-ArH), 5.50-5.35 (2 H, m, -CH=CH-), 4.55 (2 H, s, -OCH_2Ar), 3.52 (2 H, t, *J* = 6.6 Hz, -CH_2-O-Bn), 2.2-2.0 (4 H, m, -$\underline{CH_2}$-CH=), 1.8-1.6 (2 H, m, -$\underline{CH_2}$-CH_2-O-), 1.6-1.2 (m, Aliphatic backbone), 0.95 (3 H, -CH_3).

^{13}C NMR ($CDCl_3$, TMS, δ in ppm): 138.9 (-CH_2-$\underline{C}$Ar), 130.2 and 130.1 (-C=C-), 128.6 (m-Ar), 127.9 (o-Ar), 127.7 (p-Ar), 73.1 (-O-$\underline{C}H_2$-Ar), 70.8 (-$\underline{C}H_2$-O-CH_2Ar), 32.9 (-$\underline{C}H_2$CH=CH-), 32.2 (-$\underline{C}H_2$-CH_2-CH_3), 31-29 (Aliphatic backbone), 27.5 (-$\underline{C}H_2CH_2$CH=CH-), 26.5 (-$\underline{C}H_2$-CH_2-O-CH_2Ar), 23.0 (-$\underline{C}H_2$-CH_3), 14.4 (-CH_3).

Synthesis of EO, BEO and EMO.

Methyl oleate 99% (25 g, 0.084 mol), methyl oleate 90% (89 g, 0.30 mol) and bencyloleylether (36 g, 0.10 mol) were epoxidized with H_2O_2 (16%) using a quaternary ammonium tetrakis(diperoxotunstato)phosphate catalyst[33,34] and following a procedure described by Venturello.[35] EMO and BEO were purified by crystallization in 10 ml/g of acetone at -18 °C twice, filtration over a short path of silica gel using hexane/ethyl acetate 8/1 as eluent, concentrated and finally dried under vacuum for 48 h at 40 °C to yield transparent colorless oils.

EMO from 99% methyl oleate 20.6 g (78%) purity 98% (GC)

EMO from 90% methyl oleate 67.5 g (72%) purity 94% (GC)

BEO 26.6 g (71%) purity 96% (GC)

4-cis-octene (20 g, 0.178 mol) was epoxidized with dry mCPBA in DCE following a reported procedure.[36] 4-Epoxi-octene was distilled over calcium hydride at reduced pressure collecting the fraction boiling at 47-48 °C (2 mmHg) (literature 95 °C/60 mbar)[37] which was stored under argon. Yield 18.7 g (82%) purity 98% (GC).

BEO

^{1}H NMR ($CDCl_3$, TMS, δ in ppm): 7.45-7.35 (2 H, m, *o*-ArH), 7.35-7.25 (3 H, m, *m,p*-ArH), 4.51 (2 H, s, -OCH_2Ar), 3.47 (2 H, t, *J* = 6.6 Hz, -CH_2-O-Bn), 2.91 (2 H, m, epoxide), 1.7-1.5 (2 H, m, -C$\underline{H_2}$-CH_2-O-), 1.5-1.2 (m, Aliphatic backbone), 0.90 (3 H, t, -CH_3).

^{13}C NMR ($CDCl_3$, TMS, δ in ppm): 138.3 ($-CH_2-\underline{C}Ar$), 128.5 (m-Ar), 127.7 (o-Ar), 127.6 (p-Ar), 73.0 ($-O-\underline{C}H_2-Ar$), 70.6 ($-\underline{C}H_2-O-CH_2Ar$), 57.4 (-CHO), 32.0 ($-\underline{C}H_2-CH_2-CH_3$), 30.5-28.5 (Aliphatic backbone), 28.0 ($-\underline{C}H_2-CHO$), 26.8 ($-\underline{C}H_2-CH_2-CHO$), 26.3 ($-\underline{C}H_2-CH_2-O-CH_2Ar$), 22.8 ($-\underline{C}H_2-CH_3$), 14.3 ($-CH_3$).

Catalysts

Tetraisobutyldialuminoxane (TIBAO) 25 wt.% in toluene catalyst was used as received.

Tetraisobutyldialuminoxane/triisobutylaluminium (1:1) system (TIBAO/$^iBu_3Al$) was prepared "in situ" by adding the necessary amount of triisobutylaluminium (solution 1.0M in toluene), after the addition of TIBAO.

The Vandenberg catalyst $(C_2H_5)_3Al/H_2O$ (molar ratio 1:0.5) was prepared as follows. To a dry Schlenck, equipped with a teflon-coated stirring bar and a rubber seal septum, 60 mL of 25% solution of TEA in toluene (50.9 g, 111 mmol) and 30 mL of anhydrous ethyl ether were carefully transferred in this order with an argon-purged double-ended needle. The schlenck was cooled in an ice/water bath, and then distilled water (1.0 mL, 55.5 mmol) was added dropwise to the stirred solution using a microsyringe, over a 1 h period. A slight positive pressure of nitrogen was maintained throughout the apparatus to sweep away the ethane formed during the reaction. After the addition was completed, the colourless solution was stirred for 6 h to allow completion of the reaction. The aluminium concentration (1.25 M) in the resulting colourless solution was determined gravimetrically using 8-hydroxyquinoline.[38] The catalyst solution was stored in a refrigerator and aged for 1 week before it was used.

Polymerizations

Before its polymerization, EMO and BEO were dried by stirring overnight over freshly activated 4 Å molecular sieves and filtered under argon atmosphere.

All operations were performed under dry argon using standard Schlenk techniques.

Small scale polymerizations

In a typical polymerization, in a 25 mL Schlenk tube, 5 mmol of monomer and the necessary amount of anhydrous toluene to obtain a 2 M solution were introduced using a syringe. After cooling to 0 °C, the necessary amount of catalyst solution to obtain a 10/1 monomer-aluminum ratio was added using a microsyringe. The mixtures were homogenized, allowed to reach room temperature and maintained at 25 °C in a controlled bath for 72 hours. The polymerization was stopped by adding 20 mL of 5 wt.% HCl in MeOH solution and stirred for 12 hours. After sedimentation, the supernatant was decanted; the polymer was dissolved in THF and precipitated once in 5% HCl in MeOH (50 ml/g) and twice in pure MeOH (50 ml/g). The resulting white rubber-like polymer was dried under vacuum for 24 h at 40 °C.

Polymerizations with Vandenberg catalyst in the presence of THF were carried out following the same procedure but adding 0.02 mL (0.25 mmol) of anhydrous THF to the monomer solution before the addition of the catalyst.

The polymer conversion and molecular weight of the obtained polymers are collected in Table 1.

Poly(epoxioctene) (PEO)

^{1}H NMR (CDCl$_3$, TMS, δ in ppm): 3.4-3.2 (polyether backbone), 1.7-1.2 (aliphatic backbone), 1.0-0.85 (m, -CH$_3$).

^{13}C NMR (CDCl$_3$, TMS, δ in ppm): 81-79 (polyether backbone), 33-31 (-$\underline{C}$H$_2$-CHO-), 21-19 (-$\underline{C}$H$_2$-CH$_3$), 14.7 (-CH$_3$).

Poly(benzyl-epoxi-octadecenylether) (PBEO)

^{1}H NMR (CDCl$_3$, TMS, δ in ppm): 7.4-7.2 (Aromatic backbone), 4.48 (2 H, m, -O-CH$_2$-Ar), 3.44 (-CH$_2$-O-Bn), 3.4-3.2 (polyether backbone), 1.7-1.5 (2 H, m, -C$\underline{H_2}$-CH$_2$-O-), 1.5-1.2 (m, Aliphatic backbone), 0.89 (m, -CH$_3$).

^{13}C NMR (CDCl$_3$, TMS, δ in ppm): 138.9 (-CH$_2$-$\underline{C}$Ar), 128.5 (m-Ar), 127.7 (o-Ar), 127.6 (p-Ar), 82-79 (polyether backbone), 73.0 (-O-$\underline{C}$H$_2$-Ar), 70.7 (-$\underline{C}$H$_2$-O-CH$_2$Ar), 32.2 (-$\underline{C}$H$_2$-CH$_2$-CH$_3$), 31.5-29.0 (Aliphatic backbone), 28.0-26.5 (-$\underline{C}$H$_2$-CHO and -$\underline{C}$H$_2$-CH$_2$-CHO), 26.6 (-$\underline{C}$H$_2$-CH$_2$-O-CH$_2$Ar), 22.9 (-$\underline{C}$H$_2$-CH$_3$), 14.4 (-CH$_3$).

Poly(epoxidized methyloleate) (PEMO)

^{1}H NMR ($CDCl_3$, TMS, δ in ppm): 3.63 (s, $-O-CH_3$), 3.40-3.10 (m, polyether backbone), 2.27 (t, $-CH_2-CO_2-$), 1.70-1.10 (m, $-CH_2-$ aliphatic backbone), 0.85 (t, $-CH_3$).

^{13}C NMR ($CDCl_3$, TMS, δ in ppm): 173.8 ($-CO_2Me$), 82-78 (polyether backbone), 51.5 ($-OMe$), 34.2 ($-\underline{C}H_2-CO_2Me$), 32.2 ($-\underline{C}H_2-CH_2-CH_3$), 31.5-29.0 (aliphatic backbone), 28.0-26.0 ($-\underline{C}H_2-CHO$ and $-\underline{C}H_2-CH_2-CHO$), 25.2 ($-\underline{C}H_2-CH_2-CO_2Me$), 22.9 ($-\underline{C}H_2-CH_3$) 14.3 ($-CH_3$).

Table 1. Conversion and molecular weight characteristics of the polymers obtained in the polymerization of EO, BEO and EMO using TIBAO, TIBAO/$^iBu_3Al$, Vandenberg catalyst and Vandenberg catalyst in presence of THF.

Mon. 1	Mon. 2	Initiator	Yield (%)	Mnx10^{-3}	DP	Mn/Mw
EO		TIBAO	84	12.3	96	2.1
		TIBAO/$^iBu_3Al$	88	13.4	104	2.0
		Vand. Cat.	79	14.8	115	2.0
BEO		TIBAO	71	9.4	24	2.2
		TIBAO/$^iBu_3Al$	78	9.8	25	2.0
		Vand. Cat.	68	8.3	22	1.9
EMO		TIBAO	39	7.1	22	1.9
		TIBAO/$^iBu_3Al$	45	7.6	24	1.9
		Vand. Cat.	60	6.9	22	1.8
EMO	THF	Vand. Cat.	56	6.0	19	1.6
EMO*	THF	Vand. Cat.	50	6.2	19	1.7

Conditions: monomer concentration = 2M, monomer/Al ratio = 10/1. EMO/THF molar ratio 20/1. Toluene, 25 °C, 72h.
* 94% EMO (GC)

Large scale polymerization of EMO.

In a dry 250 mL flask under argon atmosphere, 31.2 g (0.1 mol) of the EMO obtained from 90% methyl oleate, 40 mL of toluene and 0.4 mL (5 mmol) of THF were introduced. After cooing to 0 °C, 8.0 mL of catalyst solution were added. The mixture was homogenized, allowed to reach room temperature and maintained at 25 °C in a controlled bath for 72 hours. The polymerization was stopped by adding 150 mL of 5 wt. % HCl in MeOH solution and stirred vigorously for 12 hours. The supernatant was decanted and the polymer was dissolved in 100 of THF and precipitated once in 1.5 L of 5% HCl in MeOH (50 ml/g) and twice in 1.5 L of pure MeOH. The resulting polymer was dried in vacuum during 48 h at 40 °C giving 15.7 g (50%) of a white solid.

Reduction tests

In a 250 mL round bottom flask under argon atmosphere, 1.88 g (6.0 mmol) of PEMO (obtained with Vandenberg catalyst) were dissolved in 60 ml of anhydrous THF. The theoretical amount of $LiAlH_4$ necessary to reduce 50% of the ester groups (57 mg, 1.5 mmol) was added in one portion and the mixture was stirred vigorously at room temperature for 1 h. After the addition of 5 ml of ethyl acetate and stirring for 15 minutes, 100 ml of a 10 % aqueous H_2SO_4 solution was slowly added. The two phases were separated, and the aqueous layer extracted with ethyl acetate. The combined organic phases were washed with H_2O, saturated $NaHCO_3$ solution, brine and dried over anhydrous magnesium sulfate. After removing the solvent on the rotatory evaporator the resulting white polymer (1.76 g) was dried at 50 °C under vacuum for 24 hours.

The same procedure was used to reduce 1.88 g (6.0 mmol) of the PEMO obtained with Vandenberg catalyst in presence of THF. Yield 1.82 g (98%)

^{1}H NMR ($CDCl_3$, TMS, δ in ppm): 3.63 (s, $-O-CH_3$), 3.65-3.55 (t, $-CH_2OH$), 3.40-3.10 (m, polyether backbone), 2.27 (t, $-C\underline{H_2}-CO_2Me$), 1.70-1.10 (m, $-CH_2-$ aliphatic backbone), 0.85 (t, $-CH_3$).

^{13}C NMR ($CDCl_3$, TMS, δ in ppm): 174.3 ($-CO_2Me$), 82-74 (polyether backbone), 62.9 ($-CH_2OH$), 51.6 (-OMe), 34.2 ($-\underline{C}H_2CO_2Me$), 32.9 ($-\underline{C}H_2-CH_2OH$), 32.1 ($-\underline{C}H_2-CH_2-CH_3$), 31-25.5 (m, aliphatic backbone), 25.2 ($-\underline{C}H_2-CH_2-CO_2Me$), 22.9 ($-\underline{C}H_2-CH_3$) 14.3 ($-CH_3$).

Characterization

GC-MS analysis were done in a 6890N gas chromatograph and a 5973 mass spectrometer (Agilent Techologies, Palo Alto, U.S.A.), using a HP-5MS capillary column of 5% phenyl polydimethyl siloxane (30 m, 0.25 mm, 0.25 μm), from Agilent Technologies, and 99.999% pure helium gas as the carrier at a flow rate of 1.5 ml min^{-1}. Samples were injected in a split/splitless injector at a split ratio of 20:1, at a temperature of 280 °C. The oven temperature of GC was initially held at 60 °C, raised to 260 °C at a rate of 6 °C min^{-1} and then held for 50 minutes. The mass spectrometer acquired data in scan mode with an m/z interval from 35 to 800. The compounds were identified by comparison with NIST08 MS library.

^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded in $CDCl_3$ and toluene d_8 using a Varian Gemini 400 spectrometer. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS), $CHCl_3$ as internal standards.

MALDI-TOF MS measurements were performed with a Voyager DE-RP mass spectrometer (Applied Biosystems, Framingham, MA) equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. 1,8,9-antracenetriol was used as matrix and potassium trifluoroacetate as dopant. Samples were prepared from a THF solution containing 40 mg/ml of matrix, 3 mg/ml of polymer and 0.1 mg/ml of dopant. The homogenized mixture was casted in the MALDI plate.

Size exclusion chromatography (SEC) analysis was carried out with an Agilent 1200 series system with PLgel 3 µm MIXED-E, PLgel 5 µm MIXED-D and PLgel 20 µm MIXED-A columns in series, and equipped with an Agilent 1100 series refractive-index detector. Calibration curves were based in polystyrene standards having low polydispersities. THF was used as an eluent at a flow rate of 1.0 mL/min, the sample concentrations were 5-10 mg/mL, and injection volumes of 100 µL were used.

Results and discussion

The main purpose of this work is the study of the ionic-coordinative polymerization of EMO. In general, internal epoxies are difficult to polymerize due to the low reactivity regarding their high steric hindrance. In addition, the presence of other oxygenated functional groups in the monomer is known to passivate the catalyst active sites and favours the occurrence of side reactions that decreases the yield and molecular weight of the resulting polymers.[26,27,39-41] To further study these effects, we chose three monomers with similar steric hindrance but different coordinative ability: EO, BEO and EMO (Scheme 1). Only monomers with cis configuration were considered as this is the dominant configuration in natural fatty acids.

Synthesis of EO was accomplished by the Prileshajev epoxidation of pure cis-4-octene with MCPBA following a modified procedure[36] and purified by fractional distillation over CaH_2. For the synthesis of BEO and EMO, benzyl-9-octadecenylether prepared from 85% oleoyl alcohol and two different methyl oleate samples with 90% and 99% of oleic acid methyl ester content were used. The peroxotungstate catalyzed epoxidation with H_2O_2[35] resulted in excellent yields of EMO and BEO with high purity. The epoxides were purified by a combination of low temperature crystallization and column chromatography dried over activated 4 Å molecular sieves. The purity of the monomers was determined by CG-MS and was found over 98% in the case of EO and the EMO obtained from the 99% methyl oleate. The purity of BEO was 94% being the major impurities the benzyl ethers of palmitoyl and stearoyl alcohols. In the case of the EMO obtained from the 90% methyl oleate, purity was 96% being the major impurities the methyl esters of palmitic, stearic, eicosanoic, docosanoic and tetracosanoic acids. Pure EMO sample was used to perform the polymerization studies whereas the EMO obtained from the less expensive methyl oleate 90plus® was used for large scale polymerizations.

Alkyl and alkoxyaluminoxane based catalyst such as Vandenberg catalyst, methylaluminoxane MAO or tetraisobutyldialuminoxane TIBAO have been described to be effective in the polymerization of long chain terminal epoxides derived from plant oils.[32,42] With these catalyst, polyethers with molecular weights up to $20x10^5$ have been described. Neat aluminum alkyls are known to not initiate the polymerization of epoxides. However, associated with aluminoxanes, effective initiators in the polymerization of epoxides and other compounds are produced.[43] The Vandenberg chelate catalyst ($Et_3Al/AcAc/H_2O$ 1:1:0.5) has also been reported to be effective in the polymerization of methyl 10,11-epoxyundecanoate and other epoxides,[44] but preliminary studies with the methyl 9,10-epoxyoctadecanoate led to very low polymer conversions. So, we selected TIBAO, TIBAO/$^iBu_3Al$ (1:1) and the Vandenberg catalyst (Et_3Al/H_2O 1:0.5) as ionic-coordinative catalysts for the polymerization studies.

Catalysts were added at 0 °C to the monomer dissolved in toluene and the polymerizations were carried out at 25 °C for three days to obtain a high monomer conversion. Preliminary studies showed that longer polymerization times did not improve polymer conversion. In all cases the analyses of the crude polymerization mixtures indicate the presence of considerable amounts of monomer together with low molecular weight oligomers. This seems to indicate that, after a certain polymerization time, the active sites in the catalyst become no longer active. Polymers were precipitated in methanol containing 5% HCl to solubilize aluminum species and were purified by precipitating twice a THF solution in an excess of methanol. This treatment efficiently removes the oligomeric fraction with no significant reduction in the yield. Typically, for the polymerization of EMO with the Vandenberg catalyst, after polymer work up and two precipitations in methanol, the yield was reduced from 67% to 56%. The soluble fraction was found to be mainly unreacted monomer. In Figure 1 the SEC traces of the PEMO fractionation process are shown. Similar behavior was observed for the rest of polymerizations. Polymer conversion and molecular weight of the different polymers are collected in Table 1. In general PEO conversions are higher than PBEO and PEMO, and PEMO gives the lowest conversion for all the tested catalysts. A similar trend can be observed from the molecular weight values which are noticeably higher for PEO than for PEMO. This is in accordance with the increasing basic character of the functional groups present in the molecule which compete with the oxiranic oxygen in the polymerization process. For PEO and PBEO polydispersities are close to 2 as expected for a cationic coordinative polymerization process. Values slightly lower were obtained for the PEMO prepared with all tested catalysts. This is probably a consequence of the fractionation process which is more effective for this polymer due to its lower molecular weight and the higher solubility in methanol of the low molecular weight oligomers due to the presence of the ester groups.

The structure, composition and characteristics of polymers were analyzed by NMR spectroscopy and MALDI-TOF-MS spectrometry.

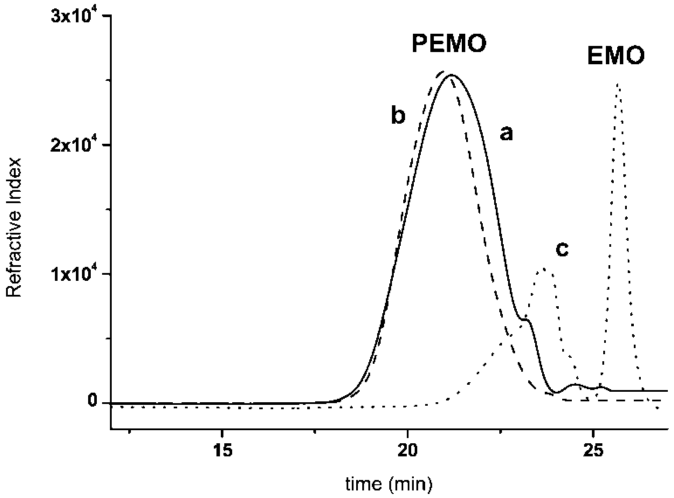


Figure 1. SEC traces of the fractions obtained from the crude PEMO prepared with Vandenberg catalyst. a) PEMO after one precipitation in methanol (continuous line), b) methanol fraction (dots line) and c) PEMO after three precipitations in methanol (dashed line).

According to the selected catalyst nature, an ionic-coordinative ring opening polymerization mechanism is expected for these monomers. Alkylaluminoxanes like methylaluminoxane (MAO) have been widely used in the polymerization of olefins but the polymerization of oxiranes with these catalysts has received much less attention.[32,43] Commercial solutions of aluminoxanes and the Vandenberg catalyst are prepared by reaction of water with a controlled excess of organoaluminum compounds.[31,45] So, according to the reaction stoichiometry TIBAO and Vandenberg catalyst are commonly formulated respectively as $(^{i}Bu)_2Al\text{-}O\text{-}Al(^{i}Bu)_2$ and $(Et)_2Al\text{-}O\text{-}Al(Et)_2$. However, the actual structure is much more complicated and not yet elucidated.[31,46] Both catalysts consist of oligomeric products in which several complex structures coexist in addition to the original component as free and bound species. This means that aluminium and oxygen atoms having different coordinative ability and nucleophilicity coexist in the catalysts.[46] The structure expected from a pure ionic-coordinative polymerization mechanism is a linear polyether ended by a nucleophilic group from the catalyst and one hydroxyl group resulting from the hydrolysis of growing aluminoxane chain end (Scheme 2a). According to the catalyst composition,

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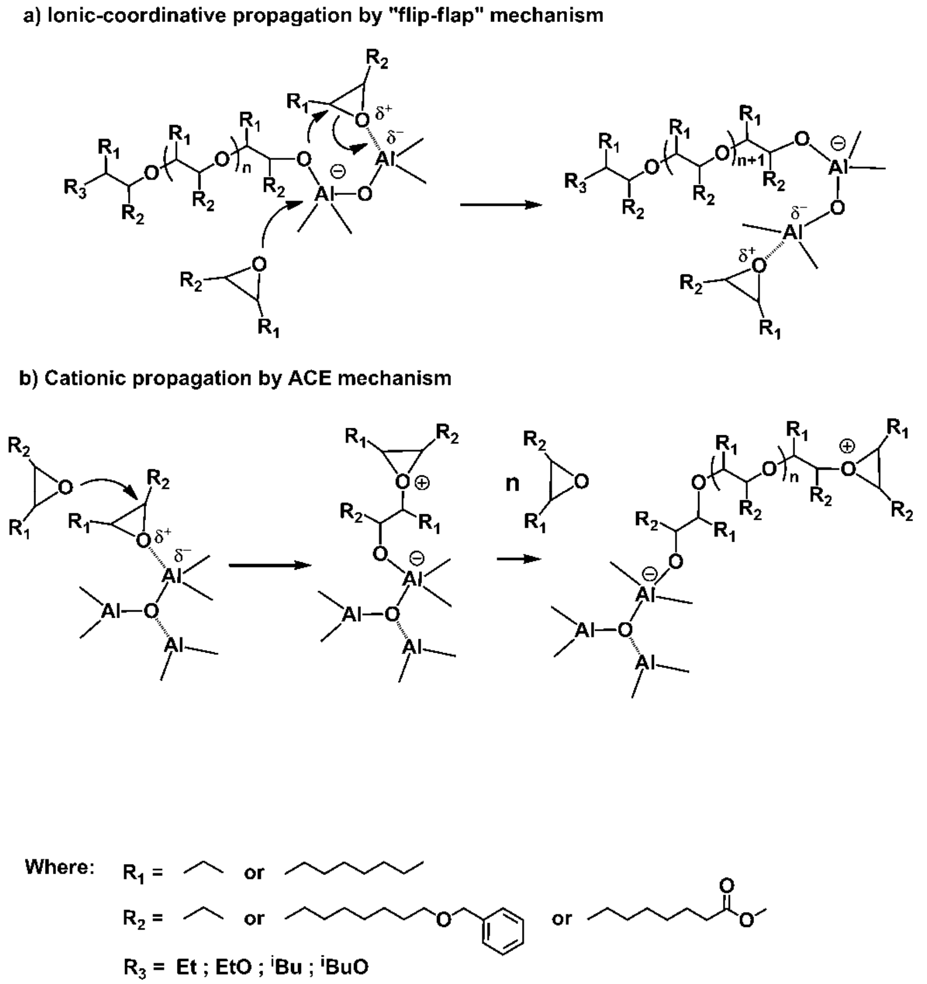
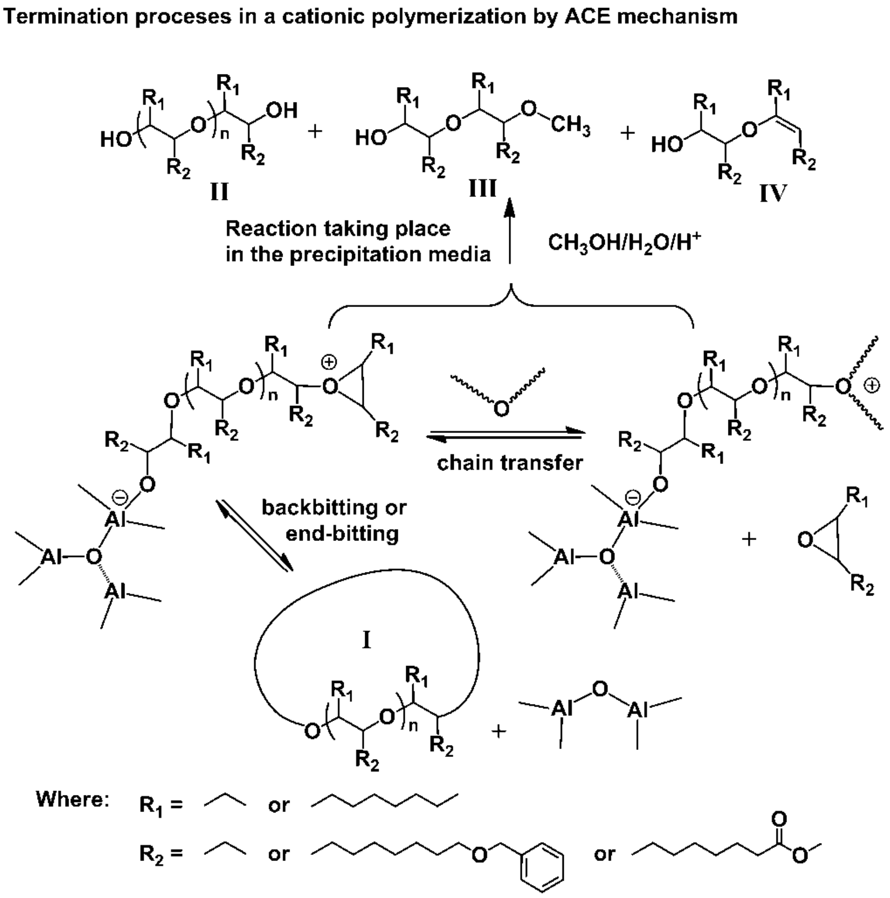
the group that initiates the polymerization by nucleophilic attack on the oxirane ring should be an alkyl group (ethyl or isobutyl) but it must be considered that hydrolysis of the aluminium alkyls can also produce alcoxy groups.



Scheme 2. Ionic-coordinative and cationic propagation mechanisms.

Ionic-coordinative polymerizations are frequently accompanied by variable amounts of linear and cyclic oligomeric fractions produced by conventional cationic polymerization[39-41] (Scheme 2b). The coexistence of these two polymerization mechanisms must be considered in this case as propagation through an ionic-coordinative mechanism involving a growing chain and a monomer respectively bonded and coordinated to two neighboring aluminum atoms. Thus, in the case of internal epoxies bearing long aliphatic chains, the steric requirements would difficult this mechanism favoring the competence of the cationic processes. The end groups expected for lineal polyethers produced by an ACE cationic polymerization mechanism[47] are hydroxy, methoxy or vinylether units (Scheme 3).



Scheme 3. Cationic termination mechanism.

MALDI-TOF-MS analysis of all samples showed a monomodal distribution with lower molecular weight than the obtained by SEC using PS standards. In all cases, several peak populations following a similar pattern can be detected up to masses of 5000-6000 Da. Moreover, in all cases the maximum peak intensity is centered at around 2000 Da. Taking into account the different molecular weight of the samples analyzed and the similarity between the obtained distributions it can be inferred that a preferential ionization/volatilization of the fractions of low molecular weight occurs.

The MALDI population pattern changes significantly from one catalyst to another but are very close for PEO and PBEO samples obtained with a same catalyst. In the case of PEMO some additional peaks are detected which are related to presence of a methyl ester group (*vide infra*). In Figure 2 the MALDI-TOF-MS spectra of PEMO obtained with the different catalysts are shown.

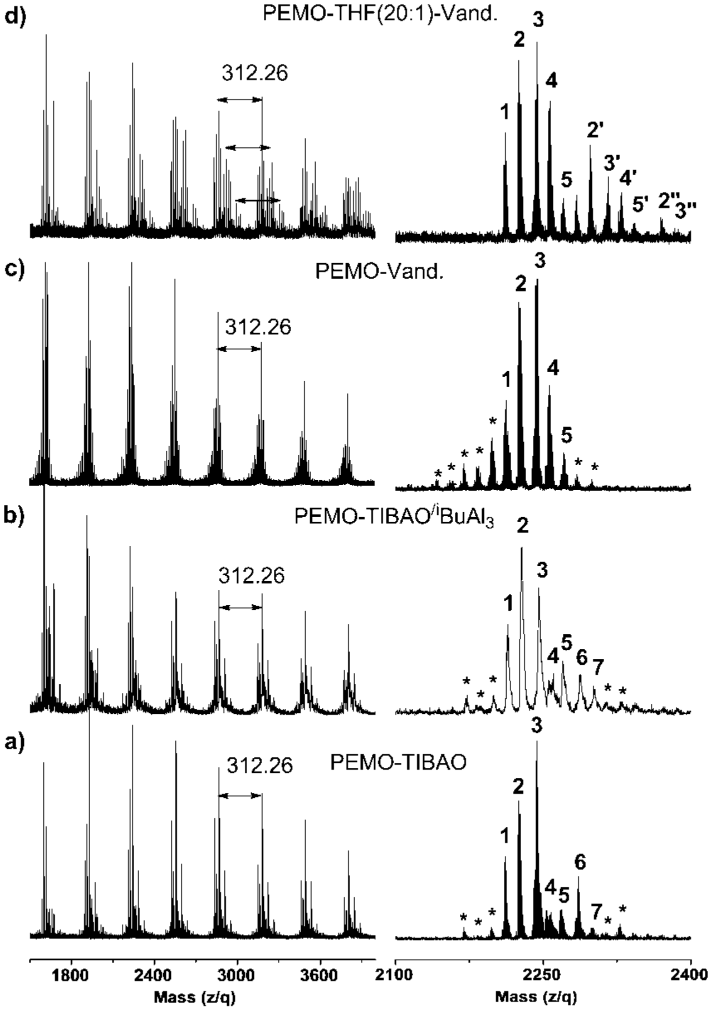
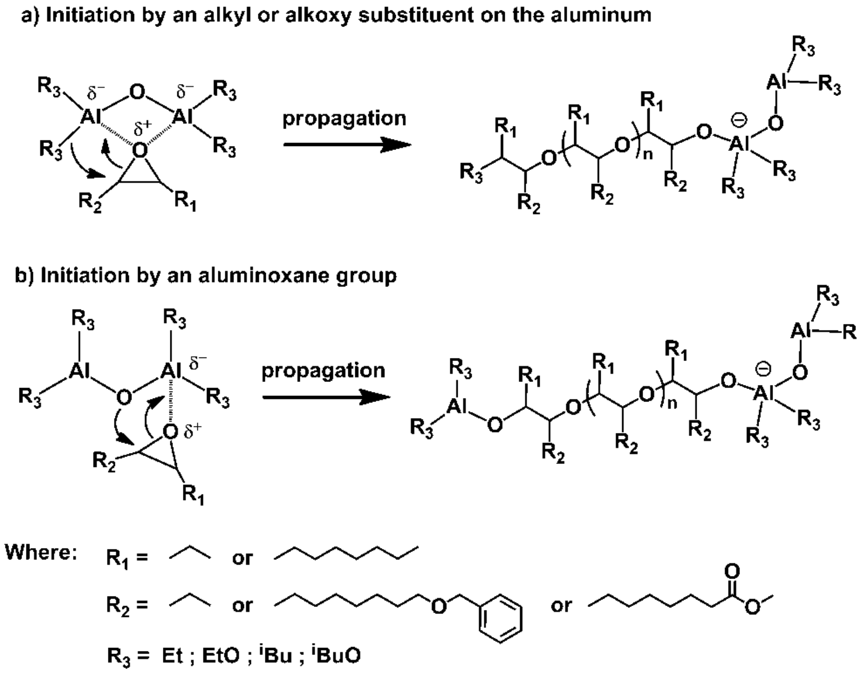


Figure 2. Left side: representative fragments of MALDI-TOF-MS spectra of the PEMO obtained with a) TIBAO; b) TIBAO/^{i}BuAl$_3$; c) Vandenberg catalyst and d) PEMO/THF (20:1) with Vandenberg catalyst. Righ side: enlargement of the peak corresponding to DP = 7.

In the case of PEMO obtained with TIBAO (Figure 2a) a cluster of at least twelve different species is observed for each polymerization degree. Peak **2** (nx312.26+K^+) can be assigned to both cyclic polyether structures (species I in Scheme 3) and linear chains terminated by C=C and OH (species IV in Scheme 3). The intensity of this peak is maximum for n = 5 and decreases rapidly for higher molecular weights. The existence of these cyclic and vinylic structures is relevant as indicates the competence of the cationic polymerization by ACE mechanism (Scheme 2b). Peak **3** (nx312.26+H_2O+K^+), which is the most intense over n = 5, corresponds to linear polyetherdiol structures. Since polymerizations are carried out in absence of water the two hydroxyl groups must be formed in a final hydrolysis step. Cationic polymerization of EMO with $HSbF_6$ in presence and in absence of water has been reported by us to yield mixtures of cyclic structures and oligoetherdiols,[22] so it cannot be excluded that some of these hydroxyl ended polyethers were formed following a cationic mechanism: water and methanol used to stop the polymerization can perform a nucleophilic attack over the different equilibrium tertiary oxonium species[48] (Scheme 3).

Florjanczyk et al. described an alternative ionic-coordinative-based mechanism for the formation of polyetherdiols in the polymerization of PO with MAO and MAO/$AlMe_3$ mixtures.[43] In an ionic-coordinative mechanism, the initiation proceeds by the attack of a nucleophilic group of the catalyst over the oxirane ring coordinated to a neighbouring metal center. In the case of aluminoxane-based catalysts it can be an alkyl or alkoxy group in the aluminum (Scheme 4a) or a whole aluminoxane moiety (Scheme 4b). In this last case the reaction depends on the nucleophylicity of the oxygen in the Al-O-Al bond system. If this oxygen is coordinated to a third aluminum atom (Scheme 2b) its nucleophilicity is poor and a cationic propagation is more likely. If it is not coordinated, their nucleophilicity is higher than the alkyl groups bonded to the aluminum. The polarizability, coordination ability and polymerization activity of Al-O-Al bonds in this kind of catalysts has been well established.[44,49,50] According to this mechanism (Scheme 4b) initiation leads to lineal polyethers with Al-O-C bonds at both ends and their acidic hydrolysis will produce a polyetherdiol. A detailed analysis of the MALDI-TOF spectra allows confirming these hypotheses. Peaks **6** (nx312.26+^{i}Bu+K^+), and **7** (nx312.26+^{i}BuO+K^+) confirm the attack of the alkyl and alkoxy groups in the Al following an ionic-coordinative mechanism, but their relative low intensity indicates that the predominant nucleophilic attack is produced by aluminoxane groups. Peak **4** (nx312.40+CH_3OH+K^+) could be also indicative of the predominance of the ionic-coordinative propagation. Linear polyethers ended by hydroxyl and methoxy groups can be formed by reaction of the oxonium species in the cationic polymerization with the methanolic precipitation media (species III in Scheme 3). The low intensity of these peaks suggests that cationic processes lead mainly to cyclic structures.[51] Moreover, as water is in low concentration in the precipitation media, the amount of polyetherdiols formed following a cationic process (species II in Scheme 3) must be low.



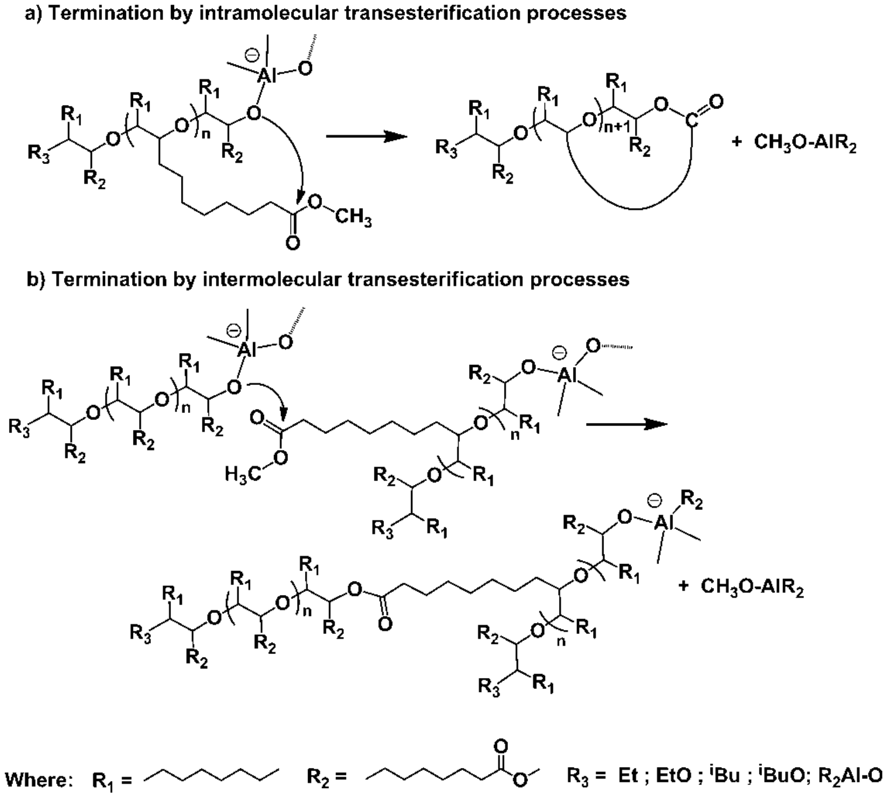
Scheme 4. Ionic-coordinative initiation mechanism.

Peak **5** (nx312.26+ CH_3OCH_3+K^+) can be related with linear polyether chains with methoxy groups at both ends. These peaks have low intensity in all the analized MALDI-TOF spectrograms and could be origined by acidic methanolysis of the chains ended by aluminum alkoxides at both ends.

The intense peak **1** and the small peaks marked with asterisks are only observed in PEMO and form a series with nx312.26-mx15+K^+ mass units. These peaks are detected in PEMO samples obtained either from 90% or 99% methyl oleate precluding the possibility of the presence of palmitoleic or other C16-C14 acid isomers. Taking into account the presence of methylester groups in the lateral chains these peaks are likely formed by interaction between the growing chain end and an ester group through a transesterification reaction with the loss of a methyl group for every transesterification process (Scheme 5). This reaction, can be intra or intermolecular and supposes, in fact, the termination of the growing chain. Intra and intermolecular transesterification processes have been fully characterized in the polymerization of lactones.[52,53] The existence of intermolecular transesterification processes is undesirable when the ultimate purpose of these polyethers is the preparation of polyols. As shown in Scheme 5 the polymer resulting from intermolecular transesterification processes contains not only ether linkages but also ester linkages in the polymer main chain, so the controlled reduction of side chain ester groups would unavoidably lead to the reduction of the main chain ester groups resulting in a dramatic decrease in the molecular weight. In the MALDI-TOF of PEMO obtained with TIBAO the intensity of peak **1**, which corresponds to a single transesterification process, is much higher than peaks marked with asterisk. This seems to indicate that some transesterification reactions are favored, likely the intramolecular between the growing chain end and its own side chain methyl ester due to its favorable entropy. Existence of transesterification reactions also implies that nucleophilic methoxy groups are formed in the media and thus it is likely that some of the polymer chains containing methoxy groups (peaks **4** and **5**) could be also the result of the initiation by these species.

It must be pointed out that in the MALDI-TOF-MS of a sample obtained after 5 h of polymerization (12% polymer conversion) only peaks **1**, **2**, **3** and with smaller intensity **6**, are detected, suggesting that intermolecular transesterification processes are mainly produced in advanced polymerization stages in which, even large amounts of monomer remain in the polymerization media, the active sites in the catalyst become no longer active for the coordinative polymerization.

In the case of PEMO obtained with the TIBAO/$^{i}Bu_3Al$ system, the MALDI-TOF spectra show the same peak populations with a similar pattern (Figure 2b). In aluminoxane/trialkylaluminum systems it has been described that alkylaluminum coordinates to Al-O-Al centers weakening the nucleophilic character of the initiator favoring the attack of monomers over and activated oxirane molecule in a cationic propagation.[43,49,50] PEO, PBEO and PEMO prepared with this initiator system were obtained in slightly higher yields and molecular weights that those prepared with TIBAO (Table 1). MALDI-TOF analysis reveals that the predominant species, along all the molecular weight range, are cyclic structures (peak **2** in Figure 2b) as expected for a higher competence of the cationic mechanism due to the presence of ^{i}BuAl$_3$.



Scheme 5. Termination by transesterification mechanism.

MALDI-TOF of PEMO obtained with Vandenberg catalyst show similar species but with a different relative intensity (Figure 2c). Cyclic structures (peak **2**) and polyetherdiols chains (peak **3**) are detected along all the molecular weight distribution but the intensity of peak **2** strongly decreases with the polymerization degree being polyetherdiols the predominant specie in the high molecular weight region (PD≥6). This agrees with the prevalence of the ionic-coordinative mechanism for this catalyst. In the case of R_3Al/H_2O catalysts it has been reported the presence of small amounts of Al-OH species, but taking into account that the hydrolysis is always carried out in presence[50] of an excess of R_3Al and that the catalyst solutions are maturated for several days, it is more likely that Al-OR groups are present in the catalyst and not free hydroxyl groups. Peaks corresponding to polymer chains initiated by ethyl groups ($n\text{x}312.26+CH_3CH_3+K^+$) which is overlapped with peak **4**, or ethoxy groups (peak **5**, $n\text{x}312.26+CH_3CH_2OH+K^+$) can be also detected with low intensity. The most staggering feature is the intensity of peak **4** ($n\text{x}312.26+CH_3OH+K^+$) which is the predominant specie in the low molecular weight region (PD≤5). This peak which corresponds to chains initiated by methoxy groups indicates that for this catalyst transesterification processes are very favored. In this way, a complete set of peaks corresponding to populations derived from these transesterification processes can be detected. This can be observed in more detail in the enlargement shown in Figure 3 in which main structure assignments are done. The peaks marked with and asterisk form a complex serie of structures that can be rationalized taking into account the occurrence of one or more transesterification reactions in combination with all above commented basic structures (cycles and hydroxyl, methoxy or ethoxy ended chains). Some representative examples of these structures are shown in Scheme 6. The main feature of all these branched structures is the presence of one or more ester linkages in the main chain.

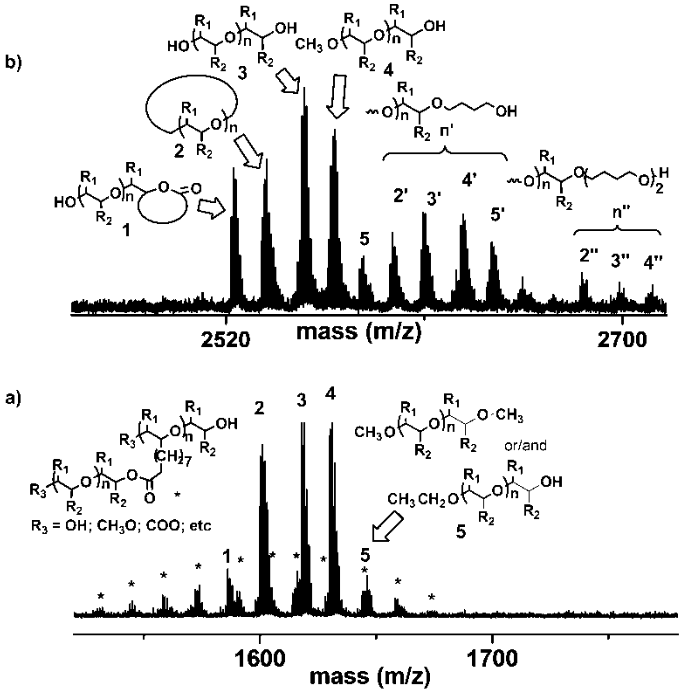
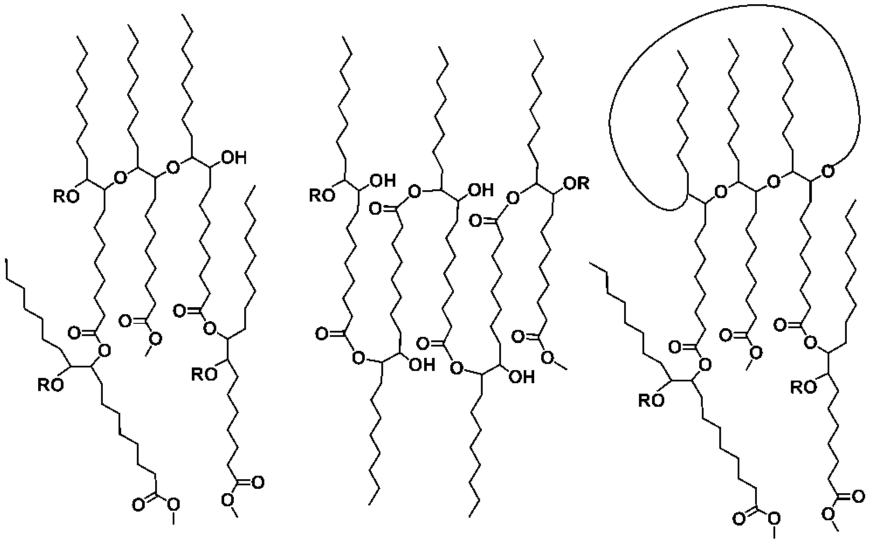


Figure 3. Enlarged detail of a peak in the MALDI-TOF-MS spectra of a) PEMO obtained with Vandenberg catalyst (DP = 5) and b) PEMO/THF (20:1) with Vandenberg catalyst (DP = 8).

According to Table 1, Vandenberg catalyst affords the best EMO conversion leading to polymers with slightly lower molecular weight than those obtained with TIBAO and TIBAO/^{i}BuAl$_3$. So, Vandenberg catalyst would be the catalyst of choice to obtain PEMO in large scale operations. MALDI analysis indicates that this catalyst produces the highest fraction of polyester type oligomers which unfortunately would lead to a decrease of the molecular weight by reduction of the ester groups.

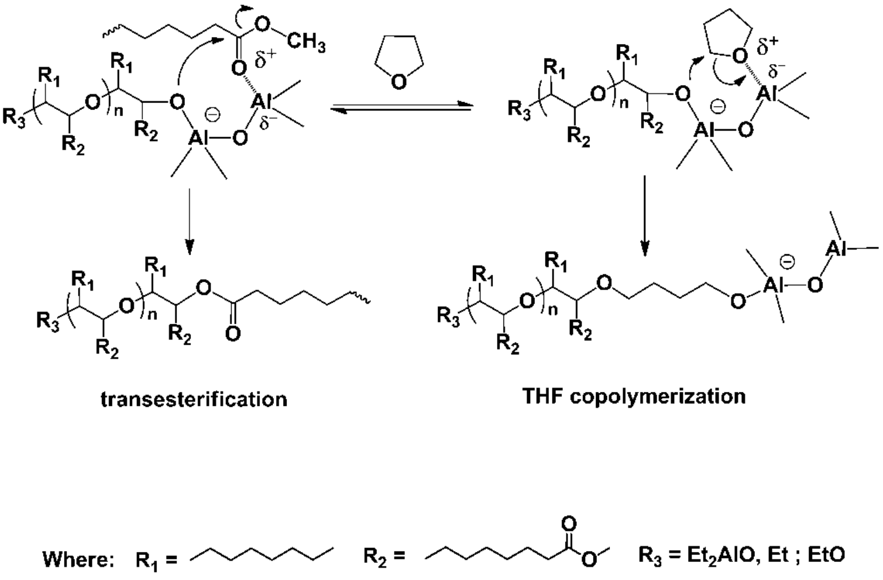


Were R = OH, CH_3O

Scheme 6. Representative polymer structures.

As in the case of PEMO obtained with TIBAO, a polymer sample obtained after 5 h of polymerization was analyzed by MALDI-TOF-MS. Again, a simpler pattern composed only by peaks **1**, **2**, **3**, **4** and **5** (peak **1** and **5** with low intensity) was observed. This demonstrates that with the exception of the intramolecular ones, transesterification processes are produced mainly at advanced polymerization stages. Unfortunately shortening the polymerization time reduces drastically the polymer yield that in this case was only 21% for 5 h.

It has been described that the relative constant rates of the processes involved in a complex polymerization system can be modified by the introduction of a comonomer in the polymerization mixture.[54] The introduction of a monomer with a different reactivity could reduce or suppress some by-side reactions and preferentially activate other propagation steps. In this way, we decided to test the EMO polymerization in presence of a small percentage of other monomer. This comonomer should be able to compete with the methyl ester groups in the reaction with the growing chain ends and must not be reactive enough to compete with EMO in the polymerization. Tetrahydrofuran was considered a good candidate as it has lower ring strain than oxiranes but higher oxygen basicity.[55] Moreover tetrahydrofuran is known to polymerize and copolymerize with cationic and ionic-coordinative initiators.[56] In this way, its polymerization proceeds at lower rates than epoxides but its coordinative ability is higher and probably enough to compete with the activation of the ester groups by the metallic centers (Scheme 7).



Scheme 7. EMO polymerization in presence of THF.

The Vandenberg catalyst copolymerization of EMO with THF in a 20:1 EMO/THF molar ratio was carried out using the same conditions. PEMO-THF was obtained in a slightly lower yield than the homopolymer but with higher yield than the polymerizations with TIBAO and TIBAO/^{i}BuAl$_3$. The SEC analysis shows a small decrease in the molecular weight but a narrower distribution (Table 1).

The MALDI-TOF analysis (Figure 2d and 3b) show some important population differences with PEMO samples obtained in absence of THF. As can be seen, the most intense peaks correspond to the cyclic and the linear polyethers ended by two hydroxyl groups or by one hydroxyl group and a methoxy or ethoxy group. The most relevant feature is the disappearance of the peaks corresponding to multiple transesterification processes with the exception of peak **1** (nx312.26-15+K$^+$) which has more o less the same relative intensity in the whole range of molecular weights. This peak, will be demonstrated (*vide infra*) to correspond to the intramolecular transesterification processes (Scheme 5a). Moreover, in the MALDI-TOF spectrogram, clusters of the same peak populations at +72 and +2x72 mass units can be detected (Figure 3b). These populations of peaks result from the incorporation of THF units at the different chains. The fact that the incorporation of THF units is only important in the high molecular weight region indicates that its copolymerization is produced by the ionic-coordinative mechanism as depicted in Scheme 7. So it can be concluded that the addition of THF as comonomer effectively suppress the intermolecular transesterification reactions by reacting with the growing chain ends without an important decrease in the molecular weight or the polymer conversion.

To gain more insight about the polymer structure a reduction experiment was carried out with PEMO samples obtained with Vandenberg catalyst with and without THF. The theoretical amount of $LiAlH_4$ was adjusted to reduce 50% of the ester groups. As can be seen in Figure 4, the SEC traces of the reduced PEMO (**1-r**) is broader than the starting PEMO (**1**) and shows a significant decrease in the molecular weight as a consequence of the reduction of the main chain ester groups formed in the transesterification. In the case PEMO-THF similar SEC were observed for starting (**2**) and the reduced product (**2-r**). This is consistent with the assumption that structures represented by peak **1** in the MALDI-TOF are cyclic esters resulting from an intramolecular transesterification process, so their reduction do not affect the molecular weight.

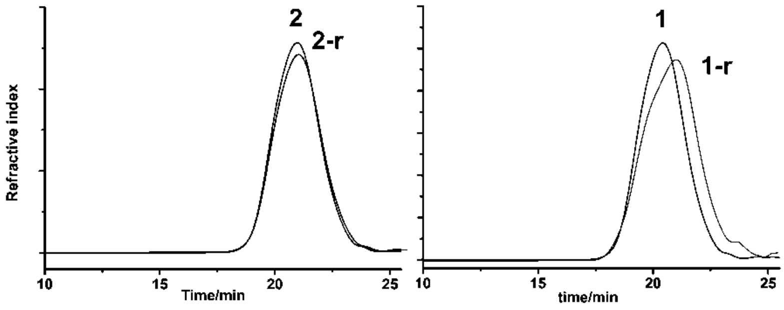


Figure 4. SEC traces of PEMO (**1**) its reduction product (**1-r**) and PEMO-THF (**2**) and its reduction product (**2-r**).

The obtained polymers were also characterized by ^1H and ^{13}C NMR spectroscopy. Moreover, in order to confirm the assignments, gHSQC correlation experiments and derivatizations with trichloroacetylisocyanate (TAI) were carried out. Figure 5 shows some representative ^1H NMR spectra with the assignments. The most outstanding feature in all these spectra is that the main chain methyne protons **a** and **b** (3.1-3.3 ppm) appear as a narrow signal whereas in the case of PEMO obtained by cationic polymerization a broad irregular signal is observed.[22] This indicates certain degree of chain regularity which further supports the predominance of the ionic coordinative mechanism. Spectrum a) in Figure 5 corresponds to PEO obtained with TIBAO. Due to its high molecular weight, signals corresponding to end groups have very low intensity. In spite of this, broad signals at c.a. 3.05 and 3.45 ppm can be detected as shoulders in the methine main chain peak. These signals are observed in all the polymers obtained with the different catalysts and are shifted when the polymer is derivatized with TAI. Thus they can be assigned to the methine protons of the hydroxylic chain end (**a'** and **b'** in structure I). Moreover in this spectrum, small signals attributable to the protons of isobutoxy end groups (**1**, **2** and **3** in structure I) can be also detected. In spectrum b), corresponding to PBEO obtained with TIBAO/^{i}BuAl$_3$ apart from the signals at 3.44 and 4.48 ppm corresponding to the Ph-CH_2-O-CH_2- side chain groups, the same end group signals can be observed but with lower intensity as expected due to its higher content of cyclic structures. Spectra c) and d) correspond respectively to PEMO and PEMO-THF (20:1) samples obtained with Vandenberg catalyst. The signals of the methylene and methyl in the -CH_2-$COOCH_3$ side chain groups appear respectively at 2.28 and 3.68 ppm. In this case end group signals can be detected with some intensity due to the lower molecular weight of these polymers. Both spectra are very similar, but in the case of PEMO-THF two new broad signals at 3.55 and 3.20 ppm are observed which can be assigned to methylenes **c** and **d** in the tetrahydrofuran moieties (structure II). Signal **c** is also shifted downfield when the polymer is derivatized with TAI and so it can be assigned to the final CH_2OH groups. Moreover, in both spectra small signals at 4.80, 4.05 and 3.77 ppm can be detected. Signal at 4.80 ppm can be assigned to the methine units bonded to an ester group (**a''** in structure III). As this signal appears in both polymers it must correspond to the intramolecular transesterified species which are the only ones in PEMO-THF and the predominant in PEMO. Methylene signals of transesterified moieties **e** overlap with the intense signal of the methylene -CH_2-$COOCH_3$ peak.

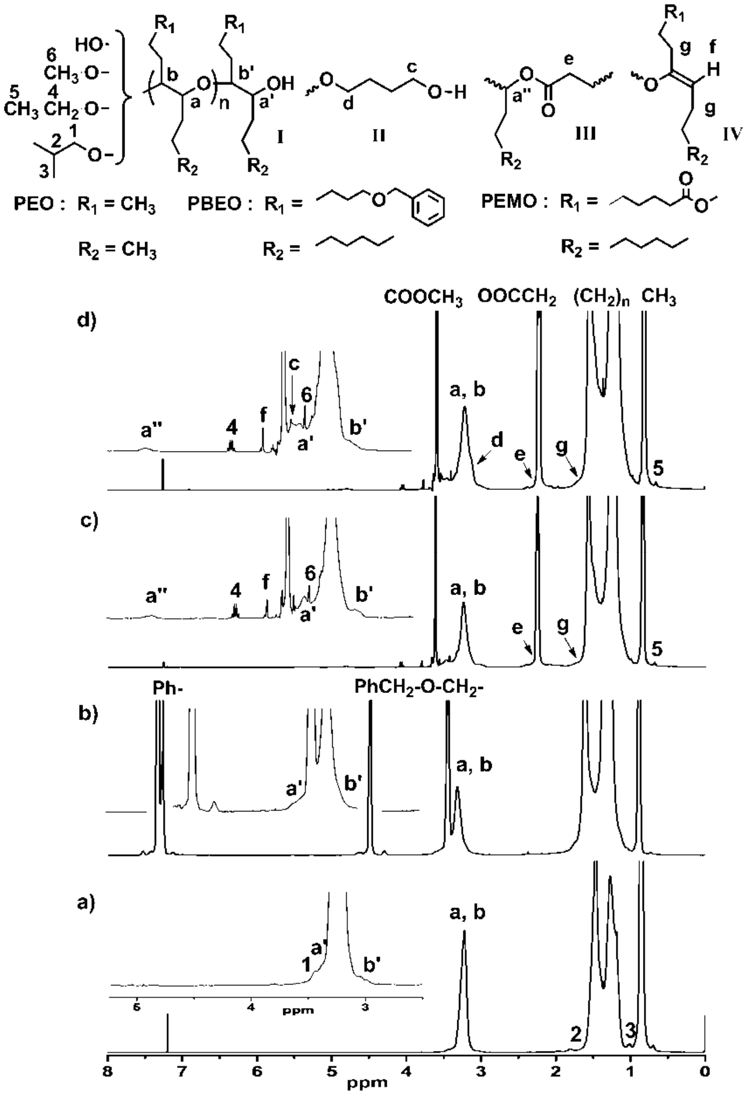


Figure 5. ^{1}H NMR spectra of a) PEO obtained with TIBAO; b) PBEO obtained with TIBAO/^{i}BuAl$_3$; PEMO obtained with Vandenberg catalyst and d) PEMO-THF (20:1) obtained with Vandenberg catalyst.

The quadruplet at 4.05 ppm corresponds to a methylene related to the methyl signal at 0.66 ppm (signal **5**) which can be assigned to an ethoxy group. In the case of Vandenberg catalyst the initiation by ethoxy groups formed during the Et_3Al controlled hydrolysis is one of the more likely coordinative mechanisms. These species (peak **5** in Figures 2 and 3) have low relative abundance in the low molecular weight region of the MALDI-TOF-MS spectra but they become more and more important as the polymerization degree increases. Moreover, it must be pointed out that ethoxy initiated species constitutes prominent peaks in the MALDI-TOF-MS spectra of PEO and PBEO obtained with the same catalyst.

Singlet at 3.77 ppm can be also observed in PEO and PBEO but its intensity is higher for polymers obtained with Vandenberg catalyst. This signal is related with a methylene that appears as a shoulder at ca. 1.75 ppm. These signals are consistent with a vinylether chain end formed by proton elimination of the growing cationic chain end (structure IV in Scheme 3). This result is very outstanding, since until now it was assumed that peak **2** in the MALDI-TOF-MS spectra corresponds only to cyclic structures. The low intensity of these vinyl signals in the case of polymers obtained with TIBAO and TIBAO/^{i}BuAl$_3$ confirms this assignment. However, for polymers obtained with Vandenberg catalyst the NMR data seems to indicate that vinylic structures also contribute in some extent.

The rest of small signals are not easily identifiable due to its overlapping and the lack of proper models but the singlet at 3.40 ppm is likely due to the methoxy chain end groups.

Figure 6 shows the ^{13}C NMR spectrum of PEMO-THF obtained with Vandenberg catalyst and the expanded region between 55 and 90 ppm a) and the expanded region for PEMO obtained with Vandenberg catalyst b). Again the most important feature in all the spectra is the shape of the methine carbons of the repeating unit which appear as a triad at 80.50, 80.02 and 89.2 ppm with maximum intensity for the former peak. Tacticity has been described for the methyne and methylene carbons of terminal long chain epoxides when polymerized with coordinative initiators[32] but in this case a selective polymerization process is hard to expect owing the similarity between the two epoxide substituents even the coordination of the ester group in the side chain could favor at least some regioselective polymerization. In the same region of the ^{13}C NMR spectra some other small intensity signals can be observed. The signal at 74.50 ppm which is a methine has been assigned to **a''** in structure III taking into account its correspondence with the signal at 4.9 ppm in the ^{1}H NMR spectrum. The signal at 71.0 ppm which appears in both polymers correspond to the methine **a'** in the hydroxylic chain ends. The small signals at 59.98 and 58.20 ppm can be assigned respectively to the ethoxy and methoxy end groups.

Moreover in the espectra of PEMO-THF two additional peaks can be observed which are related with the additional peaks at 3.55 and 3.20 ppm in the ^{1}H NMR spectrum. These signals correspond to the methylenes **c** and **d** (structure II) of the tetrahydrofuran moieties. The higher intensity of **d** indicates that not all THF units are end groups.

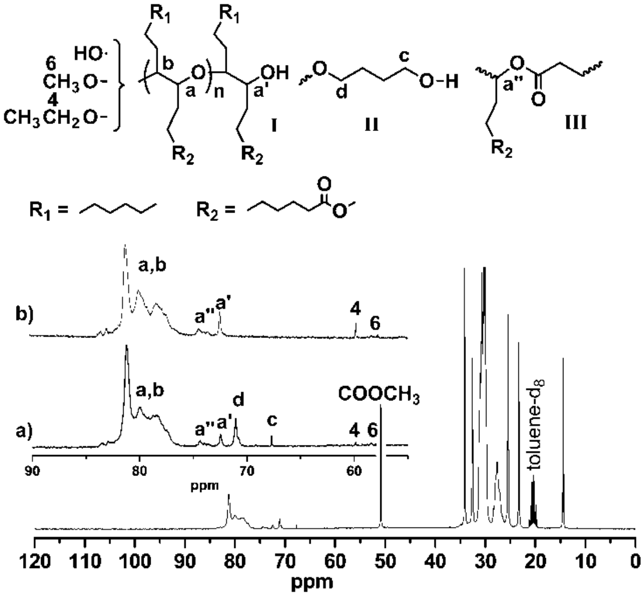


Figure 6. ^{13}C NMR spectra recorded in toluene-d8 of PEMO-THF and its expanded region from 55 to 90 ppm a) and b) expanded region for PEMO. Both obtained with Vandenberg catalyst.

Finally, even no specific study was made to optimize polymerization conditions we assayed the polymerization of EMO with the Vandenberg catalyst in presence of THF in a larger scale (0.1 mol). In this case we used EMO obtained from 90% methyl oleate which is 94% pure according to GC analysis and the same polymerization conditions. As can be seen in Table 1, the polymer conversion was slightly lower but the polymer characteristics are very similar proving that this polymerization procedure can be used to produce comb-like polyethers in acceptable good yields. The synthesis of polyether-polyols containing different hydroxyl content from PEMO and its use in the preparation of conventional and segmented polyurethanes will be discussed in a forthcoming paper.

Conclusions

The coordinative polymerization of methyl epoxyoleate, a derivative from high oleic sunflower oil, and some structural analogues, has been investigated. Under mild conditions, ionic-coordinative initiators yield polymers with higher molecular weight than the obtained with conventional cationic catalysts. MALDI-TOF-MS analysis and ^{1}H and ^{13}C NMR characterization reveals that obtained polymers consist of a mixture of cyclic and linear structures with different end groups depending on the initiator used. This can be rationalized by the coexistence of ionic-coordinative, which is predominant, and cationic propagation mechanisms. The initiator activity, in terms of polymer conversion, increases from TIBAO to TIBAO/$^{i}BuAl_3$ and to Vandenberg catalyst even a slightly decrease in the polymer molecular weight is produced. At advanced polymerization stages, transesterification processes lead to the formation of branched structures containing ester groups in the main chain. These processes, which limit the use of these polymers in the preparation of renewable polyether-polyols, can be suppressed by copolymerizing the methyl epoxyoleate with a small amount of THF. The large scale polymerization of technical grade methyl epoxyoleate and the reduction of the ester groups of the resulting polyether prove the applicability of this synthetic approach to produce fully renewable predominantly linear polyether-polyols of 6000-8000 Da molecular weights with controlled hydroxyl content.

Acknowledgements

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Biobased polyurethanes from polyether polyols obtained by ionic-coordinative polymerization of epoxidized methyl oleate

Biobased polyurethanes from polyether polyols obtained by ionic-coordinative polymerization of epoxidized methyl oleate

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Abstract

A series of poly(ether urethane) networks were synthesized from polyether polyols obtained by ionic-coordinative polymerization of epoxidized methyl oleate (EMO) using 4,4'-methylenebis(phenylisocyanate) (MDI) or L-lysine diisocyanate (LDI) as coupling agents. Moreover, a variety of segmented poly(ether urethane) networks with different hard segment contents were obtained using 1,3-propanediol (PDO) as a chain extender. The materials were characterized by differential scanning calorimetry, thermogravimetric analysis, dynamic mechanical thermal analysis and tensile properties.

Introduction

Recent years have witnessed an increasing demand on natural products in industrial applications for environmental issues, waste disposal and depletion of non-renewable resources.[1] Renewable resources can provide an interesting sustainable platform to substitute petroleum-based polymers through the design of bio-based polymers that can compete or even surpass the existing materials on a cost-performance basis with high eco-friendliness values.[2,3] Plant oils are considered as the most important renewable raw materials for the production of bio-based polymers. In recent years, a variety of polymeric materials have been developed and tested with plant oils as feedstock.[4-7]

Polyurethanes are one of the most important and versatile materials with applications ranging from flexible foams in upholstered furniture to rigid foams as insulators in walls, roofs, and appliances of thermoplastic polyurethanes used in medical devices and footwear, coatings, adhesives sealants and elastomers used on floors and automotive interiors.[8] They represent and important class of thermoplastic and thermosets since their mechanical, thermal and chemical properties can be tailored by reactions with various polyols and isocyanates. Usually, both isocyanates and polyols are petroleum based but in recent years vegetable oils, fatty acids and their

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derivatives have attracted significant attention as raw materials for the preparation of polyurethanes.[9]

For natural oils to be used as raw materials for polyol production, multiple hydroxyl functionality is required. Different ways of preparing vegetable oil-based polyols have been successfully developed: epoxidation and further oxirane ring opening,[10,11] hydroformylation,[12] ozonolysis[13] or reaction at the double bonds and subsequent reduction of the carboxyl groups that yields to polyethers containing the hydroxyl groups.[14] However, limited attention has been paid to the preparation of polyether polyols from vegetable oils. Polyether polyols with molecular weights of 200 to 10000 g/mol are important building blocks for polyurethane applications.[15] Polyols with molecular weights of about 3000 or more are used to produce flexible polyurethanes, and polyols of about 200 to 1200 g/mol are used for rigid polyurethanes. Polyether polyols are usually produced by the anionic ring-opening polymerization of alkylene oxides such as ethylene oxide or propylene oxide.

To further extend the applications of vegetable oils, our group has focused on converting these renewable resources into useful biopolymers. In a previous study we described the synthesis of polyether polyols through the combination of cationic ring opening polymerization of epoxidized methyl oleate (EMO) and the reduction of carboxylate groups to hydroxyl moieties. Polyols with different hydroxyl contents were obtained and reacted with 4,4'-methylene-bis(phenylisocyanate) (MDI) to yield polyurethanes that behave like hard rubbers or rigid plastics.[14] A series of biodegradable segmented poly(ether urethane) networks were obtained from the EMO-based polyether polyol and 1,3-propanediol (PDO) using L-lysine diisocyanate (LDI) as a non-toxic coupling agent.[16] We have also developed novel bio-based silicon-containing polyurethanes from these polyols and a silicon-containing polyol with terminal primary hydroxyl groups.[17]

Long chain internal oxiranes or functionalized epoxides show low reactivity due to a higher sterical hindrance and side reactions, and high molecular weight polymers cannot be obtained by using anionic or cationic catalysts.[18] We obtained oligomeric polyethers of about 900 to 1200 g/mol through the acid-catalyzed ring opening polymerization of EMO.[14] Coordinative ring-opening polymerization has been described for functionalized epoxides as phenylglycidylether derivatives[19] or ω-epoxy alkanoates.[20] In a previous study, we developed new polyether polyols by ionic-coordinative polymerization of EMO with molecular weights around 7000 g/mol.[21] This work seeks to broaden the physical properties of vegetable-oil based polyurethanes by using these polyethers, thus increasing the molecular weight of the polyol. Polyols were obtained by the controlled reduction of the carboxylate groups to hydroxyl moieties using lithium aluminum hydride as reducing agent and were characterized by chemical methods, spectroscopic (FTIR and NMR) and thermal (DSC) techniques. They were reacted with PDO and MDI or L-lysine diisocyanate to obtain polyurethane networks with various hard segment contents. The properties of prepared polyurethanes were studied by using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMTA).

Experimental

Materials

Methyl oleate 90plus® was kindly supplied by T+T Oleochemie . Epoxidized methyl oleate (EMO) was synthesized using a literature procedure.[22] Epoxidized methyl oleate-based polyether was synthesized in our laboratory using the procedure described earlier (M_n = 6400 M_w/M_n = 1.7).[21]

The following chemicals were obtained from the sources indicated and used as received: lithium aluminum hydride (Aldrich), 4,4’-methylene-bis(phenylisocyanate) (MDI, Aldrich) and 2,6-diisocyanato methyl caproate (L-lysine diisocyanate, LDI) (Kyowa Hakko Kogyo Co.). Chain extender 1,3-propanediol (PDO) was purchased from Aldrich and was distilled and stored at ambient temperature in a dessecator until used. Tetrahydrofuran (THF) was distilled from sodium-benzophenone immediately before use. Other solvents were purified by standard procedures.

Representative procedure for the reduction of polyether PEMO

In a round bottom flask, 5.95 g of PEMO (19.0 mmol) was dissolved in 150 ml of freshly anhydrous THF, under argon atmosphere and vigorous stirring. The desired amount of $LiAlH_4$ was added in small portions and after addition was complete, the mixture was stirred vigorously at room temperature for 30 minutes. Traces of unreacted $LiAlH_4$ were decomposed by addition of 5 ml ethyl acetate dropwise, then a 10 % H_2SO_4 aqueous solution was slowly added. The phases were separated, and the aqueous layer extracted with ethyl acetate. The combined organic phases were washed with H_2O, saturated $NaHCO_3$ solution and saturated NaCl solution, dried over anhydrous magnesium sulfate, and the solvent removed in vacuum. The polymers were dried at 50 °C under vacuum for 24 hours (see Table 1 for general properties).

^{1}H NMR ($CDCl_3$, TMS, δ in ppm): 3.63 (s, -O-CH_3), 3.65-3.55 (t, -CH_2OH), 3.40-3.10 (m, polyether backbone), 2.27 (t, -CH_2-CO_2Me), 1.70-1.10 (m, -CH_2-aliphatic backbone), 0.85 (t, -CH_3).

^{13}C NMR ($CDCl_3$, TMS, δ in ppm): 174.3 (-CO_2Me), 82-74 (polyether backbone), 62.9 (-CH_2OH), 51.6 (-OMe), 34.2 (-CH_2CO_2Me), 32.9 (-CH_2-CH_2OH), 32.1 (-CH_2-CH_2-CH_3), 31-25.5 (m, aliphatic backbone), 25.2 (-CH_2-CH_2-CO_2Me), 22.9 (-CH_2-CH_3) 14.3 (-CH_3).

Table 1. General properties of the obtained polyols

Polyol	mmol $LiAlH_4$/g polymer	OH[a] (w%)	Reduction degree (%)	*M*n (SEC)	*M*w/*M*n	Funct-ionality[b]	EW (g/eq)[c]
POH11	0.24	0.66	11	7100	1.6	2.4	2960
POH15	0.30	0.88	15	6700	1.7	3.5	1914
POH20	0.40	1.19	20	6600	1.7	4.6	1440
POH28	0.55	1.67	28	6700	1.7	5.8	1140
POH40	0.80	2.39	40	6600	1.7	9.3	710

[a] Hydroxyl content values from 1H and 19F NMR

[b] Funcionality was obtained by dividing the experimental molecular weight (Mn) by the hydroxyl content

[c] Equivalent weight calculated by dividing the experimental molecular weight (Mn) by the functionality

Representative procedure for the synthesis of polyurethanes

Polyurethanes were synthesized by reacting the appropriate amount of polyol and 1,3-propandiol for the segmented polyurethanes with a 2% molar excess of the isocyanate (MDI or LDI). Samples were prepared by vigorous stirring of the reactants at 60 °C under argon and the mixture was poured into a mold (5 cm length, 0.6 cm width) and degassed under vacuum. Mixtures were cured under argon atmosphere as follows: Polyurethanes derived from MDI (PUM) at 60 °C for 2 hours and 110 °C for 12 hours. Polyurethanes derived from LDI (PUL) at 90 °C for 2 hours and 110 °C for 12 hours. Segmented polyurethanes derived from MDI (SPUM) at 70 °C for 12 hours and 130 °C for 2 hours. Segmented polyurethanes derived from LDI (SPUL) at 110 °C for 12 hours and 130 °C for 2 hours. Chemical composition and hard segment content of the polyurethanes are shown in Table 2.

Table 2. Chemical composition of the polyurethanes

Sample Code	Polyol	Isocyanate	Molar Composition[a]	%HS[b]
PUM11	POH11	MDI	1.00/0.00/1.02	-
PUM15	POH15			-
PUM20	POH20			-
PUM28	POH28			-
PUM40	POH40			-
PUL11	POH11	LDI	1.00/0.00/1.02	-
PUL15	POH15			-
PUL20	POH20			-
PUL28	POH28			-
PUL40	POH40			-
SPUM15	POH20	MDI	1.00/1.78/2.83	15
SPUM34			1.00/5.24/6.36	34
SPUM47			1.00/9.04/10.24	47
SPUL15	POH20	LDI	1.00/2.14/3.16	15
SPUL34			1.00/5.66/6.79	34
SPUL47			1.00/10.57/11.80	47

[a] mol OH Polyol: mol OH PDO: mol isocyanate

[b] % Hard segment calculated as weight percentage of PDO and isocyanate per total material weight

Characterization

^{1}H NMR (400 MHz), ^{13}C NMR (100.6 MHz) and ^{19}F NMR (376.4 MHz) spectra were recorded in $CDCl_3$ using a Varian Gemini 400 spectrometer. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS), $CHCl_3$ and $CFCl_3$ as internal standards. The IR spectra were recorded on a Bomem Michelson MB 100 FTIR spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated total reflection (ATR) accessory with thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac-Teknokroma) was used to determine FTIR spectra.

Calorimetric studies were carried out on a Mettler DSC822e thermal analyzer using N_2 as a purge gas (20 mL/min) at a scan rate of 20 °C/min. Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N_2 or synthetic air as purge gases. The studies were performed in the 30-800 °C temperature range at a heating rate of 10 °C/min.

Size exclusion chromatography (SEC) analysis was carried out with an Agilent 1200 series system with PLgel 3 µm MIXED-E, PLgel 5 µm MIXED-D and PLgel 20 µm MIXED-A columns in series, and equipped with an Agilent 1100 series refractive-index detector. Calibration curves were based in polystyrene standards having low polydispersities. THF was used as an eluent at a flow rate of 1.0 mL/min, the sample concentrations were 5-10 mg/mL, and injection volumes of 100 µL were used.

The mechanical properties were measured with a TA DMA 2928 dynamic mechanical thermal analyzer. Specimens 2.0 mm thick, 5 mm wide and 10 mm long were tested in a three-point-bending configuration. Temperature range from -100 °C to 150, 200 or 250 °C depending on polyurethane at a heating rate of 3 °C/min and at a fixed frequency of 1 Hz. Stress-strain curves were carried out applying 0.1 N/min controlled force at 40 °C.

Hydroxyl value determination

The milimol of hydroxy groups per gram of polymer were determined by ^{1}H-NMR and ^{19}F-NMR using 2-fenylethyl-trifluoroacetate as internal standard. The samples were derivatized with trifluoroacetic acid anhydride. Reactive hydroxyl groups were calculated as follow:

$$valueOH = \frac{mmolISxIntPOH}{IntISxgPOH}$$

Where POH is the reduced polymer, IS is the internal standard, mmol IS is the amount of internal standard added to the sample in milimol and g POH is the quantity of sample measured in grams.

Results and discussion

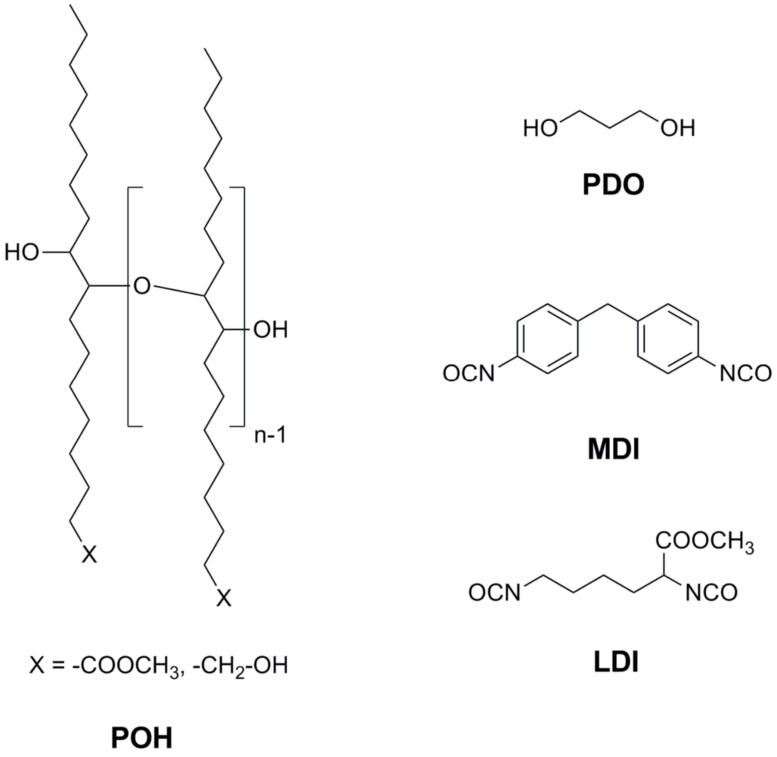
Synthesis of polyols

PEMO (M_n=6400, M_w/M_n=1.7)[21] was used as starting material for the partial reduction of the ester groups to synthesize polyols having primary hydroxyl moieties. The reduction was carried out with appropiate amounts of $LiAlH_4$ as reducing agent to obtain polyols having a 10, 15, 20, 30 and 40% of reduction degree (Table 1). We determined the hydroxyl content by ^{1}H and ^{19}F NMR spectroscopy and as can be seen, polyols POH11, POH15, POH20, POH28 and POH40 showed reduction degrees very close to the expected. FTIR spectra of the polyols showed an increase of the hydroxyl groups peak intensity (3500 cm^{-1}) whereas the decrease of the aliphatic ester carbonyl peak (1750 cm^{-1}) was observed. In the ^{1}H NMR spectra, a new signal appears at δ=3.6 ppm due to the protons of the CH_2-OH moiety. As the reduction degree increases, the intensity of this signal increases while the intensity of the peak at δ=2.3 ppm, corresponding to the methylene attached to the ester group, decreases. In this way, polyols of similar molecular weight with a range of functionalities from 2.4 to 9.3 have been obtained, which are from clear to viscous liquids at room temperature. DSC traces for POH11 exhibits a broad melting peak centered at -20 °C, which shifts to higher temperatures when the hydroxyl content value increases. Moreover, a second melting endotherm can be observed at 0 °C for POH40, with the highest functionality. Multiple peaks in these polyols should be ascribed to different crystalline forms.

Synthesis of polyurethanes

Novel biobased polyurethanes were prepared from the above mentioned epoxidized methyl oleate-based polyether polyols and MDI or LDI. Moreover, segmented polyurethanes were prepared using POH20, MDI or LDI, and PDO as a chain extender using the one-shot technique, which consists of the very efficient mixing, in one step only, in a short time, of all the raw materials involved in polyurethane preparation: polyol, chain extender and isocyanate. The chemical structure and the characteristics of the materials are shown in Scheme 1.

The chemical composition and hard segment content of the synthesized polyurethanes are shown in Table 2. The NCO/OH molar ratio was kept constant at 1.02 to compensate for isocyanates that are consumed in side reactions during the urethane synthesis. For the segmented polyurethanes, the molar composition of the POH was set at 1.00, and then the molar ratio of the PDO and isocyanate were varied to obtain polyurethanes with different hard segment contents. For the MDI-containing polyurethanes, reactants were mixed at 70 °C and cured at this temperature for 12 h before being postcured 2 h at 110 °C. The LDI-containing polyurethanes were obtained by curing 12 h at 110 °C and postcuring 2 h at 130 °C.



Scheme 1. Chemical structure of polyols, PDO, MDI, and LDI.

FTIR analysis demonstrated the urethane formation reaction during polymer synthesis. Figure 1 shows FTIR spectra before and after the curing of the polyurethane PUM28. The starting mixture shows a characteristic peak at 2240 cm^{-1} ascribed to –N=C=O stretching of the isocyanate moiety. During the curing, this peak significantly decreases and after 2 hours completely disappears. The cross-linking reaction was also monitored by the appearance of the characteristic absorbances of urethane link. The band due to the carbonyl stretching vibration of polyurethane occurs at 1723 cm^{-1},overlapped with the C=O ester band, and a combination of N-H deformation as well as C-N stretching vibrations occurs at 1533 and 1233 cm^{-1}, respectively. Peak appearing at 1309 cm^{-1} is due to –OCONH asymmetric stretching vibrations. Moreover, the broad band centered at 3500 cm^{-1}, corresponding to the O-H stretching, shifts to lower frequencies and shows a maximum at 3350 cm^{-1}, characteristic of N-H stretching.

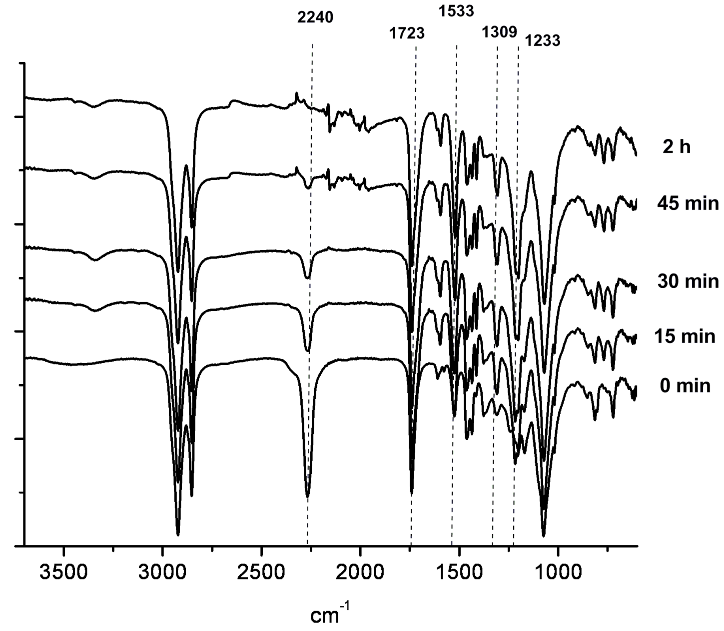
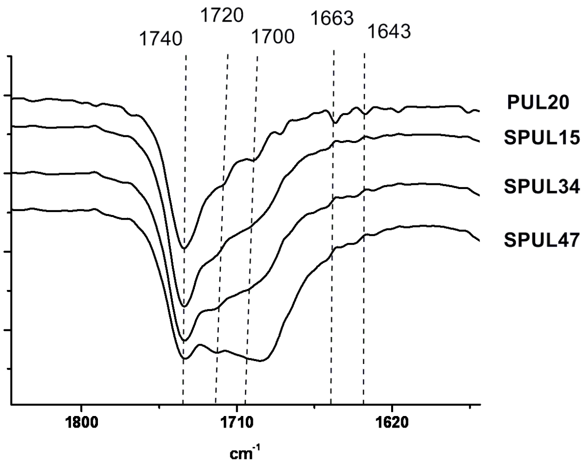


Figure 1. FTIR spectra of curing of PUM28.

FTIR spectroscopy was used to investigate the structural difference in hard and soft segments of synthesized polyurethanes with various PDO fractions. Almost all the infrared research on polyurethanes has focused on two principal vibrational regions: the N-H stretching vibration (3200-3500 cm^{-1}), and the carbonyl C=O stretching vibration amide-I region (1700-1730 cm^{-1}).[23,24] Polyurethanes are capable of forming several kinds of hydrogen bonds due to the presence of donor N-H group and C=O acceptor group in the urethane linkage. The oxygen atom of the ester or ether linkage when a polyester or a polyether soft segment is present may also act as a proton acceptor. Therefore, hydrogen bonding between hard segment-hard segment or hard segment-soft segment can exist. These bands have been widely used to characterize, at least semi-quantitatively, the hydrogen bonding state of the polymer, and to correlate this to the phase separation in the system. It is well known that in H-bonded urethane N-H and C=O bands appear at lower wavenumbers than that in free ones.[25] Figure 2 shows the FTIR spectra of C=O and N-H stretching vibration regions for synthesized polyurethanes. The band at 1740 cm^{-1} is ascribed to C=O stretching of the LDI and the remaining methyl ester groups of the polyether polyol, the broad band between 1730-1680 cm^{-1} is attributable to associated and non-associated C=O urethane groups and the small shoulders at 1663 and 1643 cm^{-1} are ascribed to associated and non-associated urea linkages which may be obtained from the reaction of some of the unreacted isocyanates with the atmospheric moisture while curing as a side reaction.



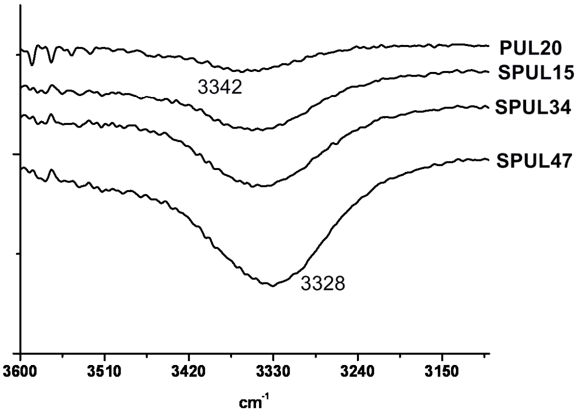


Figure 2. FTIR spectra of carbonyl (top) and amide (bottom) regions of polyurethanes.

Analysis of amide-I stretching vibration for PU sample indicates that there is a band at approximately 1720 cm^{-1}, attributable to free C=O urethane groups, and a shoulder at about 1700 cm^{-1} which is due to the H-bonded urethane. The intensity of the bands attributed to free and H-bonded urethane carbonyls increases with increasing PDO fraction, as could be expected, because increasing PDO fraction leads to increase urethane content. The intensity of the band attributed to H-bonded urethane, relative to the band attributed to the non-bonded urethane groups, increases with an increase in the hard segment content. This suggests that the SPUL34 and SPUL47 C=O urethane groups are hydrogen-bonded to a greater degree than the PUL20 and SPUL15 samples. In the amine region, the broad band ascribed to N-H stretching grows with the increase in urethane group concentration and shifts slightly to a lower wave number with increasing hard segment content, indicating an increase in the degree of association.

Thermal analysis of the polyurethanes was performed to provide insights into the morphological structure of the material. Thermal transitions are listed in Table 3 and Figure 3 shows the DSC thermograms for the segmented polyurethanes. For both series of non-segmented polyurethanes it was observed the expected trend that the T_g is higher when the functionality of the polyol used was higher, which indicates a higher degree of cross-linking. Moreover, differences can be observed for both isocyanates; the aromatic MDI leads to materials with higher T_g values than the aliphatic LDI. DSC thermograms of polyurethanes POH20/LDI extended with PDO showed an endothermic step in the heat flow at low temperatures, whereas in MDI containing samples it could not be observed. Such transitions appeared in the region of -15 to -13 °C, and were attributed to the POH soft-segment glass transition temperature. This value is a measure of relative purity of the soft-segment regions; when there are hard segments dispersed in the soft domains, the T_g of the soft segment is raised. The degree of hard segment mixing into the soft-segment domain will depend on the overall hard segment content and the affinity of one segment toward the other. In our polyurethanes, hard segment content is high enough to achieve phase separation and the experimental results revealed that the dispersion of hard segments in the soft domains seems to be low for LDI-containing polyurethanes. The results also show that the dispersion of the hard segments in the soft domain seems not to increase with the hard segment content.

Hard segment glass transition was observed at approximately 53-56 °C and 40-50 °C for SPUM and SPUL respectively. Glass transition temperatures for the hard segment depend strongly on its chemical structure and its molecular weight; it can therefore be stated that the lower hard segment T_g value in the SPUL samples could be a consequence of the irregular aliphatic structure of LDI.

No melting or crystallization peaks were found by DSC for the non-segmented polyurethanes and for the LDI containing segmented polyurethanes, according to the structure of amorphous materials. For the MDI containing segmented polyurethanes the most notable result of incorporating PDO is the appearance of melting endotherms of variable enthalpy and position, indicative of a semicrystalline structure. Melting behaviour was complex, which can be attributed to a distribution of crystallite sizes or to the presence of different crystal forms. However, it seems that the non-symmetrical diisocyanate LDI which contains methyl ester side chain produces hard segments that are unable to pack efficiently to form a crystalline hard segment domain.

Table 3. Thermal and mechanical properties of the polyurethanes

	Tg (°C)		TGA (N_2)		Young's Modulus (MPa)	Tensile Strength (Mpa)	Elonga-tion (%)
PU	½ ΔC_p	tan δ_{max}	$T_{5\% loss}$ (°C)[a]	T_{max} (°C)[b]			
PUM11	-29	-3	349	390	-	-	-
PUM15	-15	4	350	388	1.0	0.13	15
PUM20	-10	12	352	388	1.8	0.23	22
PUM28	9	23	350	392	3.5	0.20	13
PUM40	49	57	337	410	9.5	0.38	6
PUL11	-25	-10	352	392	-	-	-
PUL15	-21	-4	352	392	0.8	0.06	9
PUL20	-16	0	348	390	1.4	0.07	11
PUL28	-9	4	351	391	2.5	0.12	8
PUL40	23	29	343	412	6.0	0.18	5
SPUM15	-8, 55	26	316	321,397, 459	7.0	0.60	14
SPUM34	56	25	302	306, 408,464	30	1.80	10
SPUM47	53	24	295	303, 405,469	74	3.10	10
SPUL15	-14	13, 81	307	304, 409	1.4	0.09	13
SPUL34	-13, 51	18, 77	292	303, 417	1.8	0.13	9
SPUL47	-15, 40	19, 77	281	296, 414	-	-	-

[a] Temperature of the 5% weight loss
[b] Temperature of the maximum weight loss rate

TGA is the most favored technique for evaluation the thermal stability of polymers. Polyurethanes have relatively low thermal stability, mainly due to the presence of urethane bonds. The thermal stability of the obtained polyurethanes was studied with TGA at a heating rate of 10 °C/min in a nitrogen atmosphere and the obtained data are shown in Table 3. The shapes of the weight loss curves of non-segmented polyurethanes are almost identical, and differences in thermal stability appear to be small. It can be seen that the decomposition of the polyurethanes in a nitrogen atmosphere do not takes place below 330 °C.

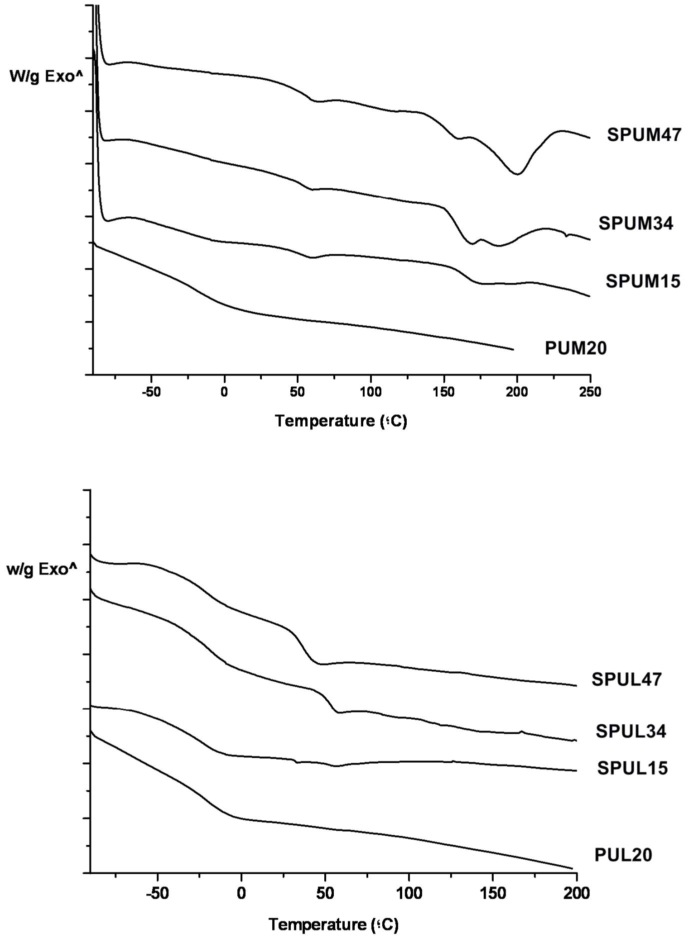


Figure 3. DSC thermograms (20 °C/min) of polyurethane networks.

The thermal decomposition of segmented polyurethanes involves at least two overlapping steps: a small drop below 300 °C is followed by the main loss weight above 300 °C (Figure 4). The first weight loss is related to the decomposition of urethane bonds, which takes place through the dissociation of to isocyante and alcohol, the formation of primary amines and olefins or the formation of secondary amines.[26] The main decomposition process is attributed to the polyether polyol chain scission, and occurs at about 410 °C. The weight loss in the first step increases as the hard segment content increases, which is in accordance to the existence of a higher amount of weaker urethane bonds.

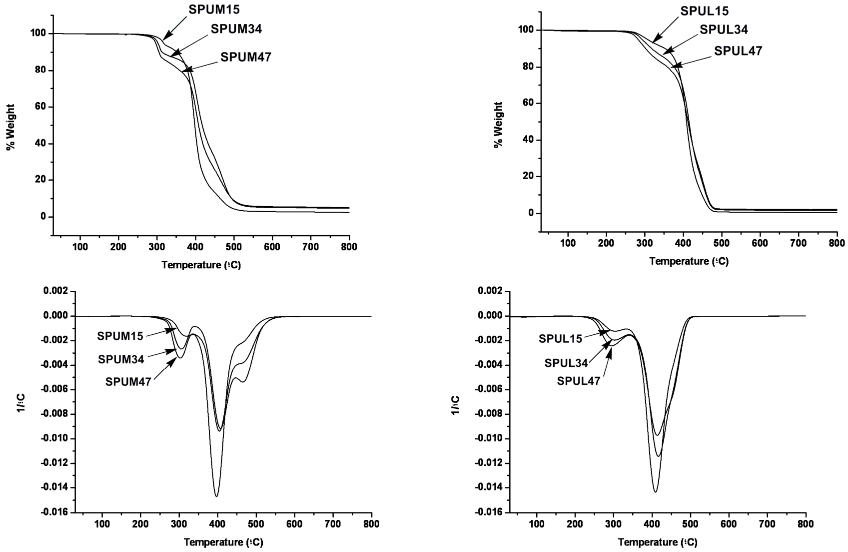


Figure 4. TGA plots (10 °C/min) and derivative curves of polyurethane networks.

The dynamic mechanical properties of the polyurethanes were obtained as a function of temperature beginning in the glassy state, through the T_g, and well into rubbery plateau of each material. Figure 5 show the temperature dependence of the storage modulus and Tan δ of the non segmented polyurethanes PUM and PUL. From the DMTA curves, the plateau of the elastic modulus in the rubbery state can be used to make qualitative comparisons of the level of cross-linking among the various polymers. Figure 5 shows that the value of the storage modulus in the rubber plateau increased as the hydroxyl content of the starting polyol increased. DMTA also makes it possible to determine the T_g of the cross-linked materials. The T_g values determined by DMTA as the maximum of Tan δ are shown in Table 3. As expected, the T_g value is higher than the $1/2\Delta C_p$ from DSC, which can be related to the heat transporting hysteresis for large scale samples in DMTA, and increase with increasing the hydroxyl content of starting polyol (Figure 5). This is caused by the higher cross-linking degree which increases the stiffness of the network structure.

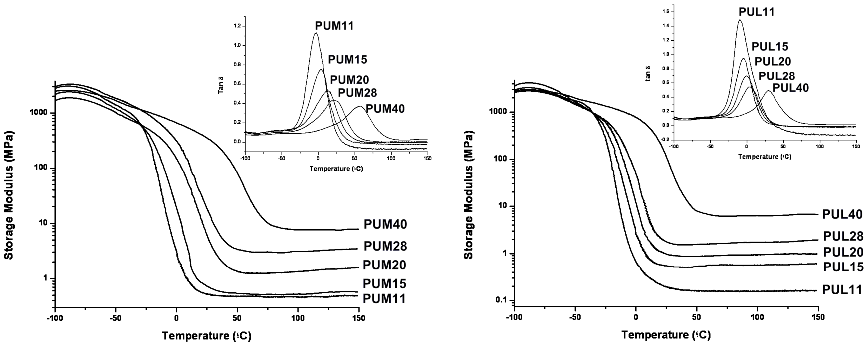


Figure 5. Storage modulus and loss factor of the non-segmented polyurethanes.

Figure 6 shows the DMTA curves of segmented polyurethanes. In the glassy region, the storage moduli E’ is higher when the hard segment content is higher due to the increased number of urethane connections and the increase in interchain interactions caused by the hydrogen bonds. It appears that the hard segments play the role of physical cross-links and fillers and this effect is more pronounced for MDI-containing polyurethanes than for LDI-containing polyurethanes. Figure 6 also shows the dissipation factor Tan δ curves as a function of temperature. While DSC does not show the glass transition of the soft segment of MDI containing polyurethanes, it was clearly visible in DMTA experiments. Reference sample shows a Tan δ peak at 12 °C for PUM20 assigned to the glass transition of the amorphous soft segment. This peak shows a shift of maxima, decreasing height and a broadening of the transition region as the hard segment content increases. This suggests greater limitations on freedom of chain mobility in the soft segment which may be explained by the phase mixing between hard and soft segments. While the Tan δ curves of SPUM polyurethanes show a unique transition, SPUL samples display the glass transition of the soft segment and a distinct transition at higher temperatures which can be attributed to the T_g of the phase-separated hard block segments of the polymer. This transition becomes more prominent when the hard segment content increases due to a more phase separated morphology. Moreover, all Tan δ curves show a low temperature transition (around -50 °C). The origin of this peak is not known, but it is generally attributed to the rotational motions of the dangling fatty acid chains.[13] This peak is larger in segmented polyurethanes than in the reference sample. This relaxation at similar temperature was observed in other polyurethanes from vegetable-oil based polyols.[14]

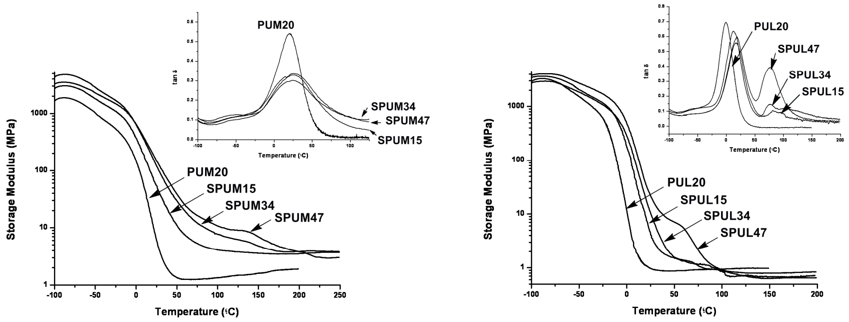
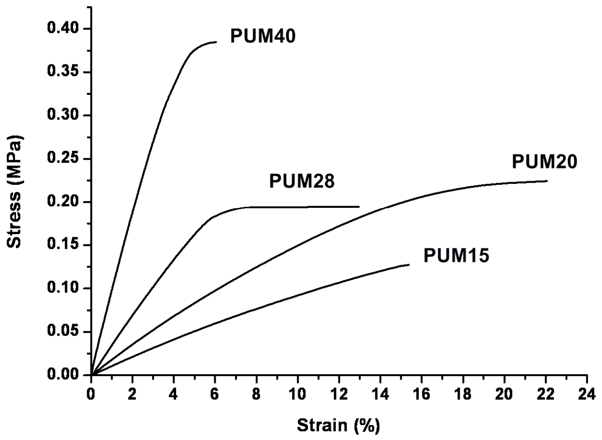


Figure 6. Storage modulus and loss factor of segmented polyurethanes.

Figure 7 shows the stress-strain curves of MDI-containing polyurethanes and Table 3 summarizes the values of the mechanical properties of all the obtained polyurethanes. Young’s Modulus and tensile strength at break increase while strain at break decreases in both, segmented and non-segmented polyurethanes, with increasing cross-linking density, which hinders molecular motion. The lower strength and modulus is a result of the higher amounts of dangling chains present which are imperfections in the final polymer network and do not support stress when the network is under load. As expected, with increasing hard segment concentration, both Young’s Modulus and tensile strength increase. Finally, the use of the aliphatic diisocyanate LDI which is weaker than aromatic diisocyanate MDI limits the Young’s Modulus and tensile strength, specially for segmented polyurethanes.



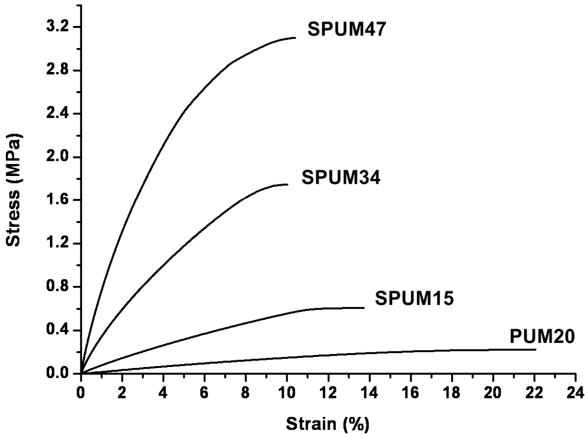


Figure 7. Stress-Strain plots of the polyurethanes.

Conclusion

As a conclusion, a variety of novel poly(ether urethane) networks were synthesized from polyether polyols obtained by ionic-coordinative polymerization of epoxidized methyl oleate. Non segmented polyurethanes show T_g values that increase as the functionality of the polyol increases and that are higher for the aromatic MDI than for the aliphatic LDI-containing materials. The segmented polyurethanes were phase segregated to varying degrees and the use of non-symmetric LDI inhibits hard segment crystallinity. All the polyurethanes are thermally stable over 300 °C and their mechanical properties increase with increasing cross-linking density and hard segment concentration.

J. Polym. Sci.: Part A: Polym. Chem., 2010, 48, 5009-5017

Acknowledgements

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Chapter II.

Polyurethanes from polyols synthesized via metathesis

METATHESIS ON VEGETABLE OIL DERIVATIVES

Olefin metathesis chemistry

Olefin metathesis has shown a constant development from the initial reports on double-bond scrambling reactions in the mid-1950s.[70] The first investigations on olefin metathesis were conducted in the early 1960s by researchers at Du Pont, Standard Oil and Philips Petroleum.[71] However, it was not until 1967 that Calderon and co-workers recognized that both ring-opening polymerization of unsaturated alicyclic compounds and the disproportionation of acyclic olefins were the same reaction and coined the term "olefin metathesis".[72] Few years later, Chauvin and Hérisson proposed as intermediates of the mechanism the formation of a metal alkylidene and a metallacyclobutane (Figure 1).[73]

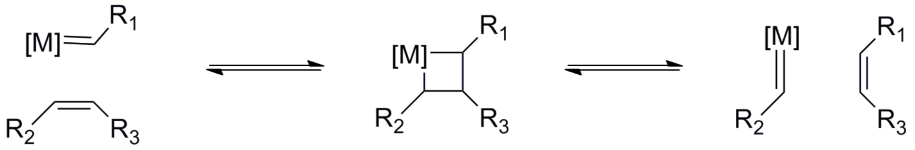

Figure 1. Olefin metathesis mechanism proposed by Chauvin and Hérisson.

The deeply study of metathesis reactions has produced a better knowledge of their potential applications. Thus, several different reactions have been developed depending on the olefinic molecules involved. In Figure 2 some of these transformations are shown. The ring-opening metathesis (ROM) takes place between a cyclic molecule and an acyclic olefin. This reaction is an equilibrium, and the reverse step is known as ring-closing metathesis (RCM). The ring-opening metathesis polymerization (ROMP) gives linear polymers from cyclic olefins. Two different acyclic olefins under metathesis reaction generate two new olefins, and this is known as cross metathesis (CM); when metathesis is applied on an α,ω-diene monomer,

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ethylene and a polymer is the result; and the reaction is named acyclic diene metathesis (ADMET) polymerization.

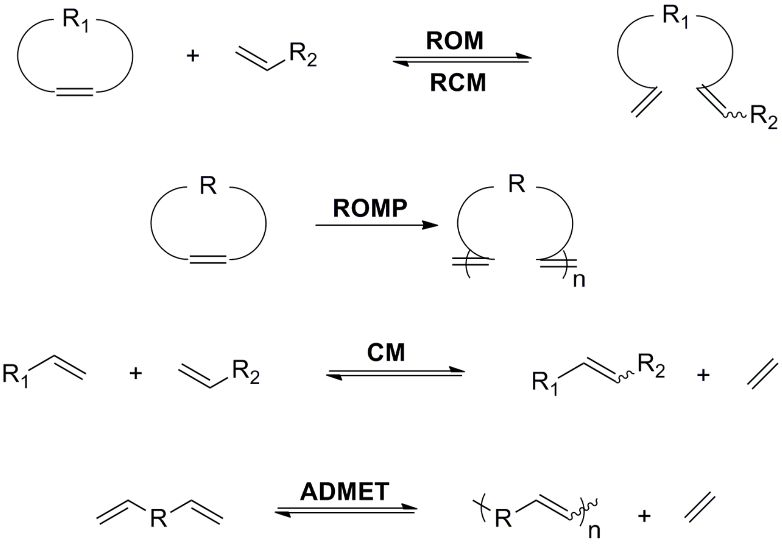

Figure 2. Most frequently studied metathesis reactions.

At the beginning, metathesis catalysts were multicomponent systems formed in situ from transition-metal halides and main-group metal alkyl cocatalysts. However, the utility of these catalysts was limited by the harsh conditions and the strong Lewis acids required, which made them incompatible with most functional groups.[74] The discovery of the olefin metathesis mechanism eventually led to the rational design of progressively more advanced, well-defined catalyst systems. Thus, in 1990 Schrock published well-defined, single-site tungsten and molybdenum alkylidene catalysts, which was a significant breakthrough in the development of metathesis.[75] However, the reactivity of these early transition metal based catalysts towards other functional groups such as alcohols, ketones, esters or aldehydes clearly limited their application. Moreover, the high oxophilicity of the metal centers makes these catalysts extremely sensitive to oxygen and moisture.[76]

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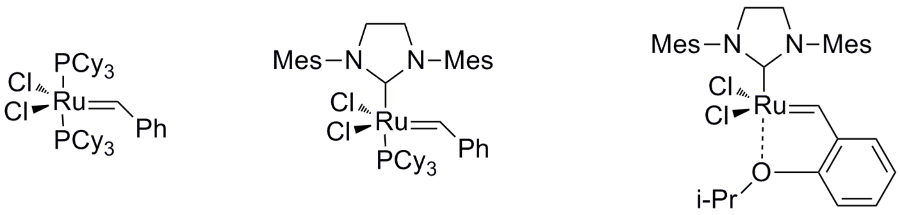
To overcome the limitations of these catalysts, other systems were studied, leading to important improvements in the synthesis of new metathesis catalysts. Among the transition metal metathesis catalysts, ruthenium reacts preferentially with carbon-carbon double bonds. The first well-defined ruthenium based metathesis catalyst (1, Figure 3), developed by Grubbs in the early 1990s, permitted the application of the olefin metathesis reactions in presence of a wide variety of functional groups. Further improvements were achieved by substitution of one of the trialkyl phosphine ligands by a N-heterocyclic carbene (NHC) (2 and 3, Figure 3). Thus, with the introduction of highly active and robust metathesis catalysts, the number of applications of metathesis has been exponentially increased.



1 **2** **3**

Figure 3. Metathesis catalysts: Grubbs 1st generation (1), Grubbs 2nd generation (2) and Hoveyda-Grubbs 2nd generation (3).

Plant oil-based polymers via metathesis

Until 1988 more than 90% of oleochemical transformations involved the fatty acid carboxy group, while less than 10% were related to the alkyl chain.[77] However, the development of metathesis reactions using catalysts more active and tolerant with functional groups has considerably increased the chemical transformations of the plant oils derivatives.

The first successful metathesis approaches with oleochemicals were reported in the 1970s by Boelhouwer et al. and dealt with the metathesis of some fatty acid methyl esters, with the WCl_6/Me_4Sn catalytic system.[78]

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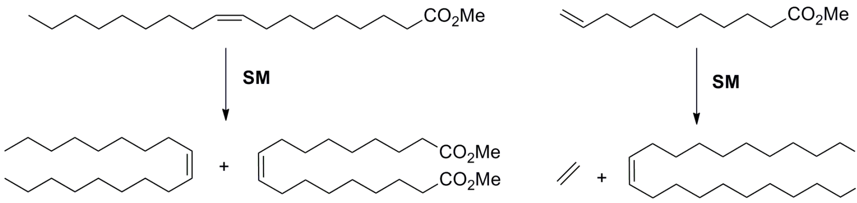
Although metathesis transformations have been used on oleochemicals for different applications, the polymer field has been highly benefited due to both the synthesis of monomers via metathesis for classical condensation polymerizations, and for the metathesis polymerization of monomers synthesized from oleochemicals.

a) *Synthesis of monomers via metathesis*

The self metathesis of fatty acid methyl esters has been intensively studied for the synthesis of long chain diesters. When a fatty acid methyl ester with internal double bond is metathesized, two products are obtained: the desired diester and the internal olefin. However, the self metathesis of fatty acid methyl esters with terminal double bonds yields the diester and ethylene as by-product (Scheme 1). By removing the ethylene generated, the equilibrium is shifted to the formation of the diester.



Scheme 1. Self metathesis of both internal and terminal double bond in fatty acid methyl esters.

Kunz and co-workers have synthesized a diester by self metathesis of methyl undecenoate. Then, the diester was polymerized by classical polycondensation methods with different diols such as ethylene glycol, 1,4-butanediol and 1,4-(bishydroxymethyl)ciclohexane (Scheme 2). [79] The obtained polyesters presented molecular weights varying from 20 to 110 KDa and melting temperatures typical of linear aliphatic polyesters. Mutlu et al. synthesized the polyamide derived from 10-undecenoic methyl ester and different aliphatic diamines.[80]

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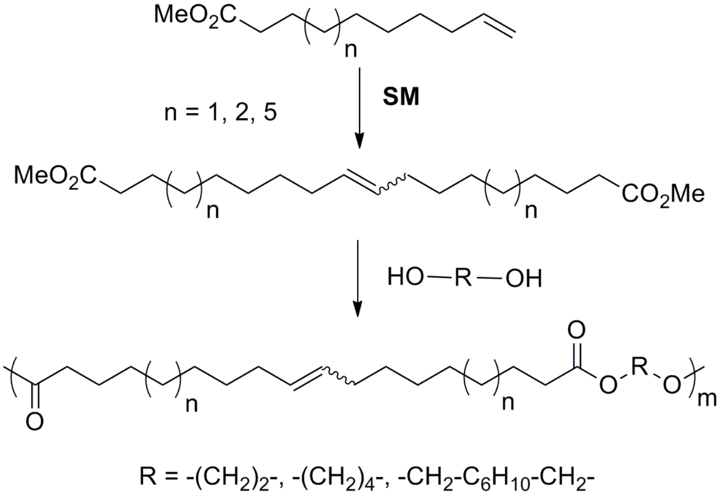

Scheme 2. Polyester synthesized from the diester derived from metathesized 10-undecenoic methyl ester.

Other route studied for the synthesis of monomers from fatty acid derivatives is its cross metathesis with functionalized olefins. Meier and co-workers have published several works in this topic; thus, by cross-metathesis of fatty acid methyl esters with methyl acrylate, different diesters were obtained, which can be used in the synthesis of polyesters and polyamides.[81] A similar method, using allyl chloride instead of methyl acrylate, has been used to obtain α,ω-difunctional monomers with potential application on polymer synthesis.[82] The cross-metathesis of fatty acid methyl esters with acrylonitrile yielded also difunctional molecules, which can be applied on polymer chemistry (Scheme 3).[83] By cross-metathesis of oleylalcohol with methyl acrylate an α,ω-difunctional monomer for polyester synthesis has been synthesized, but the protection of the hydroxyl group was a necessary step in order to achieve good conversions with small amounts of catalyst.[84]

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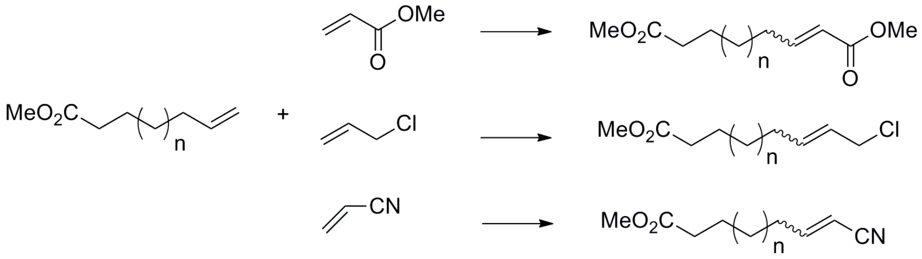

Scheme 3. Synthesis of α,ω-difunctional monomers via cross-metathesis.

b) ADMET polymerization of α,ω-dienes

Other way to synthesize vegetable oil-based polymers via metathesis reactions is to polymerize α,ω-diene monomers via acyclic diene metathesis (ADMET) polymerization. ADMET polymerization is a step-growth polymerization driven by the release of a condensate, usually ethylene. The mechanism of the ADMET polymerization cycle is well established (Figure 4).[85] The olefin coordinates to the metal centre followed by formation of a metallacyclobutane intermediate (1). At this point, the productive cleavage of 1 leads to the formation of the metathesis active alkylidene complex (2). Subsequent reaction with the double bond of a diene produces the metallacyclobutane ring (3), which subsequently leads to polymer formation. The cycle proceeds with coordination of another diene or growing polymer, followed by productive cleavage, and release of ethylene.

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[85] K. B. Wagener, J. M. Boncella and J. G. Nel, Macromolecules, 1991, 24, 2649-2657.

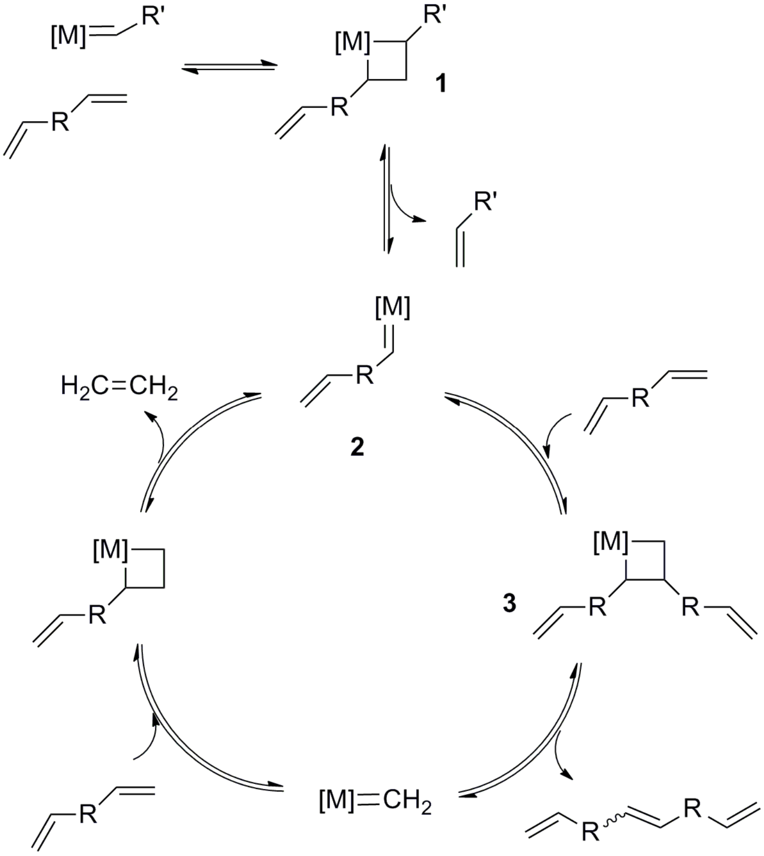
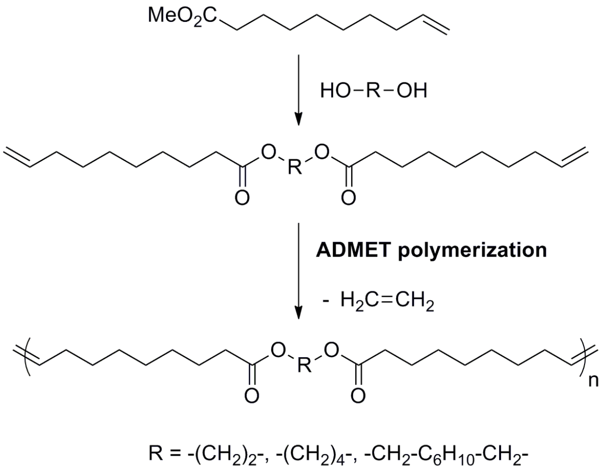


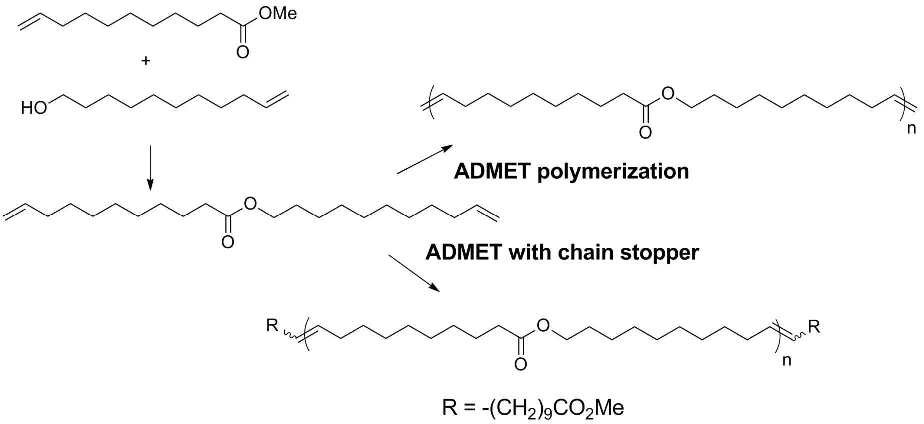
Figure 4. Generally accepted mechanism of ADMET polymerization.

Kunz and co-workers synthesized also different α,ω-dienes by transesterification of fatty acid methyl esters with diols.[79] The ADMET polymerization of the α,ω-dienes obtained yielded similar polyesters to those obtained by polycondensation of the diesters obtained via self-metathesis with the diols (Scheme 4).



Scheme 4. ADMET polymerization of the α,ω-dienes obtained by esterification of decenoic methyl esters with a diol.

Meier and co-workers described the ADMET polymerization of a fully renewable monomer synthesized by transesterification of methyl undecenoate with undecenol.[86] The unsaturated polyester showed a molecular weight of 45 kDa. Moreover, by addition of methyl undecenoate as chain stopper, it was possible to tune the molecular weight in a range from approximately 10 to 45 KDa. Finally, the application of poly(ethylene glycol) methyl ether acrylate as the chain stopper led to the preparation of ABA triblock copolymers in a one-step, one-pot procedure (Scheme 5).



Scheme 5. ADMET polymerizations of undecenyl undecenoate.

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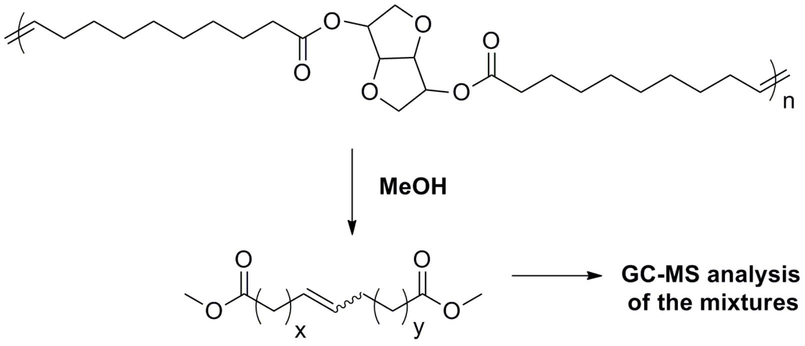
[86] A. Rybak and M. A. R. Meier, ChemSusChem, 2008, 1, 542-547.

The ADMET copolymerization of undecenyl undecenoate monomer with a phosphorous containing α,ω-diene yielded random copolymers with flame retardant properties.[87] Similar study was carried out by substituting the phosphorous free α,ω-diene by glycerol-diundecenoate monomer.[88] The obtained linear polyesters with pendant hydroxyl groups were used for the preparation of flame retardant cross-linked polymers.

The ADMET polymerization of the α,ω-diene obtained from isosorbide and 10-undecenoic acid yielded fully renewable polyester.[89] This polyester was transesterified with methanol and the degradation products were identified by GC-MS in order to study the isomerization in the metathesis reaction (Scheme 6). Similar studies were conducted on a monomer synthesized with methyl undecenoate and 1,3-propanediol.[90]



Scheme 6. Methanolysis of the polyester for the isomerization studies.

Although, in cross-metathesis reactions it has been broadly profited, the different reactivity of the olefins involved in the metathesis reaction.[91] This feature has not been exploited in ADMET polymerization until this moment. Thus, Montero de Espinosa and Meier have synthesized block- and star-copolymers by using the selectivity of olefin cross-metathesis between acrylates and terminal olefins. The monomer used in this work was 10-

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[87] L. Montero De Espinosa, J. C. Ronda, M. Galià, V. Cádiz and M. A. R. Meier, J. Polym. Sci., Part A: Polym. Chem., 2009, 47, 57605771.

[88] L. Montero de Espinosa, M. A. R. Meier, J. C. Ronda, M. Galiá and V. Cádiz, J. Polym. Sci., Part A: Polym. Chem., 2010, 48, 1649-1660.

[89] P. A. Fokou and M. A. R. Meier, J. Am. Chem. Soc., 2009, 131, 1664-1665.

[90] P. A. Fokou and M. A. R. Meier, Macromol. Rapid Commun., 2010, 31, 368-373.

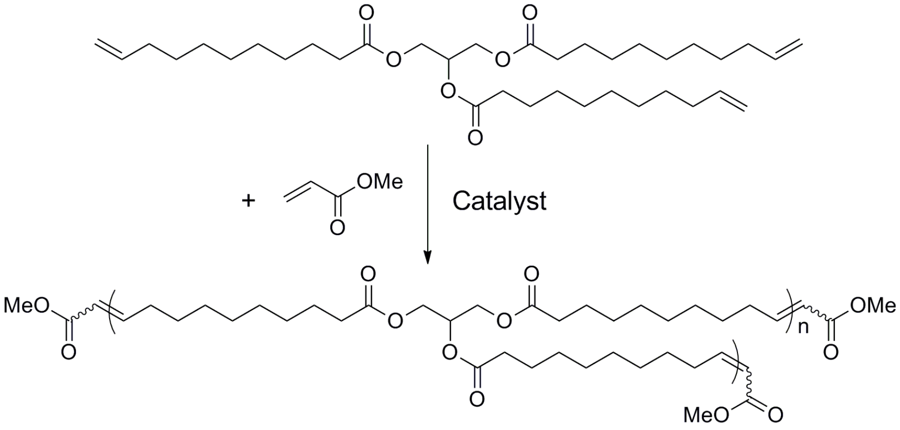
[91] A. K. Chatterjee, T.-L. Choi, D. P. Sanders and R. H. Grubbs, J. Am. Chem. Soc., 2003, 125, 11360–11370.

undecenyl acrylate, which polymerized by head-to-tail addition. Glycerol triacrylate was used as core molecule for the star-shape polymer synthesis.[92]

c) ATMET polymerization of trienes

The acyclic triene metathesis (ATMET) polymerization can be defined as the metathesis polymerization applied on a triene-containing monomer. The polymers obtained by ATMET polymerization are branched and with high polydispersity index, and can lead to cross-linked structures unless a chain stopper is used.

Meier and co-workers have synthesized branched polymers by ATMET polymerization of triglycerides with methyl acrylate as chain stopper. Two different monomers have been studied, glyceryl triundecenoate (Scheme 7) and high oleic sunflower oil. The ratio between the triglyceride as monomer and methyl acrylate as chain stopper was used to tune the molecular weight of the prepared macromolecules.[93]



Scheme 7. ATMET polymerization of glyceryl triundecenoate using methyl acrylate as chain stopper.

Despite all these examples of metathesis reactions on plant oil derivatives, the possibilities that this reaction offers are increasing faster due to the development of more active and tolerant catalyst. Moreover, the

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[92] L. Montero de Espinosa and M. A. R. Meier, Chem. Commun., 2011, DOI: 10.1039/C0CC04161K.

[93] a) P. A. Fokou, M. A. R. Meier, Macromol. Rapid Commun., 2008, 29, 1620-1625. b) U. Biermann, J. O. Metzger and M. A. R. Meier, Macromol. Chem. Phys., 2010, 211, 854–862.

number of α,ω-diene monomers chemically available is increasing day to day.

The second chapter of this thesis is focused on the synthesis of polyols via metathesis polymerization of vegetable oil-based monomers. Two different families of polyols have been synthesized:

By reaction of 10-undecenol with 1,3-dichloropropan-2-ol an α,ω-diene has been synthesized. This monomer has been polymerized with different metathesis catalysts. The best results were achieved for 2nd generation Grubbs catalyst. The polymerization of the monomer with different proportions of undecenol as chain stopper yielded a family of polyols that was reacted with MDI. The polyurethanes obtained presented good mechanical properties, and shape-memory effect was observed for semicrystalline polymer.

The second family of polyols has been synthesized by ATMET polymerization of glycerol tri-undecenoate with the Zhan catalyst, using undecenol as chain stopper. The proportion of undecenol in the polymerization mixture is the most significant parameter that affects polyols and polyurethanes properties. The polyurethanes obtained by reaction of the polyols with MDI were fully characterized, showing shape-memory effect.

Polyurethanes from polyols obtained by ADMET polymerization of a castor oil-based diene: Characterization and shape memory properties.

Polyurethanes from polyols obtained by ADMET polymerization of a castor oil-based diene: Characterization and shape memory properties.

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Abstract

The acyclic diene metathesis polymerization (ADMET) of 1,3-di-10-undecenoxy-2-propanol, a castor oil based diene, is reported. 10-Undecenol was used as renewable comonomer to end-cap polymer chains and limit the molecular weight. The polyols obtained in this way were reacted with 4,4'-methylenebis(phenylisocyanate) (MDI) to yield a series of amorphous and semicrystalline polyurethane networks. The thermal stability and the thermomechanical and mechanical properties of these thermosets have been studied and showed good shape memory properties for the semycristalline polymer.

Introduction

Recently, the use of plant oils as renewable feedstock for the development of designed polymeric materials has received particular attention due to environmental concerns.[1] The main components of vegetable oils are triglycerides, which are the product of esterification between a molecule of glycerol and three fatty acids. The chemical modification of their structure enables the synthesis of a wide variety of derivatives which can be used in different fields such as surfactants, cosmetics and lubricants.[2] Moreover, together with the well known applications in polymer science, new routes are being developed that enable access to value added polymer building blocks and controlled polymer architectures.[3] The increasing importance of polymeric materials from renewable resources has put polyols and polyurethanes derived from plant oils in the spotlight, especially due to their simple preparation yet greatly promising applications.[4,5] To extend the application possibilities of vegetable oils, we focused on converting these renewable resources into useful bioderived polymers. We described the synthesis of polyether polyols through the combination of cationic ring opening[6] or ionic-coordinative[7]

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polymerization of epoxidized methyl oleate (EMO) and the reduction of carboxylate groups to hydroxyl moieties. These polyols were reacted with 4,4'-methylenebis(phenylisocyanate) (MDI) to obtain thermosetting polyurethanes,[8] with L-lysine diisocyanate (LDI) and 1,3-propandiol to obtain biodegradable segmented polyurethanes[9] or with a biobased silicon-containing polyol to obtain silicon-containing polyurethanes with enhanced flame retardant properties.[10]

Olefin metathesis takes advantage of the synthetic potential of oleochemicals by the using inherent double bond functionality of fatty acids. Acyclic diene metathesis (ADMET) polymerization of α,ω-dienes has been shown to be an efficient tool for the synthesis of a wide variety of linear polymers and polymer architectures that are not available using other polymerization methods.[11] Essentially, ADMET is a step growth polycondensation in which two terminal olefins react to form new internal carbon-carbon double bonds and ethylene, thus affording strictly linear unsaturated polymers. It has been demonstrated that ADMET polymerization can proceed in the presence of heteroatoms, as long as the terminal olefins are far enough apart from them.[12] There are many examples of ADMET of heteroatom-containing α,ω-dienes in the literature, since the introduction of C-C double bonds in the backbone of the polymers provides different properties and permits further modifications.[13] When chain stoppers are used during the polymerization, it is possible to control the molecular weight of the final polymers.[3]

Castor oil is one of the most exploited vegetable oil as raw material for the chemical industry. From castor oil processing, like from other applications of vegetable oils as in biodiesel, glycerol is obtained as byproduct, being a platform chemical with widespread application possibilities.[14] Sebacic acid and 10-undecenoic acid are produced from castor oil via caustic fusion and pyrolisis, respectively.[15,16] Derivatives with a terminal double bond such as undecenoic acid, methyl undecenoate, undecenol, allyl undecenoate or undecylenyl undecenoate are well suited renewable raw materials for olefin metathesis reactions and other chemical transformations.[17,18] In previous studies, we synthesized a series of phosphorus-containing linear polyesters through the ADMET copolymerization of a phosphorus-based α,ω-diene with different amounts of a castor oil derived diene.[19,20] Moreover, castor oil's unique structure, where the most of the fatty acid chains bear a hydroxyl group, makes it especially attractive and a wide variety of polyurethanes have been prepared by taking advantage of the hydroxyl groups.[21] Numerous polyurethanes have been found to posses shape memory effects.[22] Generally, shape memory polymers (SMP) are stimuli-responsive materials that have the ability to store a secondary shape after deformation and restore to the originally primary shape when an external trigger is applied.[23,24] The most extensively investigated group of SMPs are thermally induced, which are triggered by heat: the shape memory is induced when a certain switching temperature is exceeded. The features of a polymer that allow for good shape memory behaviour include a sharp transition that can be used to promptly fix the secondary shape and trigger shape recovery and high deformability above the transition temperature that leads the shape recovery.

The present work describes the synthesis of several polyols using ADMET chemistry. These polyols are based on a castor oil-based diene, 1,3-di-10-undecenoxy-2-propanol (M1, Scheme 1) and 10-undecenol to end-cap the polymer chains and limit the molecular weight during the ADMET polymerization. The polyols obtained in this way were reacted with MDI to yield a series of polyurethane networks that were characterized by infrared spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and thermodynamic mechanical analysis (DMA). In this study, we also investigated the shape memory properties of these materials.

Experimental

Materials

10-undecenol, 1,3-dichloro-2-propanol, sodium hydride, ethyl vinyl ether (EVA), benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]-dichloro (tricyclohexylphosphine)ruthenium (Grubbs catalyst second generation), [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]-dichloro(*o*-isopropoxyphenylmethylene)ruthenium (Hoveyda-Grubbs catalyst second generation), [1,3-Bis(2,4,6-trimethylphenyl) -2-imidazolidinylidene]dichloro(phenylmethylene)bis(3-bromopyridine)ruthenium(II) (Grubbs third generation), 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene[2-(i-propoxy)-5-(N,N-dimethylaminosulfonyl)phenyl]methyleneruthenium(II) dichloride (Zhan Catalyst), 4,4'-methylenebis(phenylisocyanate) (MDI) were supplied by Aldrich. Anhydrous hexane and tetrahydrofuran (THF) were prepared by refluxing with sodium before used.

Synthesis of 1,3-di-10-undecenoxy-2-propanol (M1)

12 g of a 60% dispersion of NaH in mineral oil (0.30 mmol) were introduced in a two necks round bottom flask of 250 ml under argon atmosphere and equipped with magnetic stirring. The NaH was washed with anhydrous hexane twice. Then, 60 ml of anhydrous THF was added and under vigorous stirring, 65 ml of 10-undecenol (0.32 mmol) were slowly added at 25 °C. When the addition was finished, the temperature was increased to reflux for two hours and then, 11.3 ml of 1,3-dichloro-2-

propanol (0.12 mmol) were added dropwise. The reaction was maintained at reflux for 15 hours under argon atmosphere and magnetic stirring. Finally, the reaction was allowed to reach room temperature and 10 ml of water were added, and the reaction mixture was transferred into a diethyl ether/water mixture, the organic layer was separated and the aqueous one extracted with diethyl ether. The organic phases were combined and washed with HCl 5%, $NaHCO_3$ saturated solution and brine. The organic phase was dried with anhydrous $MgSO_4$ powder filtered and the solvent evaporated under reduced pressure. The product obtained was purified by crystallization in hexane at -20 °C (hexane/product = 1/1). The final yield was 65% as a light yellow liquid.

^{1}H NMR ($CDCl_3$, TMS, δ in ppm): 5.84-5.75 (m, $CH_2=C\underline{H}$), 4.96 (d, $C\underline{H_2}=CH$, Jtrans = 26.2 Hz), 4.93 (d, $C\underline{H_2}=CH$, Jcis = 20.0 Hz), 4.0-3.9 (m, $C\underline{H}$-OH), 3.55-3.35 (m, $C\underline{H_2}$-O), 2.49 (s, -OH), 2.03 (m, $C\underline{H_2}$-CH=), 1.65-1.50 (m, $C\underline{H_2}$-CH_2O), 1.45-1.10 (m, aliphatic backbone).

^{13}C NMR ($CDCl_3$, TMS, δ in ppm): 139.3 ($CH_2=\underline{C}H$), 114.3 ($\underline{C}H_2=CH$), 72.0 ($\underline{C}H_2$-O), 71.8 ($\underline{C}H_2$-O), 69.6 ($\underline{C}$H-OH), 34.0 ($\underline{C}H_2$-CH=), 29.9-29.0 (aliphatic backbone), 26.3 ($\underline{C}H_2$-CH_2-O).

ADMET polymerization (catalysts test)

0.50 g (1.26 mmol) of 1,3-di-10-undecenoxy-2-propanol and 1% of catalyst were introduced in a 3 ml conic vial. The reaction was equipped with magnetic stirring, screw cap with septum and needle to allow relaxing of the ethene evolved. The reaction was homogenized at r.t. for 10 minutes and then heated at 80 °C with stirring for 5 hours. The reaction was stopped by adding ethylvinyllether (EVE) in a EVE : catalyst ratio of 50 : 1.

^{1}H NMR ($CDCl_3$, TMS, δ in ppm): 5.5-5.25 (m, $C\underline{H}=C\underline{H}$), 4.0-3.85 (m, $C\underline{H}OH$), 3.55-3.35 (m, $C\underline{H_2}$-O), 2.6-2.4 (m, $O\underline{H}$), 2.1-1.9 (m, $C\underline{H_2}$-CH=), 1.65-1.5 (m, $C\underline{H_2}$-CH_2O), 1.4-1.2 (m, aliphatic backbone), 1.0-0.8 (m, CH3).

Self metathesis of 10-undecenol

The same conditions as above were used starting from 0.50 g (2.94 mmol) of 10-undecenol and 0.5% of catalyst were introduced in a 3 ml conic vial.

^{1}H NMR ($CDCl_3$, TMS, δ in ppm): 5.5-5.25 (m, $C\underline{H}=C\underline{H}$), 3.65 (t, $C\underline{H_2}OH$, J = 6.6 Hz), 2.1-1.9 (m, $C\underline{H_2}$-CH=), 1.7-1.5 (m, $C\underline{H_2}$-CH_2O), 1.4-1.2 (m, aliphatic backbone), 1.0-0.8 (m, CH3).

Synthesis of the polyols

1,3-di-10-undecenoxy-2-propanol (**M1**) and 10-undecenol were mixed (2 g scale) in the desired molar ratio (Table 2) in a 3 ml conic vial. Then, 0.1% of catalyst per mol of double bond was added and the reaction was equipped with magnetic stirring, screw cap with septum and needle to allow relaxing of the ethene evolved. The reaction was homogenized at r.t. for 10 minutes and then heated at 80 °C with stirring for 5 hours. The reaction was stopped by adding by adding EVE in a EVE : catalyst ratio of 50 : 1.

^{1}H NMR ($CDCl_3$, TMS, δ in ppm): 5.5-5.25 (m, $C\underline{H}=C\underline{H}$), 4.0-3.85 (m, $C\underline{H}OH$), 3.63 (t, $C\underline{H_2}OH$, J = 6.6 Hz), 3.55-3.35 (m, $C\underline{H_2}$-O), 2.6-2.4 (m, $O\underline{H}$), 2.1-1.9 (m, $C\underline{H_2}$-CH=), 1.65-1.5 (m, $C\underline{H_2}$-CH_2O), 1.4-1.2 (m, aliphatic backbone), 1.0-0.8 (m, CH_3 Iso).

Determination of the mmol of hydroxyl groups per gram of polyol

The milimol of hydroxy groups per gram of polymer were determined by ^{1}H-NMR using 2-phenylethanol as internal standard. Primary hydroxyl content was determined from signal centered at 3.63 ppm, while secondary one was calculated from signal centered at 3.92 ppm. The following equation was used:

$$valueOH = \frac{mmolISxIntPOH}{IntISxgPOH}$$

where P-OH is the Polyol, IS is the internal standard, mmol IS is the quantity of internal standard added to the sample in milimol and g P-OH is the quantity of sample measured in grams.

Synthesis of the polyurethanes

Polyol was dissolved in anhydrous toluene (50% solution) under argon atmosphere, heated at 50 °C and added to a 50% dispersion of MDI in toluene. The solution was homogenized and casted over silanized glass preheated at 90 °C. The polyurethane was maintained at 90 °C for 2 hours and at 130 °C for 3 hours.

Instrumentation

^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded in $CDCl_3$ using a Varian Gemini 400 spectrometer. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) and $CHCl_3$ as internal standards. Calorimetric studies were carried out on a Mettler DSC822e thermal analyzer using N_2 as a purge gas (100 mL/min) at a scan rate of 20 °C/min. Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with

N_2 or synthetic air as purge gases. The studies were performed in the 30-800 °C temperature range at a heating rate of 10 °C/min.

The IR spectra were recorded on a Bomem Michelson MB 100 FTIR spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated total reflection (ATR) accessory with thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac-Teknokroma) was used to determine FTIR spectra.

Size exclusion chromatography (SEC) analysis was carried out with an Agilent 1200 series system with PLgel 3 µm MIXED-E, PLgel 5 µm MIXED-D and PLgel 20 µm MIXED-A columns in series, and equipped with an Agilent 1100 series refractive-index detector. Calibration curves were based in polystyrene standards having low polydispersities. THF was used as an eluent at a flow rate of 1.0 mL/min, the sample concentrations were 5-10 mg/mL, and injection volumes of 100 µL were used.

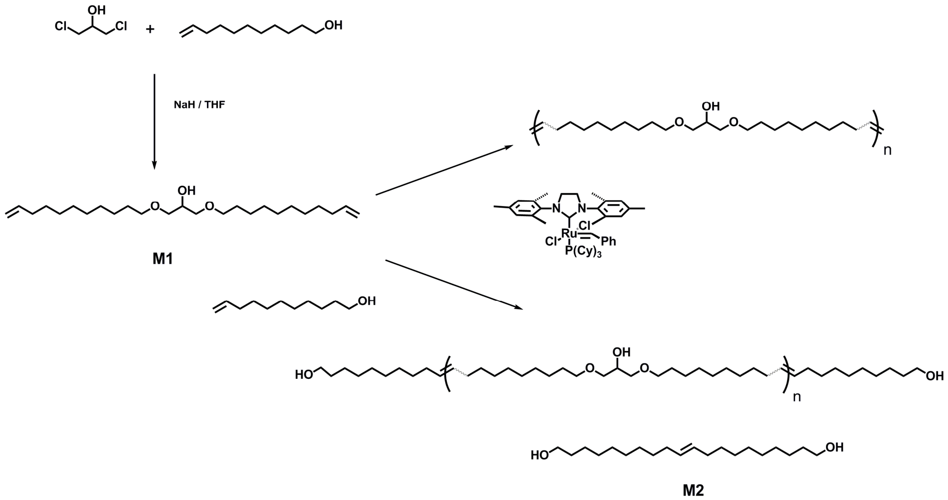
Dynamic mechanical thermal analysis (DMTA) and tensile tests properties were measured with a TA DMA 2928 dynamic mechanical thermal analyzer. Specimens 0.6 mm thick, 3 mm wide and 8 mm long were tested in a tension film configuration. For DMTA the temperature range was from -100 to 150 °C, at a heating rate of 3 °C/min and at a fixed frequency of 1 Hz. The tensile assays were performed by triplicate measuring the strain while applying a stress ramp of 1 N/min at 25 °C.

Shape-memory properties of the polyurethanes were studied in the force-controlled setup. The sample was equilibrated at 70 °C and to achieve the suitable strain, a force ramp of 0.5 N/min was applied to a previously measured stress (by a stress-strain experiment at 70 °C). Maintaining the stress applied, the sample was cooled down to 25 °C at 10 °C/min and equilibrated at this temperature for 10 minutes more. Then, the stress was released and the temperature maintained at 25 °C for 5 min. Finally, the temperature was increased at 5 °C/min to 70 °C. Three consecutive cycles were applied to each sample. Strain fixity and strain recovery ratios were measured for the three cycles.

Results and discussion

1,3-di-10-undecenoxy-2-propanol (**M1**) was synthesized by reaction of 1,3-dichloro-2-propanol with two equivalents of sodium 10-undecenolate, prepared by reacting 10-undecenol and sodium hydride (Scheme 1).[25] It must be pointed out that 1,3-dichloro-2-propanol can be obtained directly from glycerol[14] and 10-undecenol can obtained from castor oil, thus, both reagents are potentially plant oil derived, thus **M1** can be considered as 100% renewable. The compound was obtained as a yellow liquid in 65%

yield. Its ^{1}H NMR spectrum showed the expected signals at 5.8 and 4.9 ppm (CH_2=CH), at 4.0 ppm (CH-O), at 3.4 ppm (CH_2-O) and at 2.5 ppm (OH).



Scheme 1. Synthesis of monomer **M1** and ADMET polymerization.

The polymerization of **M1** was investigated with several metathesis catalysts to obtain aliphatic polyether-polyols with internal C=C double bonds (Table 1). Polymerizations were carried out in bulk under a continuous flow of nitrogen to remove the ethylene released during the metathesis reaction. SEC analysis confirmed that **M1** conversion was quantitative in all cases, as were the yields of the polymers after precipitation. Alcohol containing dienes have been polymerized via ADMET before using Grubbs 1st generation catalyst,[26] but our previous studies showed that oligomerization and poor conversion occurs probably due to catalyst degradation in presence of hydroxyl groups.[16] Second (**C1**) and third-generation (**C2**) Grubbs catalysts, the Hoveyda-Grubbs second generation catalyst (**C3**) and Zhan catalyst (**C4**) were also tested in the present work at 1% catalyst loading at 80 °C (Table 1).

Table 1. ADMET polymerization of **M1** in bulk for 5h

Sample	Catalyst (% wt)	T (°C)	Mn (x10^3)	PDI
P1	**C2** (1%)	80	2.31	1.93
P2	**C3** (1%)	80	2.46	1.93
P3	**C4** (1%)	80	2.63	1.91
P4	**C1** (1%)	80	3.71	2.05
P5	**C1** (1%)	90	3.72	2.10
P6	**C1** (1%)	70	3.02	1.95
P7	**C1** (0.5%)	80	3.62	2.04
P8	**C1** (0.1%)	80	3.50	1.96

The molecular weights of the ADMET polyethers were measured by SEC using PS standards. As can be seen the highest M_n was obtained using **C1**. When using this catalyst, no increase in M_n could be observed by increasing the reaction temperature, while lower M_n was obtained when conducting the reaction at 70 °C. Decreasing the catalyst loading led to a small decrease of M_n. On the basis of these results, polymerizations were carried out using a low catalyst loading of 0.1% of **C1** at 80 °C. The reactions could be monitored by the disappearance of the terminal olefin signals at 5.8 and 4.9 ppm together with the appearance of a multiplet at 5.4 ppm in the ^{1}H NMR spectrum (Figure 1). Moreover, new signals at 0.9 and 1.7 ppm were observed. 2nd generation ruthenium metathesis catalysts are known to promote olefin isomerization side reactions, that in the case of ADMET polymerizations lead to polymers with irregular repeating units and ill-defined end-groups.[27] The signals observed at 0.9 and 1.7 ppm can thus be attributed to CH_3 end groups formed by isomerization of terminal double bonds.

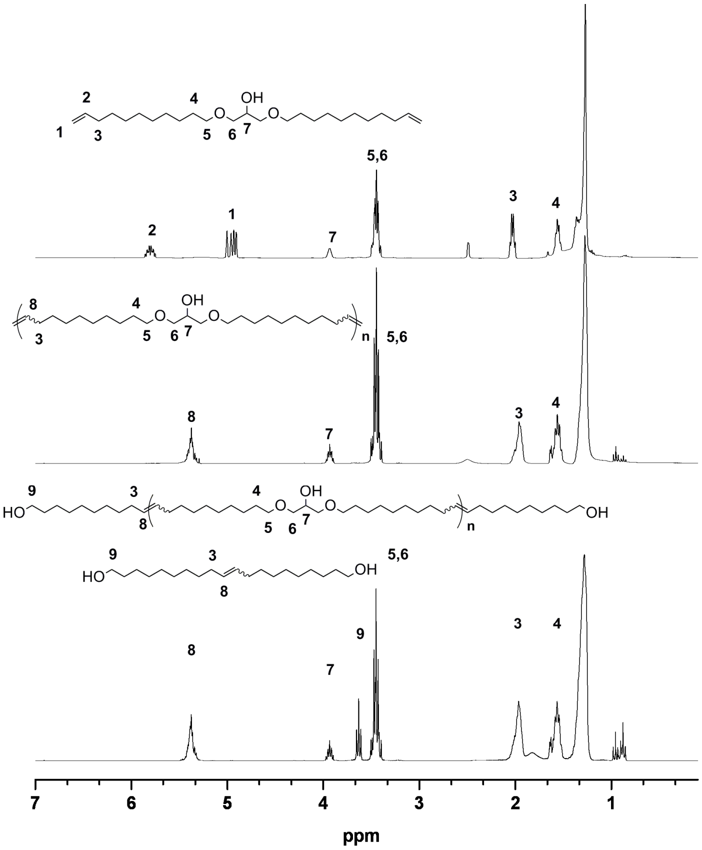


Figure 1. ^{1}H NMR spectra of **M1**, POH0, and POH2 ($CDCl_3$, TMS, 400 MHz).

We synthesized a series of polymers by performing ADMET polymerization with 10-undecenol as a monofunctional chain stopper. In this way, telechelic polymers of different molecular weight are obtained, containing mainly primary alcohols as end groups (Scheme 1). First, the metathesis of 10-undecenol was investigated using the established reactions conditions. Using 0.1% of **C1** at 80 °C, a 70% of conversion was obtained. Isomerization of the double bond was detected in an amount of 27%, leading to internal olefins. Due to the higher reactivity of terminal olefins, if compared to the internal double bonds, the isomerized products remained unaltered in the reaction conditions employed. In the synthesis of polyols, the amount of chain stopper was varied to increase **M1**/ chain stopper ratio from 1:0.1 to 1:5 (Table 2). As expected, isomerization of terminal double bonds took place and thus the reaction mixture was vacuum distilled at 70 °C to remove the low molecular weight by-products. The distillation residue was analyzed by SEC and the percentage of self-metathesis of chain stopper was found to increase as the amount of 10-undecenol does, as expected. Moreover, the molecular weights decrease as the amount of chain stopper increases as reported previously.[15,28] The total hydroxyl content as well as the percentage of primary and secondary alcohols were determined by ^{1}H NMR spectroscopy. The total hydroxyl content and the percentage of CH_2-OH increase while the percentage of CH-OH decreases when the amount of chain stopper increases. DSC traces for the polyols are collected in Figure 2. As can be seen, **POH0** exhibits multiple melting endotherms centered at 3, 20 and 40 °C that should be ascribed to different oligomers. When the amount of chain stopper increases, the number of lower temperature peaks increases and the enthalphy of the peak at higher temperature decreases, according to the existence of a lower molecular weight species.

Table 2. ADMET polymerization of **M1** using 10-undecenol as chain stopper

Sample	M1/CS[a]	SM (%)[b]	Mn (x10^3)[c]	PDI[c]	mmol OH/g[d]	CH_2-OH (%)[e]	CH-OH (%)[f]
POH0	1:0	-	3.50	1.96	2.93	0	100
POH0.1	1:0.1	8	2.80	1.82	3.20	11.5	88.5
POH0.3	1:0.3	9	2.42	1.70	3.35	22.9	77.1
POH0.5	1:0.5	11	1.99	1.60	3.61	29.3	70.7
POH1	1:1	16	1.63	1.45	3.94	42.3	57.7
POH2	1:2	25	1.34	1.35	4.47	58.3	41.7
POH3	1:3	32	1.23	1.33	4.70	67.6	32.4
POH5	1:5	42	1.11	1.26	5.18	77.4	22.6

[a] M1/10-undecenol molar ratio
[b] Percentage of 10-undecenol self-metathesis
[c] Determined by SEC
[d] Hydroxylic content determined by NMR
[e] Primary hydroxilic groups determined by NMR
[f] Secondary hydroxilic groups determined by NMR

The ADMET of **M1** in the presence of 10-undecenol is a pathway to mixtures of polyether polyols of different molecular weights that include different amounts of the self-metathesis product **M2** (Scheme 1)**.** Novel biobased polyurethanes were prepared by reacting these mixtures with MDI. The polyurethanes were synthesized by dissolving the reactants under argon atmosphere in anhydrous toluene, mixing at 50 °C and casting the mixture over a silanized glass plate preheated to 90 °C. The polyurethanes were then cured at 90 °C for two hours and post-cured at 130 °C for three hours. FTIR analysis demonstrated the urethane formation reaction during polymer synthesis by the disappearance of the band at 2240 cm^{-1} ascribed to the –N=C=O stretching of the isocyanate moiety and the appearance of the characteristic absorbances of the urethane link at 1730 cm^{-1}. Moreover, the broad band centered at 3500 cm^{-1}, corresponding to the O-H stretching, shifts to lower frequencies and shows a maximum at 3315 cm^{-1}, characteristic of the N-H stretching of urethanes.

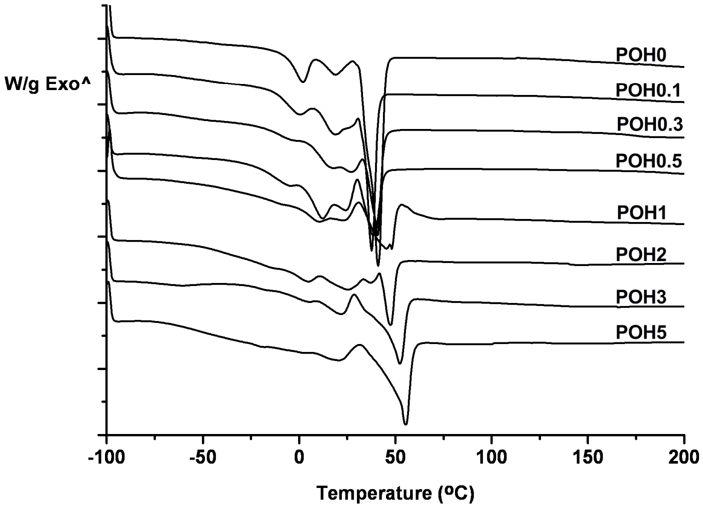


Figure 2. DSC thermograms (20 °C/min) of the polyols.

The thermal behaviour of polyurethanes was investigated by DSC (Figure 3). The glass transition temperature of the polyurethane PU0 measured by DSC is 8 °C. The most notable result of increasing the **M2** content in the mixture and decreasing the molecular weight of the polyols is an upward shift in the T_g and the appearance of a melting endotherm for PU5. The lower molecular weight of the polyols and the increasing of crosslinking would cause a restriction of segmental mobility, therefore, an increasing of T_g values. Since the starting material in the preparation of the polyurethanes is a mixture of polyether polyol and diol, with primary and secondary hydroxyl groups, the relative reactivity of functional groups is not equal. As a result, structurally inhomogeneous systems containing various domains with different sizes are obtained, which consist of alternate polyol or diol isocyanate sequences. Part of the domain is chemically crosslinked, with covalent bonds between polyol and isocyanate and part results from the physical crosslinking of the linear diol-isocyanate segments through hydrogen bonding. The chemical crosslinks would reduce the mobility of molecular chains and restrict the effective packing into crystals. When increasing amounts of a shorter diol are employed, the effective packing of polymer chains into crystals seems to be promoted and a semicrystalline material is obtained for PU5. When this sample was run a second time after melting, no melting peaks were observed, probably as a result of the miscibility of polyol and M2 fragments above the melting point. To check this, PU5 was annealed at 40 °C for several hours and left to cool slowly to room temperature to promote phase separation and crystallization. In the DSC thermograms after annealing a small endotherm appears, that shifted to a higher temperature and increased in enthalphy as the annealing time increased.

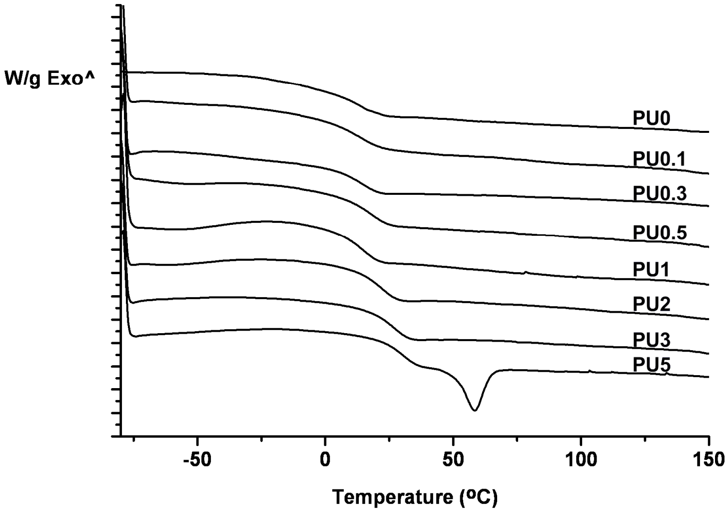


Figure 3. DSC thermograms (20 °C/min) of the polyurethanes.

The thermal stability of polyurethanes was studied by TGA in a nitrogen atmosphere and the obtained data are shown in Figure 4 and Table 3. The shapes of the weight-loss curves of all the polyurethanes are almost identical and the differences in the thermal stability appear to be small. The decomposition of the polyurethanes in a nitrogen atmosphere does not take place below 290 °C. The derivative curves reveal that more than one process occurs during thermal degradation: a first drop below 400 °C is followed by the main loss weight above 400 °C. The first weight loss is related to the decomposition of urethane bonds, which takes place through the cleavage to isocyanate and alcohol, the formation of primary amines and olefins or the formation of secondary amines.[29] The main decomposition process is attributed to the polyether polyol chain scission, and occurs at about 450 °C. The weight loss in the first step increases as the hydroxyl content of the polyol increases, which is in accordance to the existence of a higher amount of weaker urethane bonds.

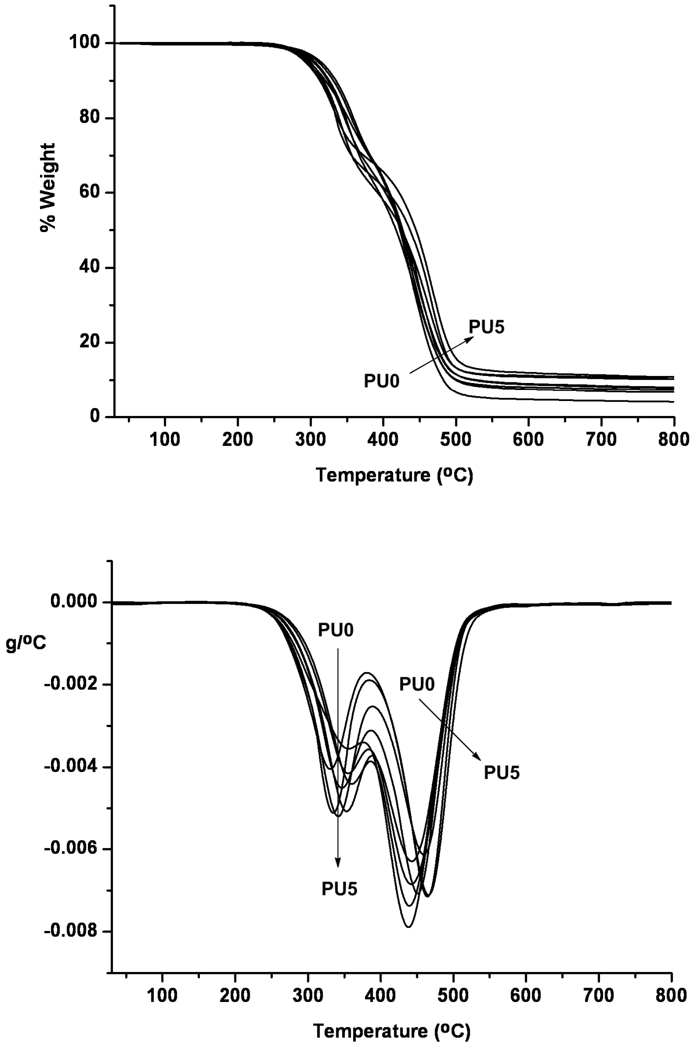


Figure 4. TGA plots (10 °C/min) and first derivative curves of polyurethanes.

The dynamomechanical behaviour of these polyurethanes was investigated by DMTA. Figure 5 shows the elastic modulus and the dissipation factor as a function of the temperature. Like crosslinked polymeric networks, at low temperatures there is a glass state with E’ at a high modulus plateau and at higher temperatures there is a rubbery state with a lower E’. The storage moduli at the rubbery plateau decrease when the low molecular weight diol **M2** content increase, according to a lower crosslinking density. As can be seen, all the polymers behave like homogeneous networks. An unique broad transition is observed for semicrystalline PU5, that according to DSC results must correspond to the glass transition and the melting of the crystalline phase.

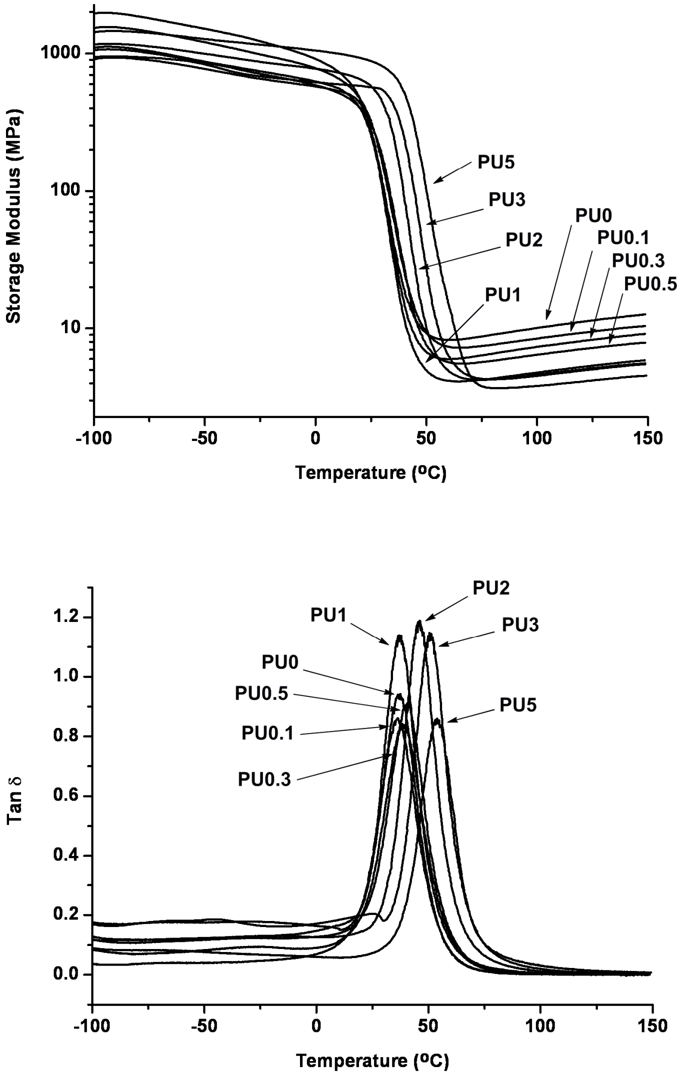


Figure 5. Storage moduli and Loss factor of polyurethanes.

The glass transition temperature determined from the peak of Tan δ is higher than the one determined by DSC (Table 3), which can be related to the heat transporting hysteresis for large scale samples in DMTA. Consistent with DSC results, this peak shows a shift of maxima when increasing the **M2** content in the mixture and decreasing the molecular weight of the polyols.

The height of the Tan δ peak increases as the content of **M2** increases, according to the lower crosslinking density that causes lower limitations on freedom of chain mobility. However, the peak value of Tan δ for PU5 is lower even though its **M2** content is higher. This can be explained by the presence of microcrystalline domains in the polymer, as has been observed by DSC, which restricts the chain mobility.

Table 3. Thermal properties of polyurethanes

	Tg (°C)	TGA (N_2)				
Polyurethane	½ΔC_p	$T_{5\%}$ (°C)	$T_{max\ 1}$ (°C)	$T_{max\ 2}$ (°C)	$Yield_{800°C}$ (%)	Tan δ_{max}
PU0	8	298	356	438	4	36
PU0.1	12	314	360	439	7	39
PU0.3	13	310	355	442	8	39
PU0.5	9	306	353	443	7	41
PU1	10	303	347	451	8	37
PU2	23	299	341	459	11	46
PU3	25	295	335	464	10	51
PU5	28	293	331	466	11	54

Figure 6 shows the stress-strain curves of the polyurethanes and Table 4 summarizes the values of the mechanical properties of all the obtained polyurethanes. Young’s Modulus and tensile strength at break increase while strain at break decreases when increasing the **M2** content in the mixture and decreasing the molecular weight of the polyols. What is most notable is the enhanced modulus and tensile strength at break of PU5 as expected from its semicrystalline nature.

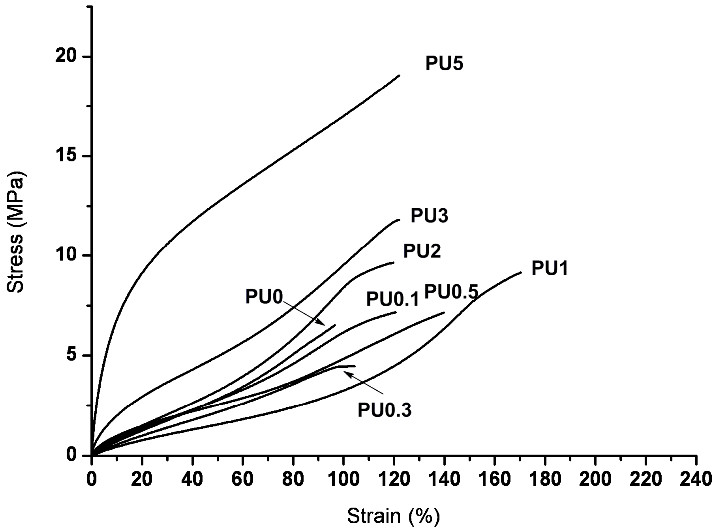


Figure 6. Stress-strain plots of the polyurethanes.

Table 4. Mechanical properties of the polyurethanes

Polyurethane	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)
PU0	7.3	6.5	96
PU0.1	9.7	7.0	120
PU0.3	6.5	4.5	100
PU0.5	8.8	7.6	140
PU1	4.7	9.3	171
PU2	11.4	8.0	120
PU3	25.0	11.8	120
PU5	90.0	19.0	121

The shape memory properties have been evaluated with cyclic tensile tests (Figure 7). In such tests, samples were heated above the switching temperature and stretched to the desired temporary shape. In the next step, the materials are cooled down to 25 °C to fix the temporary shape and shape recovery is triggered by heating the sample above the transition temperature. The tensile test was performed consecutively for two more times on the same sample. Samples PU0 to PU3 showed no capability to fix strain, i.e., the strain diminished to zero as the stress was released. In contrast, semicrystalline PU5 showed a sharp recovery only after heat was applied. Below the switching temperature the sample keeps its shape because of the crystallinity of the switching segments and after reaching the melting temperature the material restores under entropic force.

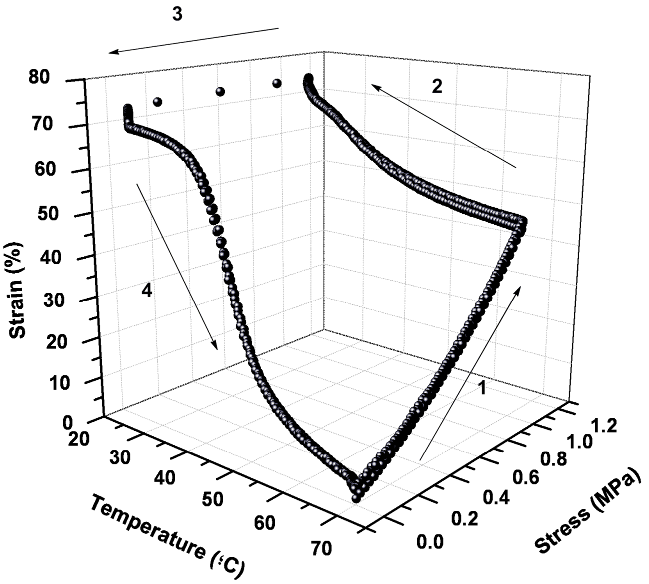


Figure 7. Stress-temperature-strain plot showing the shape memory cycle of PU5.

Two main parameters define the quality of the shape memory material: the strain recovery rate R_r and strain fixity rate R_f.

$$Rf(N) = \frac{Lu(N)}{Lm(N)} x100\%$$

$$Rr(N) = \frac{Lm(N) - Lf(N)}{Lm(N) - Lf(N-1)} x100\%$$

Where L_u is the fixed strain of the film unloaded and stabilized at 25 °C, L_m is the strain of the polyurethane before release of the stress, L_f is the final strain of the sample at 70 °C and N is the number of cycles. R_r indicates the quality of the restoration of the primary shape after reheating and R_f expresses how well the material can maintain the total strain of the

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secondary shape after releasing the force on the sample. Strain fixity and recovery in the first experiment are high (R_f = 94% and R_r = 88%) and subsequent two cycles are superimposable with both parameters remaining high (R_f=93% and R_r=93%), thus showing remarkably shape memory properties.

Conclusions

A castor oil based α,ω-diene containing hydroxyl groups (**M1**) has been successfully polymerized via ADMET polymerization using the second generation Grubbs catalyst. The molecular weight of the polyols has been reduced using 10-undecenol as renewable chain stopper and mixtures of varying amounts of polyether polyols and diol **M2** have been obtained. Novel biobased polyurethanes were prepared by reacting these hydroxyl containing mixtures with MDI. The most notable result of decreasing the molecular weight of the polyols and increasing the **M2** content in the mixture is an upward shift in the T_g and the switch to a semicrystalline material for the highest **M2** content (PU5). The shape memory properties of polyurethanes have been evaluated with cyclic tensile test and PU5 showed outstanding values of strain fixity and recovery.

Acknowledgements

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Shape memory polyurethanes from branched polyols obtained by ATMET polymerization of glyceryl triundec-10-enoate and 10-undecenol

Shape memory polyurethanes from branched polyols obtained by ATMET polymerization of glyceryl triundec-10-enoate and 10-undecenol

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Keywords: metathesis, polyurethanes, ATMET, shape memory, renewable resources

Abstract

The synthesis of branched polyols from glyceryl triundec-10-enoate by acyclic triene metathesis polymerization is reported. 10-undecenol was used as a monofunctional renewable comonomer to end-cap polymer chains, functionalize the periphery of the resulting branched materials and to control the molecular weight. The thus obtained polyols were reacted with 4,4'-methylenebis(phenylisocyanate) (MDI) to yield a series of semicrystalline polyurethane networks. The investigation of the thermal stability and the thermomechanical and mechanical properties of these thermosets revealed good shape memory properties.

Introduction

In recent years, the utilization of renewable materials such as plant oils and natural fatty acids for replacing petroleum derived raw materials for the production of polymeric materials has attracted great attention.[1] The main components of vegetable oils are triglycerides, which are the product of esterification between a molecule of glycerol and three fatty acids. Many of these fatty acids have double bond functionalities in the aliphatic chain, which, in combination with the development of olefin-metathesis,[2] offers manifold new possibilities for the utilization of these renewable resources for organic and polymer chemists.[3] The polymer field has probably benefited most from this development by applying metathesis chemistry for the synthesis of renewable monomers[4] for step-growth polymerizations and the possibility to polymerize plant oil based α,ω-dienes via acyclic diene metathesis (ADMET) polymerization.[5] Moreover, ADMET was shown to be an efficient tool for the synthesis of a wide variety of linear polymers and polymer architectures that are not available using other polymerization methods.[6] It has been demonstrated that ADMET polymerization can proceed in the presence of heteroatoms as long as the terminal olefins are far enough apart from them.[7] Many examples of ADMET of heteroatom-containing α,ω-dienes exist in the literature, since the introduction of functionalities to the backbone of a polymers provides different properties and permits further modifications.[8]

The development of ADMET polymerization and the possibility to control the polymer molecular weight using chain stoppers has opened new possibilities to obtain desired polymer architectures.[9] Moreover, chain stopper strategies have recently been exploited with the aim of polymerizing monomers with functionalities higher than two in order to avoid cross-linking. The thus named acyclic triene metathesis (ATMET) polymerization has been used in order to obtain branched polymers. In this way, glyceryl triundec-10-enoate (**1**), synthesized from glycerol and methyl undec-10-enoate, was polymerized using methyl acrylate as chain stopper in presence of Hoveyda-Grubbs second generation catalyst. The relative amount of added methyl acrylate made it possible to tune the molecular weight of the hyperbranched polymers, to functionalize them in their periphery and to completely avoid their crosslinking.[10] This strategy has also been used with success in the ATMET polymerization of high oleic sunflower oil.[11]

In a previous work, we reported the ADMET polymerization of 1,3-di-10-undecenoxy-2-propanol using 10-undecenol as renewable comonomer to end-cap polymer chains and limit the molecular weight. The linear polyols obtained in this way were reacted with MDI to yield a series of amorphous and semicrystalline polyurethane networks that showed good shape memory properties.[12] Shape-memory materials can be deformed and fixed into a temporary shape, and afterwards recover their original and permanent shape by exposure to an external stimulus.[13,14] Usually, heat or light have been used as stimulus for shape memory polymers (SMP).[15] Moreover, the indirect actuation of the shape memory effect has also been carried out by using irradiation with infrared light, application of electric fields, alternating magnetic fields or immersion in water.[16] Applications of SMPs can be found, for example, in heat-shrinkable tubes for electronics or films for packaging, self deployable sun sails in spacecraft, intelligent medical devices, or implants for minimally invasive surgery.[17]

In this work, we focused on the synthesis of branched polyols to take advantage of their properties including lower viscosity and increased solubility, if compared to their linear analogs. We have used ATMET polymerization of **1** as trifunctional monomer and 10-undecenol **2** as chain stopper (see Scheme 1) to obtain hyperbranched polyols that are functionalized in their periphery. By varying the ratio between **1** and **2**, it was possible to vary the molecular weight and hydroxyl number and to avoid crosslinking.

These polyols have been reacted with 4,4'-methylene-bis(phenylisocyanate) (MDI) to obtain a series of polyurethanes that were characterized by infrared spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and thermodynamic mechanical analysis (DMTA). In this study, we also investigated the shape memory properties of these materials.

Experimental

Materials

10-undecenol, ethyl vinyl ether (EVE), benzylidene[1,3-*bis*(2,4,6-trimethylphenyl)-2-imidazolidinylidene]-dichloro(tricyclohexylphosphine)-ruthenium (second generation Grubbs catalyst), [1,3-*bis*(2,4,6-trimethylphenyl)-2-imidazolidinylidene]-dichloro(*o*-isopropoxyphenylmethylene)ruthenium (second generation Hoveyda-Grubbs catalyst), [1,3-dimesityl-2-imidazolidinylidene]dichloro (phenylmethylene)*bis*(3-bromopyridine)-ruthenium(II) (third generation Grubbs catalyst), 1,3-*bis*(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene[2-(i-propoxy)-5-(N,N-dimethylaminosulfonyl)phenyl]-methyleneruthenium(II) dichloride (Zhan Catalyst), and 4,4'-methylenebis(phenylisocyanate) (MDI) were supplied by Aldrich. Glyceryl triundec-10-enoate (**1**) was synthesized following a previously reported method.[10]

Synthesis of the polyols

Glyceryl triundec-10-enoate (**1**) and 10-undecenol (**2**) were introduced in a 3 ml conic vial in the desired molar ratio. The reaction was equipped with magnetic stirring and screw cap with septum. The mixture was homogenized at room temperature for 10 minutes and 0.3 mol % of catalyst was added and the reaction was equipped with N_2 purge and heated at 50 °C with stirring for 3 hours. Then, a second 0.1 mol % of catalyst was added and the mixture was stirred for an additional 3 hours at 80 °C. The reaction was stopped by adding EVE in a 50 : 1 EVE : catalyst ratio.

^{1}H NMR ($CDCl_3$, TMS, 400 MHz, δ in ppm): 5.45-5.30 (m, CH=CH), 5.28-5.22 (m, CH_2-$C\underline{H}$(O)-CH_2), 4.32-4.24 (dd, *J* = 4.5 and 12.0 Hz, O-$C\underline{H}_2$-CH), 4.16-4.09 (dd, *J* = 6.0 and 11.8 Hz, O-CH_2-CH), 3.62 (t, *J* = 6.8 Hz, $C\underline{H}_2$-OH), 2.30 (t, *J* = 7.5 Hz, $C\underline{H}_2$-COO), 2.05-1.90 (m, $C\underline{H}_2$-CH=CH), 1.70-1.50 (m, $C\underline{H}_2$-CH_2-COO), 1.40-1.20 (m, aliphatic backbone), 0.95 (t, *J* = 7.2 Hz, =CH-CH_2-$C\underline{H}_3$), 0.87 (t, *J* = 7.2 Hz, CH_2-CH_2-$C\underline{H}_3$).

FTIR (cm^{-1}): 3370, 2923, 2852, 1744.

Determination of hydroxyl content

The milimol of hydroxy groups per gram of polymer were determined by ^{1}H NMR spectroscopy using 2-phenylethanol as internal standard (3.85 ppm). Primary hydroxyl content was determined from signal centered at 3.62 ppm. The following equation was used:

$$valueOH = \frac{mmolISxIntPOH}{IntISxgPOH}$$

Where P-OH is the Polyol, IS is the internal standard, mmol IS is the quantity of internal standard added to the sample in milimol and g P-OH is the quantity of sample measured in grams.

Synthesis of the polyurethanes

Polyol was dissolved in anhydrous toluene (1/1 w/w) under argon atmosphere, heated to 50 °C and added into a dispersion of MDI in toluene (1/1 w/w). The solution was homogenized and casted over a silanized glass preheated to 70 °C. The polyurethane was maintained at 70 °C for 2 hours and at 120 °C for 3 hours.

FTIR (cm^{-1}): 3353, 2924, 2852, 1738, 1596

Instrumentation

^{1}H NMR (400 MHz) spectra were recorded in $CDCl_3$ using a Varian Gemini 400 spectrometer. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) and $CHCl_3$ as internal standards.

Calorimetric studies were carried out on a Mettler DSC822e thermal analyzer using N_2 as a purge gas (100 mL/min) at a scan rate of 20 °C/min. Thermal stability studies were carried out on a Mettler

TGA/SDTA851e/LF/1100 with N_2 as purge gases. The studies were performed in the 30-800 °C temperature range at a heating rate of 10 °C/min.

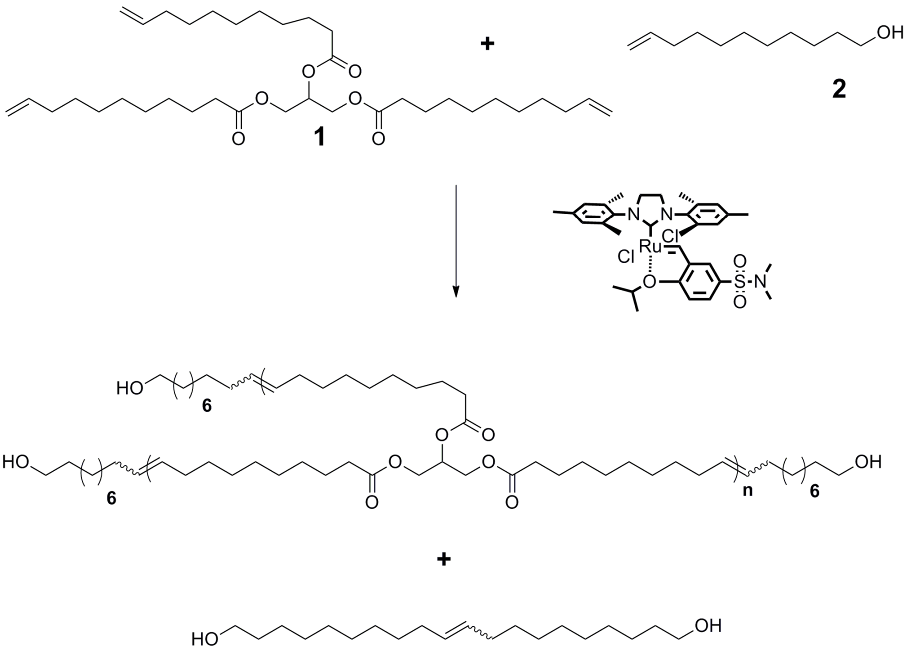
The IR spectra were recorded on a Bomem Michelson MB 100 FTIR spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated total reflection (ATR) accessory with thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac-Teknokroma) was used to determine FTIR spectra.

Size exclusion chromatography (SEC) analysis was carried out with an Agilent 1200 series system with PLgel 3 µm MIXED-E, PLgel 5 µm MIXED-D and PLgel 20 µm MIXED-A columns in series, and equipped with an Agilent 1100 series refractive-index detector. Calibration curves were based in polystyrene standards having low polydispersities. THF was used as an eluent at a flow rate of 1.0 mL/min, the sample concentrations were 5-10 mg/mL, and injection volumes of 100 µL were used.

Dynamic mechanical thermal analysis (DMTA), tensile tests properties and shape-memory effect were measured with a TA DMA 2928 dynamic mechanical thermal analyzer. Specimens 0.6 mm thick, 3 mm wide and 8 mm long were tested with a tension film clamp. For DMTA the temperature range was from -90 to 150 °C, at a heating rate of 3 °C/min and at a fixed frequency of 1 Hz. The tensile assays were performed by triplicate, measuring the strain while applying a stress ramp of 1 N/min at 25 °C. The shape-memory effect was quantified in the controlled-force setup as follow: the sample was equilibrated at 100 °C and a force ramp of 0.5 N/min was applied until a determined stress (previously estimated by a stress-strain experiment at 100 °C) to achieve the desired strain. Maintaining the stress applied, the sample was cooled down to 25 °C at 10 °C/min and equilibrated at this temperature for 10 minutes. Then, the stress was released and the temperature maintained at 25 °C for 5 min. Finally, the temperature was increased at 5 °C/min to 100 °C. Three consecutive cycles were applied to each sample. Strain fixity and strain recovery ratios were measured for the three cycles.

Results and Discussion

The ATMET polymerization of **1** in presence of 10-undecenol **2** as chain stopper was carried out using a total of 0.4 mol % of Zhan catalyst (Scheme 1). Grubbs second generation catalyst needed double amount of catalyst to achieve a similar degree of polymerization. Grubbs third generation and Hoveyda-Grubbs second generation catalysts showed very low conversion for the reaction.



Scheme 1. Synthesis of branched polyols via acyclic triene metathesis (ATMET) of triglyceride **1** with chain stopper **2**.

If the Zhan catalyst was added in one portion, the reaction mixture with the lowest proportion of chain stopper gave crosslinked byproducts. However, it was found that a stepwise addition of the catalyst provided a better control of the branching reaction avoiding cross-linking. Thus, in the first step, 0.3% of catalyst per mol of total double bond was added and the reaction was heated at 50 °C, three hours later a second batch of catalyst (0.1%) was added and the temperature was increased to 80 °C and maintained for three more hours.

Five polyols were synthesized by varying the **1**:**2** ratio (Table 1). As it is well known, metathesis polymerizations proceed with some migration of the terminal double bond to internal position. Thus, isomerized 10-undecenol was removed after the reaction by applying high vacuum at 70 °C for 12 hours. The resulting polyols were analyzed by SEC (Figure 1) and the percentage of self-metathesis of **2** was found to increase while the molecular weights decreased with increasing rations of **2**:**1**. Thus, polyols with a smaller amount of chain stopper have higher molecular weight and higher polydispersity, which is in agreement with previously reported ATMET polymerization results.[10,11] One of the most important parameters of the polyols for the synthesis of polyurethanes is the amount and nature of hydroxyl groups. The synthesized polyols have primary hydroxyl groups and their content, as determined by ^{1}H NMR spectroscopy (Table 1), increases as the amount of 10-undecenol does.

Table 1: Synthesis and characterization details of the studied polyols.

Polyol	**2**:**1**ratio	M_n (x 10^3)[a]	M_w/M_n[a]	% diol[b]	mmolOH/g[c]
POH1.5	1.5	3.00	6.23	9	1.36
POH2	2	2.67	4.67	12	1.76
POH3	3	2.07	2.91	16	2.27
POH5	5	1.71	2.42	24	2.94
POH8	8	1.39	1.81	31	3.40

[a] determined by SEC

[b] percentage of 10-undecenol self-metathesis

[c] hydroxyl value as determined by ^{1}H NMR

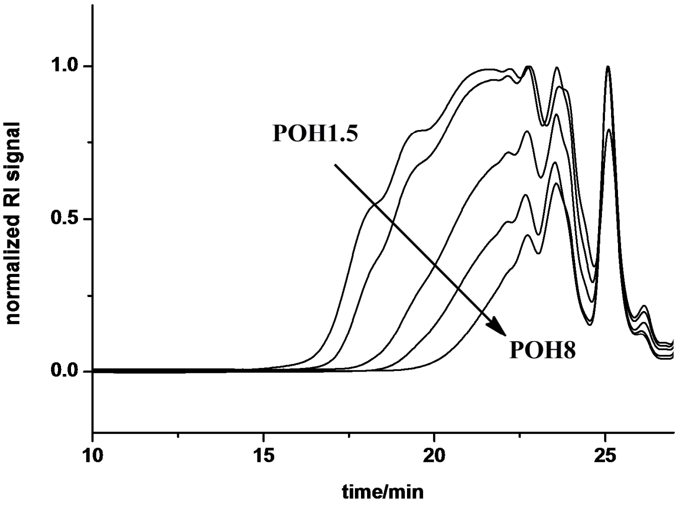


Figure 1. GPC traces of the prepared polyols POH1.5-POH8 (compare Table 1).

The polymerizations were also monitored by ^{1}H NMR spectroscopy (Figure 2). Terminal double bond signals (5.8 and 4.9 ppm) disappeared for the five formulations, and a signal corresponding to the internal double bond formed in the metathesis reaction appeared at 5.4 ppm. Signals below 1 ppm attributable to methyl groups were observed, which can be explained by isomerization of the terminal double bond to internal ones.[18] Thus, the obtained polyols contain some non functionalized branch ends, which would remain as dangling chains in the final cross-linked polyurethanes.

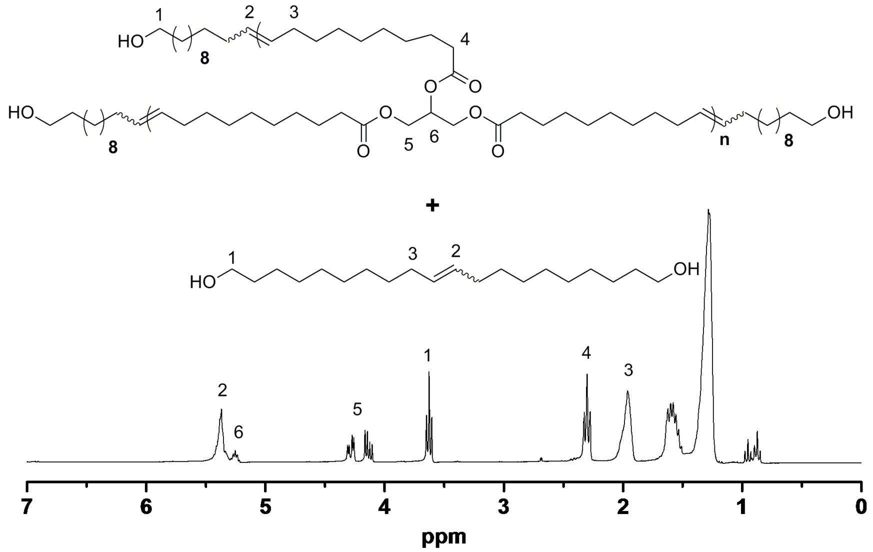


Figure 2. ^{1}H NMR with peak assignment of polyol POH2 (compare Table 1).

The DSC curves of these polyols show several endothermic peaks (Figure 3) that should be ascribed to the presence of different oligomers or crystalline forms. For the polyols with lower proportion of chain stopper, the endothermic peaks are observed between 0 and 40 °C, while for those synthesized with a higher content of 10-undecenol, a sharp endothermic peak appears at around 50 °C. According to the higher percentage of self-metathesis of chain stopper, this peak could be attributed to the melting of the lineal diol originated in the self metathesis of 10-undecenol.

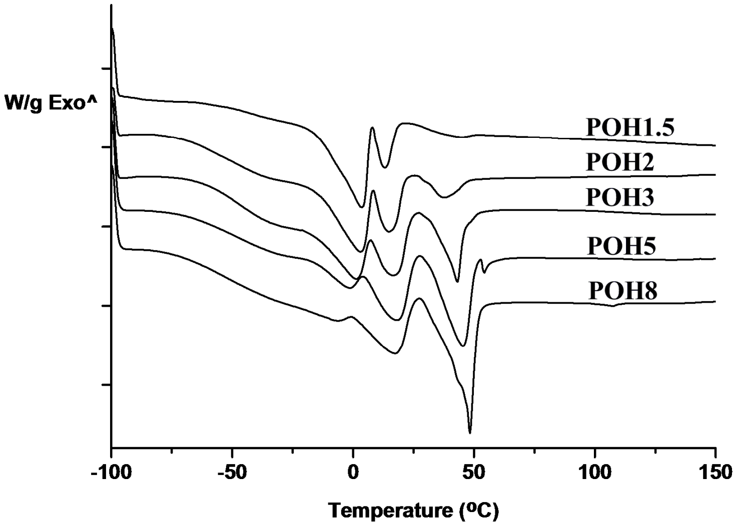


Figure 3. DSC traces (20 °C/min) of polyols POH1.5-POH8 (compare Table 1).

Polyurethanes were then synthesized from the above described polyols by dissolving the reactants, in the desired stoichiometry, in anhydrous toluene and under argon atmosphere. The reactant solutions were mixed, casted over a silanized glass plate preheated to 70 °C, cured at 70 °C for 2 hours and post- cured at 120 °C for 3 hours. Characterization of the polyurethanes by FTIR/ATR showed the disappearance of the isocyanate and hydroxyl stretching bands at 2240 and 3370 cm^{-1}, respectively. New bands appeared due to the urethane group: the stretching of N-H bonds at 3353 cm^{-1} and of the C=O bonds, which is partially overlapped with the carbonyl band of the fatty acid moiety, at 1738 cm^{-1}. The intensity of these bands increase as the hydroxyl content of the starting polyol does, as expected.

The thermal behavior of the polyurethanes was investigated by DSC (Figure 4, Table 2). They show glass transition temperatures below 0 °C that increase as the hydroxylic content increases, according to a higher degree of crosslinking. Moreover, the lower molecular weight of the polyol and the higher percentage of the diol cause a restriction of segmental mobility, increasing T_g values and hindering the detection of T_g by DSC for PU8. Moreover, as a result of the higher hydroxilic content of the starting polyol, melting endotherms appear in the DCS plots. Since the starting material in the preparation of the polyurethanes is a mixture of polyol and diol, structurally inhomogeneous systems containing various domains with different sizes are obtained, which consist of alternate polyol or diol isocyanate sequences. Part of the domain is chemically crosslinked, with covalent bonds between polyol and isocyanate and part results from the physical crosslinking of the linear diol-isocyanate segments through hydrogen bonding. The chemical crosslinks would reduce the mobility of molecular chains and restrict the effective packing into crystals. When increasing amounts of the shorter diol are employed, the effective packing of polymer chains into crystals seems to be promoted and semicrystalline materials are obtained.

The thermal stability of the polyurethanes in nitrogen atmosphere was studied by TGA (Table 2). The shapes of the weight-loss curves show the typical degradation behavior of polyurethanes. Differences in thermal stability appear to be small and the decomposition takes place at ca. 280 °C. There is a first weight loss (related to the decomposition of urethane bonds) that increases as the hydroxyl content of the polyol increases, in accordance to the existence of a higher amount of weaker urethane bonds. The main decomposition process is related to the polyol chain scission above 450 °C.

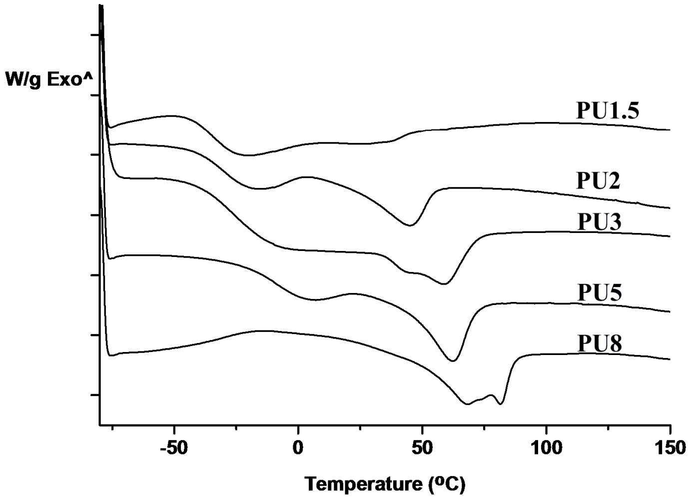


Figure 4. DSC traces of polyurethanes (20 °C/min) that were obtained from polyols POH1.5-POH8 (compare Table 1) with MDI.

Table 2. Thermal properties of the prepared polyurethanes

PU	T_g (°C)^a	T_m (°C)	ΔH (J/g)	T_g (°C)^b	$T_{5\%}$ (°C)^c	Yield$_{800°C}$(%)	T_{max} (°C)^d
PU1.5	-34	-	-	-7	288	7	298-457
PU2	-28	45	5	-4	288	8	296-461
PU3	-24	59	7	-1	287	10	293-465
PU5	-5	62	8	13	281	10	290-466
PU8	-	81	13	13	276	10	289-465

[a] ½ ΔCp from DSC data
[b] Tan δ_{max} from DMTA data
[c] temperature of the 5% of weight loss
[d] temperature of the maximum weight loss

Dynamic mechanical thermal analysis of the polyurethane films was performed in the range of temperatures between -90 and 150 °C. In Figure 5, storage modulus curves for the PUs are presented. All polyurethanes showed two transitions, which can be related to the already discussed DSC traces.

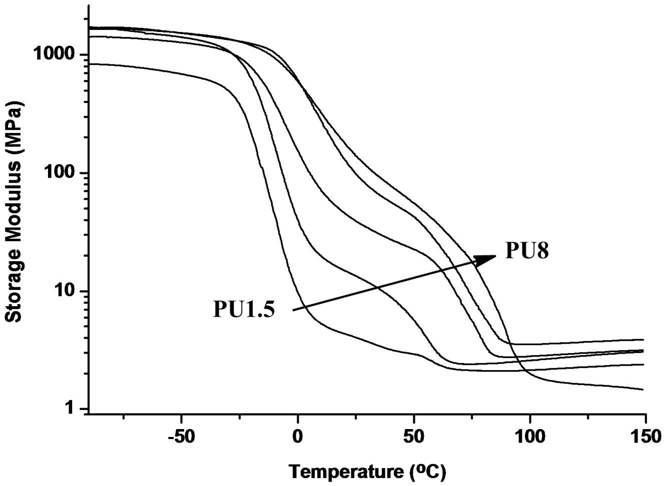


Figure 5. Storage moduli of the prepared polyurethanes.

The first drop in the storage modulus, assigned to the glass transition of the materials, appears close to 0 °C. The second transition, originated by melting of the crystalline domains, is centered at 55 °C for PU1.5 and PU2, while, for the rest is close to 75 °C. Both transitions are shifted from lower temperatures for PU1.5 to higher for PU8. Moreover, the intensities of the steps are different for each sample: PU1.5 has a first main transition below -10 °C with a small step close to 55 °C. Upon increase of the diol proportion in the polyurethane, the second step become more important, which is in agreement with the fact that the crystalline phase is originated by reaction of the diol obtained by self-metathesis of **2** with MDI. The storage modulus value in the rubbery plateau increases with the increment of the diol proportion, according to a lower cross-linking density.

The maximum of the Tan δ curves was used to determine the glass transition of the polyurethanes. Figure 6 shows that the maximum of the curve moves from -7 °C for PU1.5 to 13 °C for PU8 (Table 2). These values, assigned to the glass transition, are in good agreement with the tendency observed by DSC. The shape of the peak gives information about the cross-link density, thus, for PU1.5 the highest and sharpest peak indicates a lower cross-linking, whereas PU8 has lowest and broad peak indicating that the cross-linking density is higher. This behavior is due to both, covalent cross-linking points for urethane bonds and crystalline domains, which also act as net points.

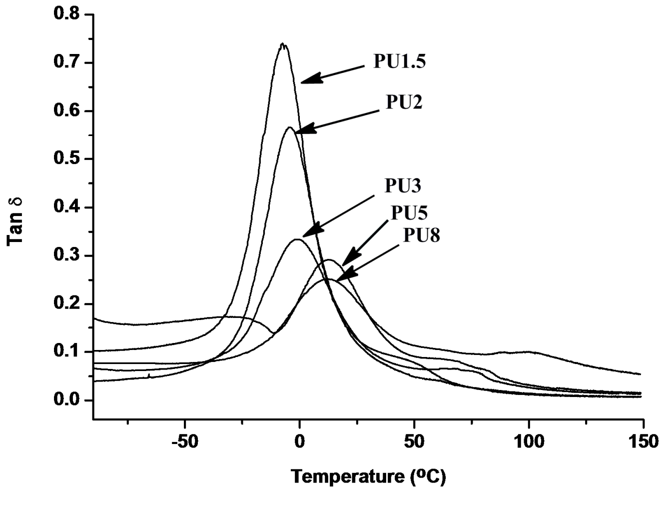


Figure 6. Tan δ and loss factor of the prepared polyurethanes.

Figure 7 shows the stress-strain curves for the different polyurethanes. PU1.5 presented the lowest values for the stress applied at break, final strain and Young's modulus. By increasing the diol proportion and, therefore, the crystalline phase of the polyurethane, the resistance of the film is improved. Thus, the maximum stress for PU1.5 was of 1.2 MPa much lower than that of the PU8 which is 9.1 MPa. In the same way, the percentage of strain at the break point for PU1.5 was 65%, while it was above 250% for PU8. The other polyurethanes showed intermediate values as can be seen in Table 3.

Table 3. Mechanical properties of the polyurethanes

PU	Stress (MPa)	Strain (%)	Young's Modulus
PU1.5	1.2	65	3.4
PU2	3.1	150	7.6
PU3	5.5	174	23
PU5	7.6	198	38
PU8	9.1	265	61

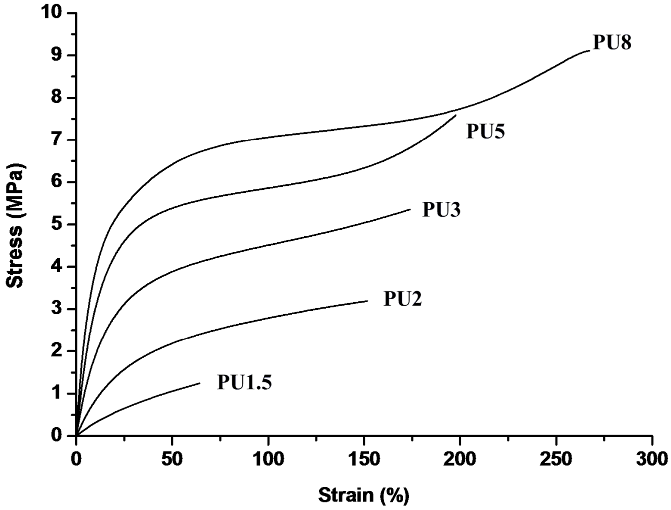


Figure 7. Stress-strain plots of the investigated polyurethanes.

The obtained polyurethanes showed a shape-memory effect, which was quantified by applying the cyclic tensile tests described in the experimental part. Samples were heated above the switching temperature and stretched to the desired temporary shape. In the next step, the materials were cooled down to 25 °C to fix the temporary shape and shape recovery was triggered by heating the sample above the transition temperature. The tensile test was performed for three consecutive runs on the same sample and the strain fixity rate R_f and the strain recovery rate R_r were calculated (Table 4).

$$Rf(N) = \frac{Lu(N)}{Lm(N)} x100\%$$

$$Rr(N) = \frac{Lm(N) - Lf(N)}{Lm(N) - Lf(N-1)} x100\%$$

Where L_u is the fixed strain of the film unloaded and stabilized at 25 °C, L_m is the strain of the polyurethane before release of the stress, L_f is the final strain of the sample at 100 °C and N is the number of cycles. R_r indicates the quality of the restoration of the primary shape after reheating and R_f expresses how well the material can maintain the total strain of the secondary shape after releasing the force on the sample, thus, ideal values for R_f and R_r are 100%.

Table 4. Shape-memory results for the characterized polyurethanes

	R_f			R_r			Stress	Strain
	Cycle 1	Cycle 2	Cycle 3	Cycle 1	Cycle 2	Cycle 3	(MPa)	(%)
PU3	70	76	75	79	95	94	0.8	110
PU5	75	78	80	89	98	98	0.8	120
PU8	92	95	95	92	98	99	0.5	140

Polyurethanes PU1.5 and PU2 showed no capability to fix strain, while polyurethanes PU3, PU5 and PU8 showed a shape-memory effect (Figure 8). For PU3, the force ramp applied to the film produces a different final strain (L_m) for each cycle. It is clear that the second and third cycles are quite similar, and indicate a clear R_r and R_f improvement compared to the first one. This small training effect is due to the occurrence of some chain relaxation during the mechanical cycle which is characteristic of shape memory polymers.[19] For PU5 and PU8 the three consecutive thermomechanical cycles are superimposable. Both the shape fixing and shape recovery increased significantly for PU5. PU8 show almost complete shape fixing and recovery as can also be seen from the high R_f and R_r values that were almost unchanged through the cycles. Since the obtained polyuretanes are covalently cross-linked semicrystalline networks, the secondary shape is fixed by crystallization while the permanent shape is established by chemical cross-linking. The improvement on the shape memory properties from PU3 to PU8 can be related to a lower cross-linking density and a higher percentage of diol, which would increase the remaining crystallinity that keeps the material in its secondary shape.

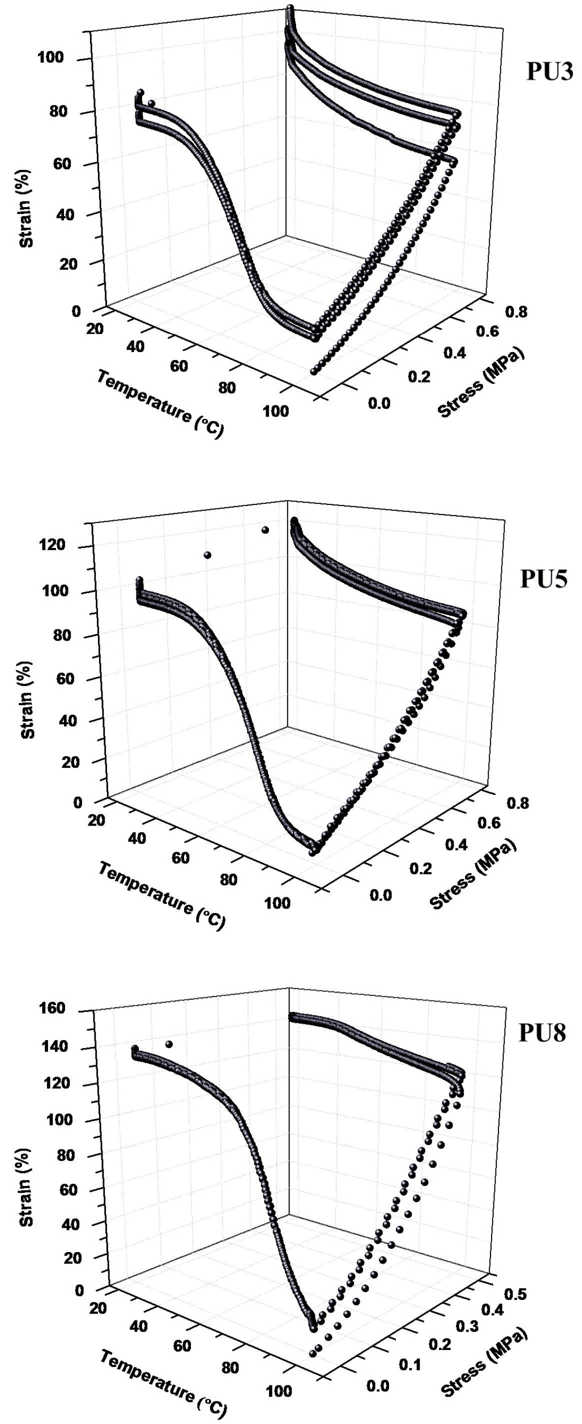


Figure 8: Stress-strain plots of the investigated polyurethanes.

Conclusion

Branched polyols were prepared via a one step one pot procedure by applying acyclic triene metathesis polymerization to a triglyceride. By using different amounts of a chain stopper in comination with this triglyceride, polyols of varying molecular weight and OH value could be obtained. using these polyols, novel biobased polyurethanes were prepared by reacting them with MDI. The resulting polyurethanes were fully characterized and their mechanical properties were investigated in detail. Some of the covalently crosslinked semicrystalline networks obtained showed good shape memory properties

Acknowledgement

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Chapter III.

Polyurethanes from polyoxazoline-polyols synthesized via cationic ring opening polymerization and thiol-ene coupling

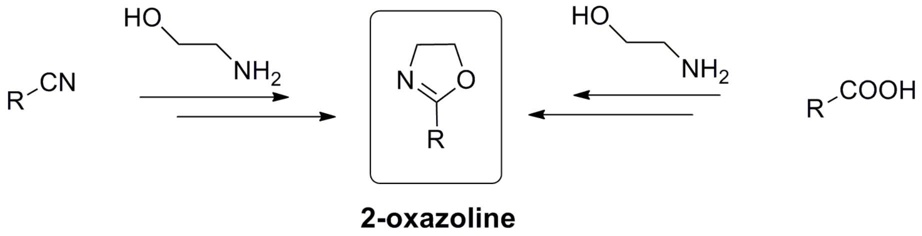
RING OPENING POLYMERIZATION OF 2-OXAZOLINES

Synthesis of 2-oxazolines

Oxazolines are five-membered heterocycles with an internal double bond. Depending on the position of the double bond, oxazolines have three structural isomers; 2-oxazoline, 3-oxazoline, and 4-oxazolines. Among them, 2-oxazolines are by far the most well-known and extensively studied ones, and have an endo-imino ether (-N=C-O-) group. Historically, 2-oxazolines are known since the end of 19th century. The first oxazoline synthesis was made in 1884 via dehydrohalogenation of allylurea, but its chemical structure was confused.[94] Five years later, the first successful synthesis of oxazolines was reported and then the chemistry of oxazolines started to be increasingly investigated.[95]

The formation of an oxazoline ring was postulated in the cyclodehydration of the peptide linkages constituted by the α-amino-β-hydroxy acids, serine, or threonine.[96]

In polymer chemistry, 2-substituted-2-oxazolines are the most important ones. The substituent in the 2-position is determinant in tuning the properties of the polymer. The most common synthesis of 2-oxazoline monomers involves the reaction between acids or nitriles with aminoethanol (Scheme 1). However, many other methods have been described.[97]



Scheme 1. Synthesis of 2-oxazolines from nitriles and carboxylic acids.

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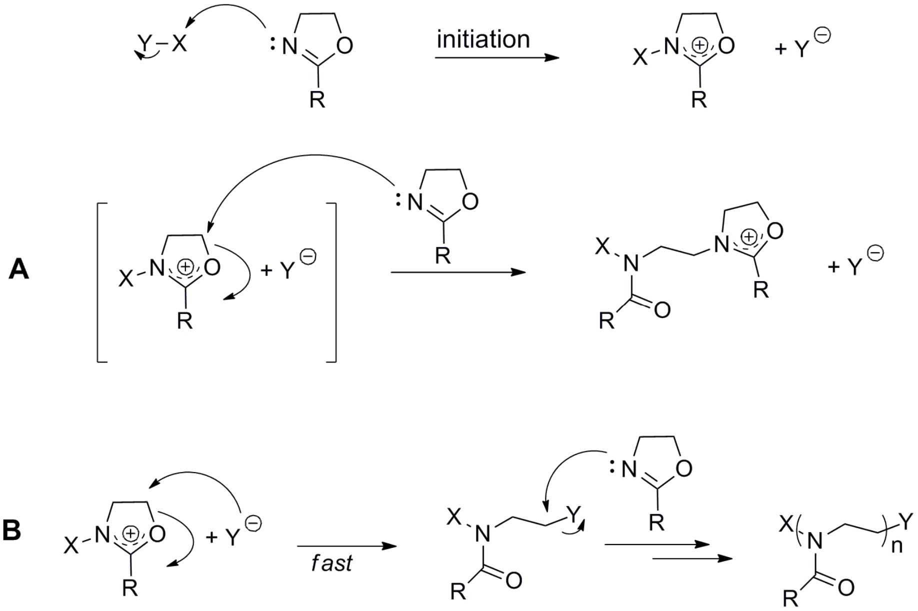
Polymerization of 2-oxazolines

Although oxazolines react with a great number of functional groups, the polymerization reaction is the most intensively studied. The polymerization process is thermodynamically favorable due to both the release of the ring strength and the formation of an amide group from the less stable imino ether.

The ring opening polymerization of 2-oxazolines proceeds cationically and is commonly initiated using alkyl halides or other alkylating agents like alkyl triflates. The initiation step in the cationic ring opening polymerization (CROP) proceeds by attack of the oxazolinic nitrogen to the electrophilic carbon of the initiator. This attack produces the activation of the oxazolinic ring as a cation. Depending on the initiator, the propagation of the polymerization can follow two different ways, through ionic species or through covalent ones (Scheme 2).[98]



Scheme 2. Polymerization mechanism of 2-oxazolines. Propagation by ionic species (A), and propagation by covalent species (B)

In the propagation through ionic species, the nitrogen of the monomer attacks to the carbon in the five position of the propagating 2-oxazolinium

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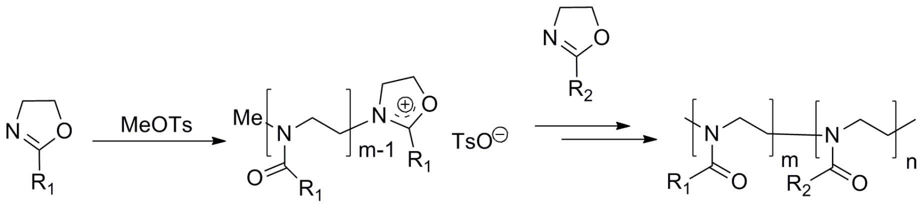
specie resulting in a O-C(5) bond cleavage and the isomerization to give an acylethylenimine unit. When the initiator generates a strong nucleophile in the initiation step the polymerization proceeds via covalently bonded species. In this case, the ring of the generated 2-oxazolinium salt is rapidly opened by the attack of the counteranion of the initiator.

In general, once all the monomer has been consumed in the polymerization, the polymer chains are still active, and the addition of a nucleophile is generally used to stop the reaction. But the addition of fresh monomer re-starts the polymerization.

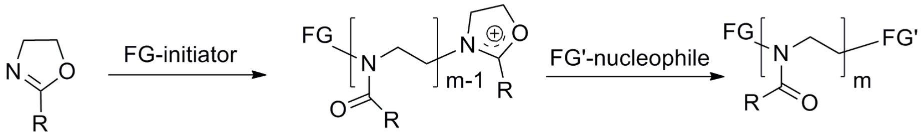
So the cationic ring opening polymerization (CROP) of 2-oxazolines is a living polymerization, which allows to obtain a desired molecular weight by controlling the proportion of the initiator to monomer, and the obtained polymers are characterized by a narrow molecular weight distribution. The living polymerization can be used also to obtain block-co-polymers by addition of a second monomer once the polymerization of the first one is finished (Scheme 3).



Scheme 3. Synthesis of block-co-poly(2-oxazoline)s by one-pot two-steps strategy

Beside of the possibilities offered for the living polymerization nature we have to add the synthesis of poly(2-oxazoline)s with complex architectures. The initiators generally used in the polymerization of 2-oxazolines can have an unique point of initiation, but the use of initiators with two or more initiation points allows to obtain telechelics or star-shape polymers.

The living CROP of 2-oxazolines provides easy and direct access to a wide variety of well-defined polymers, in which the end-group functionality can be controlled during the initiation and termination steps (Scheme 4). Furthermore, the properties of poly(2-oxazoline)s can be tuned simply by varying the side chain of the 2-oxazoline monomer. Thus, polyoxazolines with, for example, methyl groups in the 2-position are soluble in water, whereas with long alkyl chains as in the case of nonyl-oxazoline are insoluble in water. By controlling the monomer composition and distribution it is possible to tune some properties as hydrophobic behavior, lower critical solution temperature, and so on.



Scheme 4. Poly(2-oxazoline) functionalization in the initiation and termination steps

The controlled synthesis of a polymer allow to study the self-assembly behavior of polyoxazolines, and tuning the lower critical solution temperature open up a completely new research area on thermoresponsive materials. Moreover, polyoxazolines have a peptide-like backbond, thus, in recent years, the use of poly(2-oxazoline)s in biomedical applications has evolved as a result of their biocompatibility.[99]

Functionalization of polyoxazolines by click chemistry

Together with the possibilities offered by choosing the oxazolinic monomers and controlling the polymerization process, the combination of polyoxazolines with click chemistry might be an important stimulus for the broader application of poly(2-oxazoline)s.

The first report on poly(2-oxazoline)s and click chemistry was published by Luxenhofer and Jordan.[100] The homopolymerization of 2-(pent-4-ynyl)-2-oxazoline and copolymerization with 2-methyl-2-oxazoline and 2-ethyl-2-oxazoline yielded well-defined alkyne-functionalized polymers. Various azides were subsequently coupled quantitatively to the polymer by the Huisgen 1,3-dipolar cycloadition catalyzed by copper(I) (Scheme 5).

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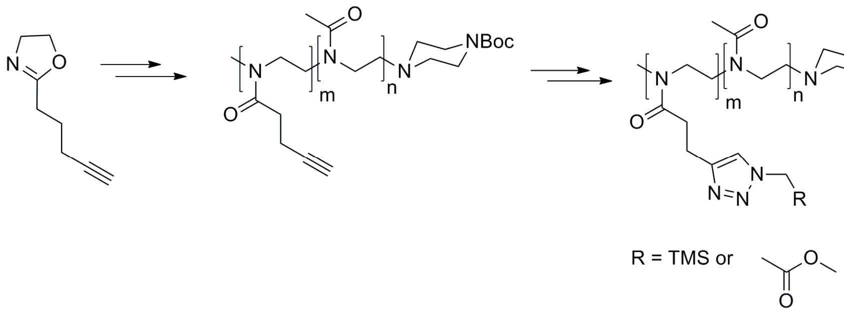
[99] a) N. Adams and U. S. Schubert, Adv. Drug Delivery Rev., 2007, 59, 1504-1520. b) H. Schlaad, C. Diehl, A. Gress, M. Meyer, A. L. Demirel, Y. Nur and A. Bertin, Macromol. Rapid Commun., 2010, 31, 511-525. c) R. Hoogenboom, Angew. Chem. Int. Ed., 2009, 48, 7978-7994.

[100] R. Luxenhofer and R. Jordan, Macromolecules, 2006, 39, 3509-3516.



Scheme 5. Side chain functionalization of co-poly(2-pent-4-ynyl-2-oxazoline) via azide-alkyne cycloaddition

Binder et al. reported the synthesis of poly(2-oxazoline)s with azide groups in the side chain.[101] Poly(2-oxazoline)s end-functionalized with alkyne groups and subsequent click functionalization was reported by Hoogenboom and coworkers and used for the formation of star-shaped poly(2-oxazoline)s.[102]

Cortez and Grayson have fixed terminal azide at one end of poly(2-ethyl-2-oxazoline) to prepare star polymers, diblock copolymers, and cylic polymers.[103] Also Volet et al. have functionalized with an azido group at one or both ends of the poly(2-methyl-2-oxazoline) and the Huisgen 1,3-dipolar cycloaddition has been investigated between the azido-functionalized polyoxazoline and different terminal alkynes.[104] In this way, telechelic polymers with several functional groups have been obtained, as well as block copolymers with polyethylene glycol (Scheme 6).

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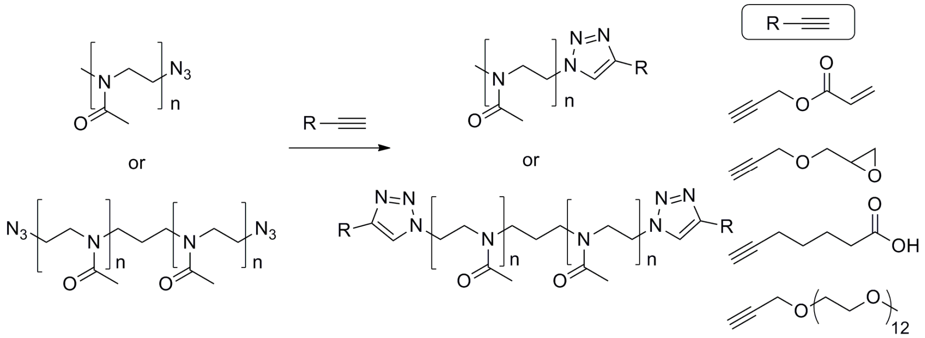
[101] W. H. Binder and H. Gruber, Macromol. Chem. Phys., 2000, 201, 949-957.

[102] M.W. M. Fijten, C. Haensch, B. M. van Lankvelt, R. Hoogenboom and U. S. Schubert, Macromol. Chem. Phys., 2008, 209, 1887–1895.

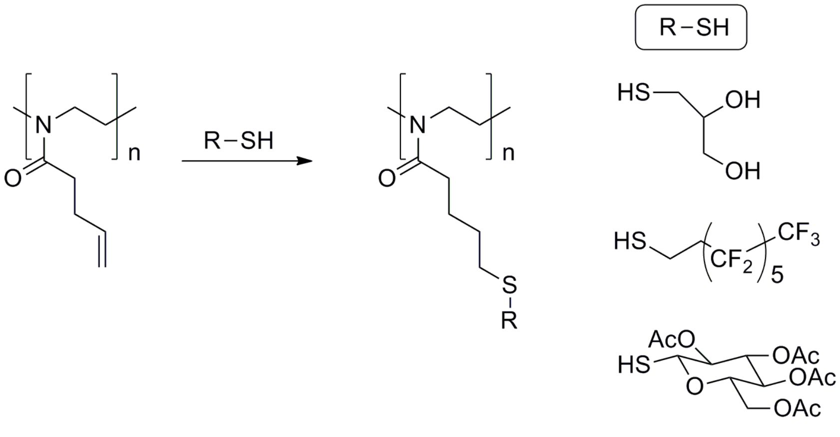
[103] a) M. A. Cortez and S. M. Grayson, Polym. Mater. Sci. Eng., 2008, 98, 436-437; b) M. A. Cortez and S. M. Grayson, Polym. Mater. Sci. Eng., 2008, 98, 438-439; c) M. A. Cortez, B. Cafferty and S. M.Grayson, Polym. Prepr., 2010, 51, 466-467.

[104] G. Volet, T. X. Lav, J. Babinot and C. Amiel, Macromol. Chem. Phys., 2010. DOI: 10.1002/macp.201000556.



Scheme 6. Azide-alkyne cycloaddition on a poly(2-oxazoline) functionalized at the initiation and/or termination step

Thio-click functionalization of poly[2-(but-3-enyl)-2-oxazoline] (co)polymers was reported by Schlaad and co-workers.[105] The alkene side-chain-functionalized polymers were modified with a variety of thiol compounds, including hydroxyl-functionalized compounds, fluorinated chains and sugars (Scheme 7). The thiol-ene coupling of the 2-isopropenyl-2-oxazoline with different thiol-compounds and subsequent polymerization has been carried out by Grayson and co-workers.[106]



Scheme 7. Thiol-ene functionalization of poly(2-oxazoline)

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[105] A. Gress, A. Völkel and H. Schlaad, Macromolecules, 2007, 40, 7928-7933.

[106] A. Mallory, M. A. Cortez and S. M. Grayson, Macromolecules, 2010, 43, 4081-4090.

Finally, the preparation of anthracene end-functionalized poly(2-oxazoline)s was performed by Müllen and co-workers, who used 9-bromomethylanthracene as initiator.[107] The resulting polymers might be suitable candidates for Diels-Alder click reactions.

In the third chapter of this thesis, the obtention of copolymers of 10-undecenoic and decanoic derived 2-oxazolines by cationic ROP is described. The thiol-ene functionalization with 2-mercaptoethanol produces a set of lineal polyoxazoline-polyols. The polyols obtained were reacted with MDI to obtain polyurethane networks.

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[107] T. Bartz, M. Klapper and K. Müllen, Macromol. Chem. Phys., 1994, 195, 1097-1109.

Poly-2-oxazoline derived polyurethanes. A versatile synthetic approach to renewable polyurethane thermosets

Poly-2-oxazoline derived polyurethanes. A versatile synthetic approach to renewable polyurethane thermosets.

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Summary

2-Nonyl-2-oxazoline and 2-(9-decenyl)-2-oxazoline have been copolymerized in different proportions by cationic ring opening polymerization (CROP) to obtain a series of random linear copolymers with tailored molecular weight and double bond functionality in the side chains. Thiol-ene addition of 2-mercaptoethanol has been used to produce a set of polyoxazoline-polyols under mild conditions and with quantitative double bond transformation. The polyols obtained in this way were reacted with methylene-bis(phenylisocyanate) (MDI) to yield a series of amorphous and semicrystalline polyurethane networks. The thermal stability and the thermomechanical properties of these termosets have been studied and related with the structure of the parent polyols.

Introduction

The depletion of world oil pool, rising price of crude oil and increased environmental concerns are pressurizing the scientists for the use of renewable natural resources in different fields of applications as they are eco-friendly and cost-effective materials.[1] In this regard vegetable oils are one of the most promising renewable raw materials because of their availability, structural variety and chemical versatility. Vegetable oils containing unsaturated fatty acids can be used in polymerizations to make biobased polymers.[2-5] Moreover, numerous fatty acids are now available in a purity that makes them attractive for synthesis and as raw materials for the chemical industry.[6]

Polyurethanes (PUs) are one of the most important and versatile classes of polymers and can vary from thermoseting to thermoplastic materials. Polyurethanes exhibit better abrasion resistance, toughness, chemical resistance and mechanical strength compared to other polymers such as polyesters and polyesteramides. Moreover, their mechanical, thermal and chemical properties can be tailored by reactions with various isocyanates and polyols. Usually, both isocyanates and polyols are petroleum based, but in

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recent years, vegetable oils, fatty acids and their derivatives have attracted significant attention as raw materials for the preparation of polyurethanes.[7] For natural oils and derivatives to be used as raw materials for polyol production multiple hydroxyl functionality is required.[8] This can be accomplished by various strategies like the epoxidation of carbon-carbon double bonds and further oxirane ring opening with alcohols and other nucleophiles,[9,10] the transesterification with multifunctional alcohols[11,12] and the hydroformilation or ozonolysis and subsequent reduction of the carbonyl groups[13,14]. Unfortunately, these strategies usually lead to complex mixtures of polyols with different hydroxyl content, molecular architecture and molecular size. In a recent work, we prepared a set of polyether polyols for PUs synthesis by polymerization of the methyl 9,10-epoxyoleate and subsequent controlled reduction of the pendant side ester groups.[15-17] This new strategy allowed an excellent control of the polyol hydroxyl content but failed in the control of the polyol molecular weight and molecular architecture due to the nature of the cationic and ionic-coordinative polymerizations used. On the contrary, the living nature of the cationic ring-opening polymerization (CROP) of 2-substituted-2-oxazolines allows the facile preparation of well-defined homo and copolymers with an excellent control of their molecular weights, end group functionalities, and molecular architecture allowing an accurate control of the final properties.[18-24] Moreover, 2-oxazoline monomers can be readily prepared directly from the carboxylic acids or their nitrile derivatives following various synthetic pathways.[25-30] In this way, 2-oxazolines are excelent candidates to transform unsaturated carboxylic fatty acids in polymers with tailored structure and functionality. Copolymerization of saturated and unsaturated 2-oxazoline monomers allows the preparation of lineal copolymers with prefixed molecular weights and the desired amount of pendant double bonds in a random or blocks arrangement.[31-33] Side chain double bond hydroxylation can be accomplished in different ways. Hydroboration/oxidation techniques have been applied successfully to polymers like polybutadiene,[34] poly(3-hydroxyundecen-10-enoate),[35] poly(4-allyloxyphenyloxazoline)[36] and poly[2-(9-decenyl)-2-oxazoline[37] but this approach needs low temperature conditions, a complex work up and uses expensive reagents and strongly basic and oxidizing media what is undesirable in oxazoline based polymers. Thiol-ene chemistry, which implies the free-radical addition of thiols onto double bonds, is a highly efficient tool that has been applied to polymer synthesis.[38-40] Click chemistry reactions have also been used in polyoxazolines[41] and recently efficient thiol-ene modification of poly[2-(3-butenyl)-2-oxazoline][42] poly[2-isopropyl/3-butenyl)-2-oxazoline][43] and 2-oxazoline monomers[44] has been described.

The present work describes the synthesis of random copolymers of 2-nonyl-2-oxazoline and 2-(9-decenyl)-2-oxazoline by CROP and its thiol-ene functionalization with 2-mercaptoethanol to produce a set of lineal polyoxazoline-polyols under mild conditions, quantitative double bond transformation, and with control of the molecular weight and the hydroxyl content. The polyols obtained in this way were reacted with methylene-bis(phenylisocyanate) (MDI) to yield a series of polyurethane networks that were characterized by infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and thermodynamic mechanical analysis to establish the polyol structure-PU properties relationship.

Experimental

Materials

2,2-Dimethoxy-2-phenylacetophenone (DMPA), 10-undecenoic acid, 2-mercapto ethanol and methylene-bis(phenylisocyanate) (MDI) were purchased from Aldrich. Benzyl bromide and thionyl chloride were obtained from Fluka, and decanoic acid and ethanolamine from Merck. Tetrahydrofuran (THF) and acetonitrile (ACN) from Aldrich were dried with sodium-benzophenone and P_2O_5 respectively and distilled immediately before use.

Synthesis of monomers

2-Nonyl-2-oxazoline and 2-(9-decenyl)-2-oxazoline were synthesized starting from the corresponding acids and ethanolamine following general reported procedures.[45-48] The monomers were purified by fractional distillation over barium oxide under vacuum and stored under argon. The physical properties and spectral characteristics were in accordance with those described in the literature.[31,47] Purity was estimated over 98% by GC.

Random polymerization

The copolymerization of 2-nonyl-2-oxazoline (NonOx) and 2-(9-decenyl)-2-oxazoline (DecOx) was carried out with benzyl bromide in anhydrous acetonitrile (ACN) at 100 °C for 24 h. Polymerizations and work up were carried out following a similar procedure previously described.[48]

In a typical copolymerization procedure the appropriate amounts of NonOx and DecOx (30 mmol) were placed in a flame-dried screw capped shlenck flask under argon. Next, the necessary amount of anhydrous ACN was added to reach a 2M solution. The mixture was stirred at room temperature and the necessary amount of anhydrous benzyl bromide was added by means a precision syringe. The polymerization mixture was heated and kept at 100 °C for 24 h. After cooling to 50 °C, the polymerization was stopped by adding few drops of 10% KOH solution in water and stirring for one hour. The resulting solution was concentrated under vacuum, the residue dissolved in ethyl acetate and the extracts washed several times with brine, dried with anhydrous $MgSO_4$ and concentrated. The isolated polymer was dried at 40 °C under vacuum for 24h. Results are summarized in Table 1.

Thiol-ene polymer modification

In a shlenck flask under argon 2.1 g of POx (1.5 mmol of POx1, 2.0 mmol of POx2, 3.0 mmol of POx3) were dissolved in 5ml of anhydrous THF. DMPA (1% respect to the C=C) as initiator and mercaptoethanol (2.5 equivalents respect to the C=C) were added. The mixture was stirred and irradiated at 365 nm (18 w) for 2 h at room temperature. Excess of reagent was removed by washing with brine several times and the polymer dried at 40 °C under vacuum for 48 h.

Polyurethane synthesis

Around 2-3 g of polyol were dissolved under argon in anhydrous toluene to achieve a 50% (w/w) solution. The solution was heated at 50 °C and added to a 50% (w/w) dispersion of MDI in toluene. In all cases a ratio of 1.02 equivalents of isocyanate group per hydroxyl was employed. The mixture was stirred under argon until was homogeneous and casted over silanized glass plaques preheated at 90 °C. The polyurethane was maintained at 90 °C for 2 h and at 130 °C for 3 h. producing films with 0.03 to 0.04 mm thickness.

Determination of hydroxyl content

Quantification of the hydroxyl content was carried out using ^{1}H-NMR spectroscopy and 2-phenylethanol as internal standard using the signal at 2.85 ppm as reference. Accurate weights of polyol and the internal standard were introduced in a NMR tube. The intensity of the partially overlapped signals at 3.79-3.70 ppm (side chain -$\underline{CH_2}OH$ and chain-end -$\underline{CH_2}OH$) and the signal at 2.71 ppm (-S-$\underline{CH_2}$-CH_2-OH side chain groups) was compared with the intensity of the signals at 3.86 and 2.85 ppm (Ph-$\underline{CH_2}$-$\underline{CH_2}$-OH) of internal standard. The hydroxyl content in milimol of hydroxyl groups per gram of polyol was calculated using Equation 1.

$$ValueOH = \frac{mmolIS \times IntPOH}{IntIS \times gPOH} \qquad \text{Equation1}$$

Where mmolIS is the internal standard amount in mmol, IntPOH is the integral value of the polyol, IntIS is the integral value of the internal standard and gPOH is the amount of polyol in grams.

Characterization

GC-MS analysis were done in a 6890N gas chromatograph and a 5973 mass spectrometer (Agilent Techologies, Palo Alto, U.S.A.), using a HP-5MS capillary column of 5% phenyl polydimethyl siloxane (30 m, 0.25 mm, 0.25 μm), from Agilent Technologies, and 99.999% pure helium gas as the carrier at a flow rate of 1.5 ml min^{-1}. Samples were injected in a split/splitless injector at a split ratio of 20:1, at a temperature of 280 °C. The oven temperature of GC was initially held at 60 °C, raised to 260 °C at a rate of 6 °C min^{-1} and then held for 50 minutes. The mass spectrometer acquired data in scan mode with an m/z interval from 35 to 800. The compounds were identified by comparison with NIST08 MS library.

^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded in $CDCl_3$ using a Varian Gemini 400 spectrometer. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) as internal standard.

FTIR spectra were recorded on a Bomem Michelson MB 100 FTIR spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated total reflection (ATR) device with thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac-Tknokroma) was used.

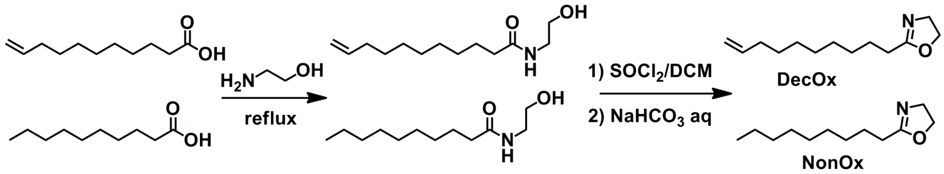
MALDI-TOF MS measurements were performed with a Voyager DE-RP mass spectrometer (Applied Biosystems, Framingham, MA) equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. 1,8,9-antracenetriol was used as matrix and potassium trifluoroacetate as dopant. Samples were prepared from a THF solution containing 40 mg/ml of matrix, 3 mg/ml of polymer and 0.1 mg/ml of dopant. The homogenized mixture was casted in the MALDI plate.

Size exclusion chromatography (SEC) analysis were carried out with an Agilent 1200 series system with PLgel 3 μm MIXED-E, PLgel 5 μm MIXED-D and PLgel 20 μm MIXED-A columns in series, and equipped with an Agilent 1100 series refractive-index detector. Calibration curves were based in polystyrene standards having low polydispersities. THF was used as an eluent at a flow rate of 1.0 mL/min, the sample concentrations were 5-10 mg/mL, and injection volumes of 100 μL were used.

Calorimetric studies were carried out on a Mettler DSC822 differential scanning calorimeter using N_2 as a purge gas (20 mL/min). Dynamic mechanical thermal analysis (DMTA) and tensile tests were performed using a TA DMA 2928 in the Controlled Force-Tension Film mode with a preload force of 0.1 N, an amplitude of 10 μm and at a fixed frequency of 1 Hz in the -80 to 170 °C range and at a heating rate of 3 °C/min. The tensile assays were performed by triplicate on rectangular samples (10 x 5 x 0.5 mm^3) measuring the strain while applying a ramp of 0.5 N/min at 25 °C. A preload force of 0.05 N and a soak time of 3 min were used. Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N_2 as purge gas. The studies were performed in the 30-800 °C temperature range at a scan rate of 10 °C/min.

Results and discussion

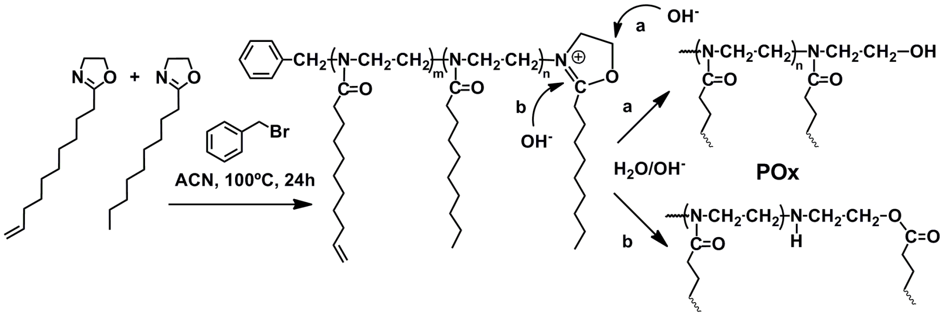
As commented, the main purpose of this work is preparing tailor-made thermosetting PUs from comb-like copoly-2-oxazolines functionalized with hydroxyl groups in the side chain. To prepare the starting 2-oxazoline monomers we chose 10-undecenoic acid and decanoic acid as unsaturated and saturated precursors respectively. Both starting materials are from renewable origin. 10-undecenoic acid is the main product of castor oil caustic fusion or pyrolisis[49] and decanoic acid occurs naturally in coconut and palm kernel oils and is the major component eml seed oil (60-70%).[50] The synthesis of the 2-oxazoline monomers was accomplished using the standard two steps procedure consisting of the reaction of the acid with ethanolamine followed by treatment with thionyl chloride and basic hydrolysis[45-47] (Scheme 1).



Scheme 1. Synthesis of the fatty acid-derived oxazoline monomers.

The resulting 2-oxazolines were purified by fractional distillation under vacuum giving colorless oils in good yield (76% for NonOx and 82% for DecOx). Physical properties and structural characteristics were in accordance with those described in the literature.[31,47]

NonOx was copolymerized with the necessary molar amount of DecOx to obtain copolymers with a 15%, 20% and 30% of unsaturated comonomer. The copolymerizations were carried out at 100 °C in anhydrous ACN using benzyl bromide as initiator (Scheme 2). Each mixture of monomers was polymerized using three different monomer/initiator ratios 8/1, 14/1 and 20/1. These initiator ratios were selected to obtain copolymers with a theoretical DP of 8, 14 and 20 respectively.



Scheme 2. Cationic ring opening copolymerization of oxazoline monomers and possible chain termination mechanism.

In this way, nine different copolymers varying composition and molecular weight were obtained essentially with quantitative conversions. Results determined by SEC and ^{1}H NMR are collected in Table 1, together with the theoretical values expected from the monomer-initiator ratio used. All copolymers were obtained in quantitative conversion and so the comonomer composition should match with the feed.

Table 1. Composition and molecular weight of POx copolymers.

Sample	DecOx (a)	NonOx (a)	Ox/BnBr ratio	Mnx10^{-3} (b)	Mnx10^{-3} (c)	Mnx10^{-3} (d)	DP (e)	Mn/Mw (d)
POx1a	0.85	0.15	8/1	1.70	2.09	2.24	11.2	1.08
POx1b	0.85	0.15	14/1	2.89	3.20	3.23	16.2	1.08
POx1c	0.85	0.15	20/1	4.09	4.12	4.09	20.5	1.11
POx2a	0.80	0.20	8/1	1.70	2.16	2.24	11.2	1.08
POx2b	0.80	0.20	14/1	2.90	3.25	3.28	16.4	1.08
POx2c	0.80	0.20	20/1	4.10	4.20	4.17	20.9	1.15
POx3a	0.70	0.30	8/1	1.71	1.97	2.21	11.0	1.08
POx3b	0.70	0.30	14/1	2.92	3.20	3.25	16.1	1.09
POx3c	0.70	0.30	20/1	4.12	4.40	4.20	20.9	1.13

a) Molar percentage in the feed.
b) Theoretical from the Ox/BnBr ratio.
c) Determined by ^{1}H NMR.
d) Determined by SEC using PS standards.
e) Calculated from SEC results.

The ^{1}H NMR spectra (Figure 1a) shows the expected signals for copolymers obtained via a CROP initiated by benzyl bromide. In addition to the main and side chain proton signals of both comononer units, some other low intensity signals can be observed. These signals do not disappear or change their intensity by precipitating the polymer and so it can be assumed that they are due to end groups instead of polymer impurities. Signals between 7.40-7.12 ppm and 4.65-4.47 ppm can be assigned to the starting benzyl moieties, whereas the signals at 3.77 and 3.63 ppm can be assigned to the final hydroxyethyl groups formed in the termination step by reaction with water. This was confirmed by "in situ" derivatization of the polymer with trichloroacetylisocyanate (TAI) which produces a downfield shift of 0.48 ppm for the signal at 3.77 ppm in the ^{1}H NMR spectrum. The relative intensity of signals at 4.6-4.5 ppm was used to estimate the molecular weight by comparing with the main chain methylene signal at 3.42 ppm. The signals at 4.15 and 2.90-2.60 ppm could be assigned to an ester end group which can be formed alternatively by attack of water to the position 2 of the growing oxazolinium group as it has been established by Schubert et al (Scheme 2).[51]

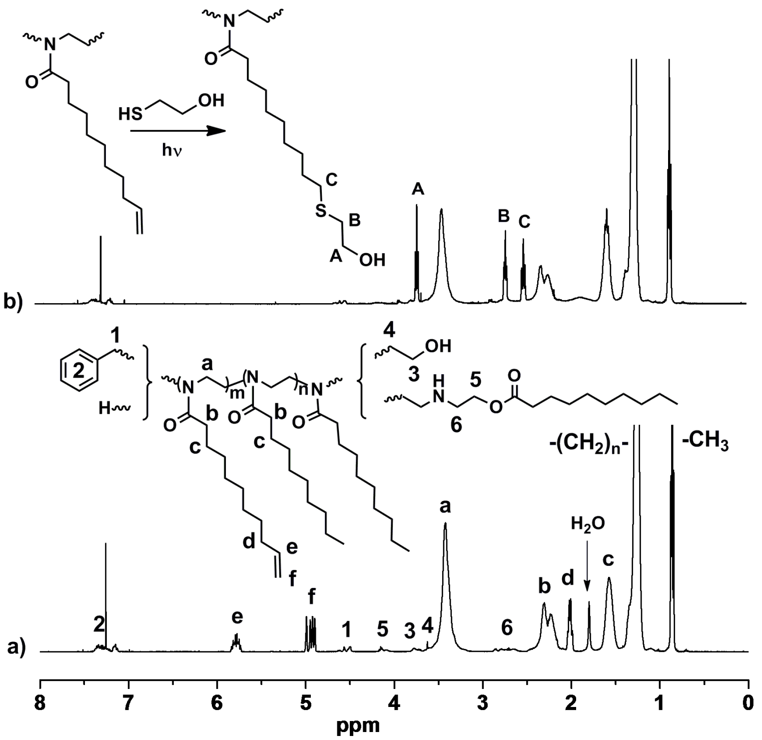


Figure 1. ^{1}H NMR spectra of POx2c a) and thiol-ene addition product POH2c b).

SEC chromatograms of polymers (Figure 2) show in all cases narrow monomodal distributions with polydispersities around 1.08 with the exception of the polymers obtained with 20/1 monomer/initiator ratio that presents a slightly higher polydispersity (1.11-1.15) (Table 1). The M_n values obtained by SEC were somewhat higher than the theoretical ones especially in the case of the low molecular weight polymers.

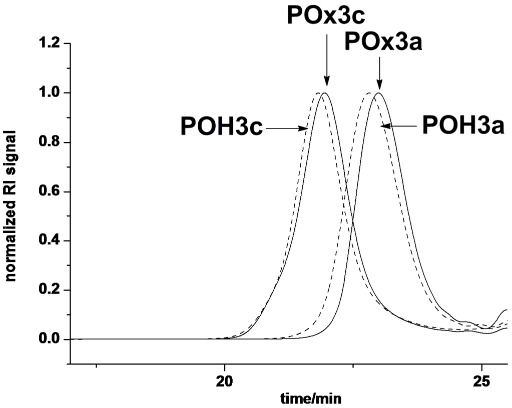


Figure 2. SEC chromatograms of POx3a and POx3c (continuous line) and the corresponding thiol-ene reaction products POH3a and POH3c (dashed line).

Molecular weights estimated by ^{1}H NMR were also higher than the expected probably because of the existence of other possible side initiations that were not taken into account in the measurements. To gain insight about the structure of these polymers, MALDI-TOF-MS analysis was performed. In Figure 3a the representative spectra obtained for POx2b is shown. In all samples at least two different Gaussian peak distributions can be observed.

The main distribution fits with de expected structure for a random copolymer with benzyl and hydroxyl end groups and presents molecular weight distributions close to the observed by SEC. Each peak in the main distribution presents a fine structure which can be associated to the different comonomer composition as is shown in the expanded zone of the peak corresponding to DP 14 in Figure 3b. As can be seen, the peaks of poly(NonOx$_{14}$), poly(NonOx$_{13}$/DecOx$_1$), poly(NonOx$_{12}$/DecOx$_2$) and up to poly(NonOx$_7$/DecOx$_7$) can be observed varying its relative intensity with the amount of DecOx comonomer in the POx3b.

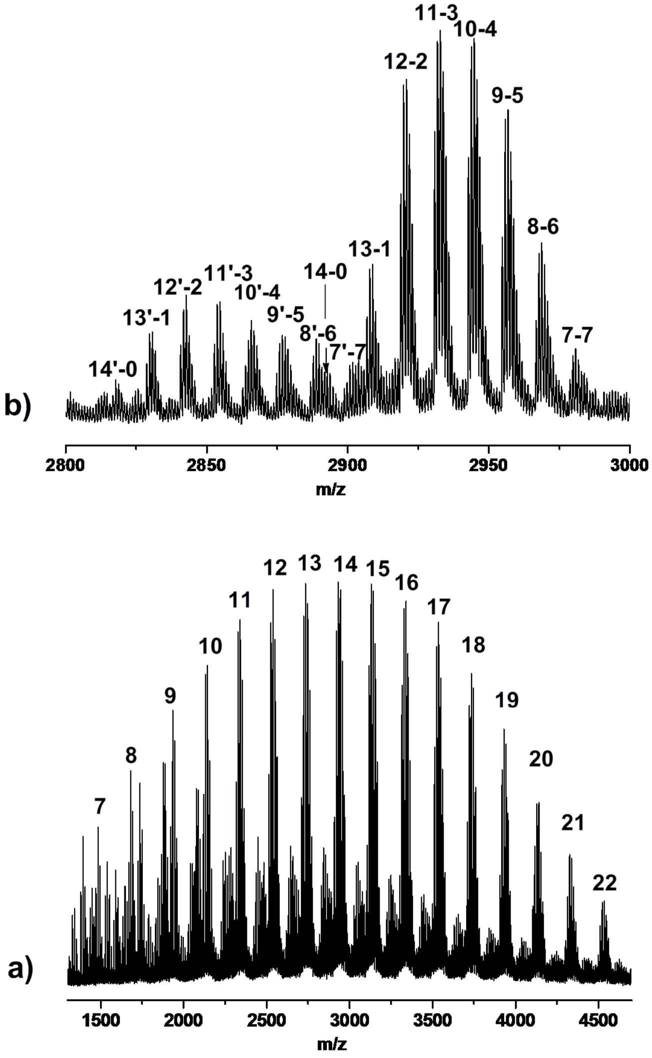
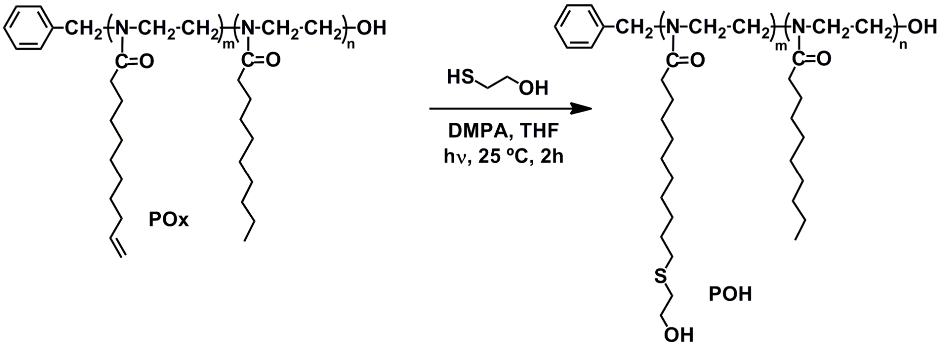


Figure 3. a) MALDI-TOF-MS spectra of POx3b, numbers indicate the DP. b) Amplification of the peak corresponding to DP=14. Numbers indicate the copolymer composition: the first indicate the number of saturated monomeric units and the second the number of unsaturated ones. The series with apostrophe correspond to the polymers chains not initiated with benzyl groups.

The same MALDI-TOF-MS patterns are observed for POx1 and POx2 copolymer series. In all cases a secondary peak distribution is observed. The mass of these secondary peaks fits with a random copolymer with hydrogen and hydroxyl end groups (difference of 91 Da with the main series peaks). These peaks can be explained on the basis of known chain transfer reactions which take place during the polymerization of oxazolines[52] leading to hydrogen-initiated and enamine chains. Alternatively, these species can be formed as result of chain-transfer processes with traces of water or H-nucleophiles present in the polymerization media.[53] This secondary set of peaks follows the same comonomer composition than the main peak series but not a Gaussian distribution. As expected for species formed in chain transfer processes, the peaks are more intense in the low molecular weight region and its intensity decreases progressively as the polymerization degree increases. According to the relative peak intensity the amount of chain transfer species is more important in POx1c, POx2c and POx3c which is in agreement with their wider molecular weight distribution observed by SEC. The presence of copolymer chains not initiated by benzyl groups also explains why the ^{1}H NMR molecular weight calculation gave higher values than the theoretical ones.

We used photoinitiated thiol-ene addition of 2-mercaptoethanol to functionalize the pendant copolyoxazoline double bonds (Scheme 3). After 2h of irradiation and a simple work up, the polyoxazoline-based polyols were obtained in quantitative yield.



Scheme 3. Thiol-ene functionalization of the copolyoxazolines.

^{1}H NMR analysis (Figure 1b) show the absence of double bond signals and the appearance of three new signals at 2.51 ppm (-$\underline{CH_2}$-S-CH_2CH_2-OH), 2.71 ppm (-CH_2-S-$\underline{CH_2}CH_2$-OH) and 3.71 ppm (-CH_2-S-$CH_2\underline{CH_2}$-OH) corresponding to the 2-hydroxyethylthioether group. SEC analysis of polyoxazoline polyols (Figure 2 and Table 2) shows a similar molecular weight distribution and polydispersity than the starting unfunctionalized polyoxazoline, thus indicating the absence of degradation and side chain processes. MALDI-TOF-MS spectra shows a complex pattern with several series of peaks separated by 78 mass units which corresponds to the -S-CH_2CH_2-OH moiety. These series of peaks could be assigned to the copolymers initiated with H- and Bn- groups and cationized either by sodium or potassium.

Table 2. Molecular weight, hydroxyl content and thermal properties of POH polyols.

Sample	$Mnx10^{-3}$ (Mn/Mw) (a)	mmolOH/gPol. (b)	mmolOH/gPol. (c)	Tg (°C) (d)	Tm (°C) (d)	ΔH (J/g) (d)
POH1a	2.34 (1.11)	0.79	1.22	-11.6	50,7	14.1
POH1b	3.41 (1.11)	0.80	1.08	-9.0	58.3, 81.0, 88.3	40.7
POH1c	4.31 (1.11)	0.80	0.89	-2.5	58.3, 87.3, 101.3	41.3
POH2a	2.42 (1.11)	1.08	1.45	-10.9	56.3	22.9
POH2b	3.57 (1.11)	1.09	1.34	-7.4	59.0, 84.3	40.6
POH2c	4.56 (1.16)	1.09	1.18	-3.6	58.3, 82.7, 93.7	41.9
POH3a	2.50 (1.10)	1.20	1.66	-11.7	54.7	21.1
POH3b	3.62 (1.11)	1.23	1.47	-6.6	57.7, 78,7	40.1
POH3c	4.58 (1.14)	1.21	1.32	-3.9	60.3, 84.7	41.8

a) Determined by SEC using PS standards.
b) Side chain OH content determined by ^{1}H NMR.
c) Side chain plus chain-end OH content determined by ^{1}H NMR.
d) Determined by DSC.

The hydroxyl number of all polyoxazoline-polyols was determinate by ^{1}H NMR measuring the amount of hydroxyl end groups and chain hydroxyl groups. The intensity of the signals at 3.80-3.70 ppm corresponding to side chain $–CH_2OH$ and chain-end $–CH_2OH$ groups was compared with the intensity of the signals at 3.86 and 2.85 ppm (Ph-$\underline{CH_2}$-$\underline{CH_2}$-OH) of a known amount of phenylethanol as internal standard. Also the intensity of the signal at 2.71 ppm corresponding to the -S-$\underline{CH_2}$-CH_2-OH was measured in order to calculate the hydroxyl content due exclusively to side chain groups. Both hydroxyl contents expressed in mmol of OH per gram of polymer are collected in Table 2. The calculated side chain hydroxyl values are in good agreement with the theoretical ones taking into account the copolymer composition thus confirming the efficiency of the functionalization under the mild conditions used. For each POH1, POH2 and POH3 polyol series the total hydroxyl content increases as the molecular weight decreases due to the contribution of the chain end hydroxyl groups.

The resulting polyoxazoline-polyols were yellowish clear waxy solids. DSC analysis shows its semicrystalline nature with T_g values below 0 °C and multiple melting endotherms in the range of 50 to 100 °C (Table 2). Both, first and second order transitions increase with molecular weight for all copolymer series. Low molecular weight copolyols showed a single melting endotherm at ca. 50 °C whereas the rest of polyols show complex endotherms. According to results, the different thermal behaviour of these samples seems to be related to the differences in molecular weight rather than to the hydroxyl group content.

These polyoxazoline-based polyols were used to prepare polyurethane thermosets by reaction with MDI in solution of toluene. In all cases a slight excess of isocyanate group over the theoretical amount based on the polyol hydroxyl content was used. The PU prepolymers were casted onto glass plaques and cured at 130 °C for 3 h to produce flexible to hard yellowish transparent materials as films with 0.03 to 0.04 mm thickness. The synthesized polyols, having primary hydroxyl groups showed an excellent compatibility with the MDI toluene suspension leading to homogeneous systems before the curing cycle.

FTIR analysis (Figure 4) demonstrated the completion of the reaction by the disappearance of the band at 2240 cm^{-1} corresponding to the –N=C=O stretching of the isocyanate group and the appearance of the characteristic absorbances of the urethane links at 1728 cm^{-1} which appears clearly differentiated to the band at 1641 cm^{-1} corresponding to the C=O stretching of the polyoxazoline amide groups. The C=O of these urethane linkages appears as a broad band between 1745 and 1690 cm^{-1} with a maximum at 1728 cm^{-1} and a shoulder at 1710 cm^{-1} which are attributable to the associated and non associated C=O urethane groups. No additional shoulders at ca. 1660 cm^{-1} attributable to urea linkages were observed. Moreover the broad band centred at 3500 cm^{-1}, corresponding to the O-H stretching, shifts to lower frequencies and shows a maximum at 3315 cm^{-1}, characteristic of the N-H stretching of urethanes.

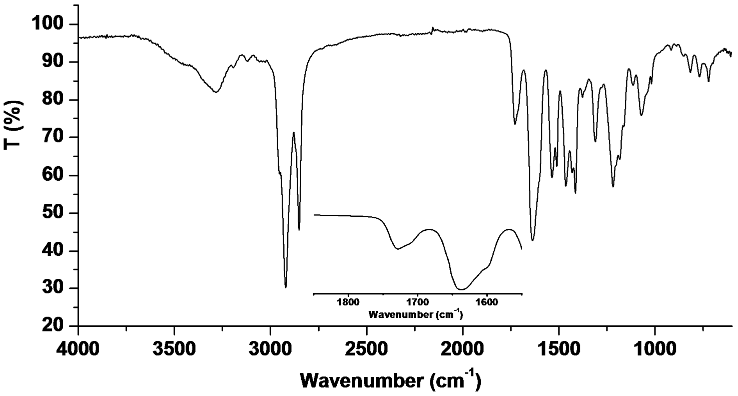


Figure 4. FTIR-ATR spectrum of PU2c.

The thermal properties of polyurethanes were investigated by DSC (Figure 5 and Table 3). The most significant feature is the appearance of a melting endotherm at 57-58 °C for PUs obtained from polyols of medium (2900 Da) PUb and high (4100 Da) PUc molecular weight. In these cases, the crystallinity is higher for the PUs obtained from the higher molecular weight polyoxazoline polyols. When comparing PUs obtained from polyols of the same molecular weight but increasing hydroxyl content (PU1b, PU2b, PU3b and PU1c, PU2c, PU3c series) a decrease in its relative crystallinity degree is observed, which can be related to the increasing difficulty in the chain packing as the cross-linking degree increases.

Table 3. Thermal properties of PUs.

	Tg (°C)		Tm		TGA (N_2)	
Sample	1/2ΔCp (a)	Tanδ$_{max}$ (b)	T_{max}(°C) (a)	ΔH (J/g) (a)	$T_{5\%}$(°C)	T_{max}(°C)
PU1a	12	49	---	---	299	224, 415
PU1b	20	56	58.3	8.3	319	413
PU1c	26	64	57.7	9.7	315	414
PU2a	20	51	---	---	296	219, 410
PU2b	20	50	57.2	2.9	295	238, 410
PU2c	23	53	57.0	6.1	303	272, 410
PU3a	24	52	---	---	259	233, 411
PU3b	21	51	---	---	284	246, 409
PU3c	18	48	58.1	1.8	261	252, 410

a) Determined by DSC.
b) Determined by DMTA.

The glass transition temperature for all PUs is around 20 °C showing a slight increase with the starting polyol molecular weight (Series PU1 and PU2) but not in the case of PU3 series. This complex behaviour can be related to the ocurrence of two different effects. Lower molecular weight polyols have higher hydroxyl content and consequently leads to PUs with higher number of urethane links, however PUs from high molecular weight polyols have crystalline regions which act as physical crosslinks restricting mobility. In absence of other effects PUs made from polyol of similar molecular weight but increasing hydroxyl content, should lead to an increase in the number of urethane links and consequently in the T_g values. This behaviour is effectively observed in PUs obtained from similar comb-like amorphous polyetherpolyols.[15] In this case, it must be considered the semicrystalline nature of these PUs and the fact that the strong polar interactions between polyoxazoline amide groups can be disrupted as the amount of urethane links increases. This consideration is supported by the fact that polyoxazoline-polyols with the similar molecular weight but different hydroxyl content (ie. POH1c, POH2c and POH3c) have very close T_g values (Table 2).

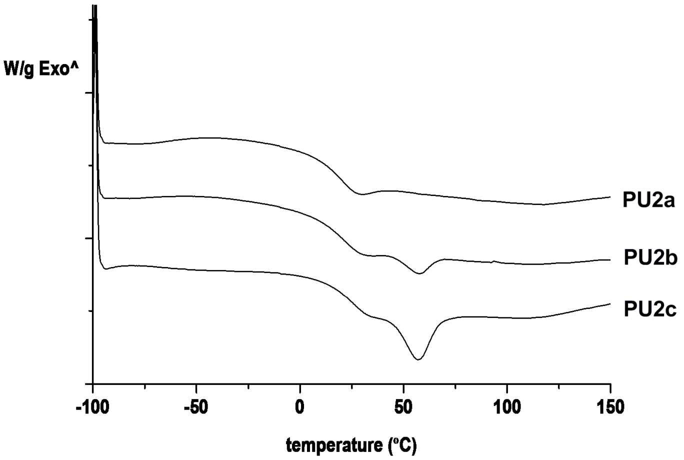


Figure 5. Second heating DSC traces of PU2a, PU2b and PU2c.

The thermal stability of polyurethanes was studied in N_2 atmosphere (Table 3). The shapes of the weight-loss curves were very similar for all PUs and differences in the thermal stability seem to be negligible. The decomposition shows two main stages for most of the PUs (Figure 6a). The first has a maximum that increases from 219 °C to 272 °C in the PU2 series and from 233 °C to 252 °C in the PU3 series in a parallel way with the increase of molecular weight of the starting polyol. The weigh-loss associated (5-10% of the total mass) decreases with the same parameter and so this decomposition process can be associated in part to the polyol fragmentation. This can be inferred when comparing the TGA curves of a PU, its parent polyol and the original polyoxazoline (Figure 6b). As can be seen, all polymers have a main degradation process with a maximum around 400 °C, but the polyoxazoline polyol and the polyurethane present an additional low temperature degradation process that is not observed in the polyoxazoline polymer. This seems to indicate that this degradation process is related in part with the cleavage of the $–S-CH_2-CH_2-O-$ moieties.

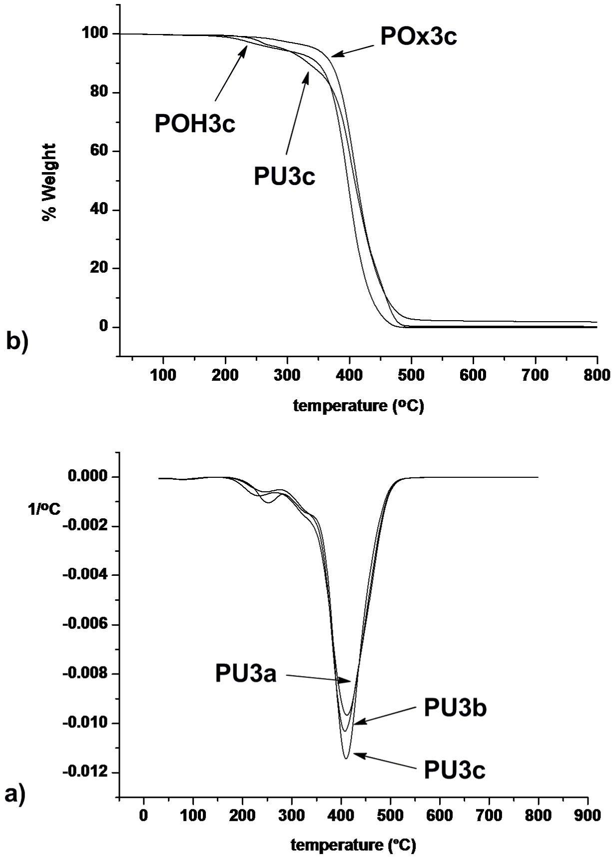


Figure 6. a) First derivative curve of the TGA plots of PU3a, PU3b and PU3c. b) TGA plots of POx3c, POH3c and PU3c.

A second degradation step appears as a shoulder around 335-340 °C for all samples and can be associated to the initial decomposition of the urethane links. The third and main decomposition step has a maximum at 410-415 °C for all PUs and supposes the complete degradation of the polyoxazoline and urethane moieties leading to a carbonaceous residue of about 1% of the initial weight in all cases.

The dynamomechanical behaviour of PUs was studied by DMTA. Typical DMTA plots for cross-linked polymeric networks were observed in all cases. A glass state with a high modulus plateau E’ at lower temperatures and a rubbery state with lower E’ at higher temperatures are observed. For all PU series the storage moduli at the rubbery plateau slightly increases with the molecular weight of the starting polyol. Polyurethanes behave like homogeneous networks with a unique broad transition that according to DSC corresponds to the glass transition in the amorphous PU and the glass transition and melting in the semicrystalline PUs.

Figures 7a and 7b show the representative Tan δ of some synthesized PUs. Consistent with DSC results, this peak shows a slight shift of maxima when increasing the molecular weight of the parent polyol for series PU1 and PU2 which is consistent with the increase in its crystallinity degree.

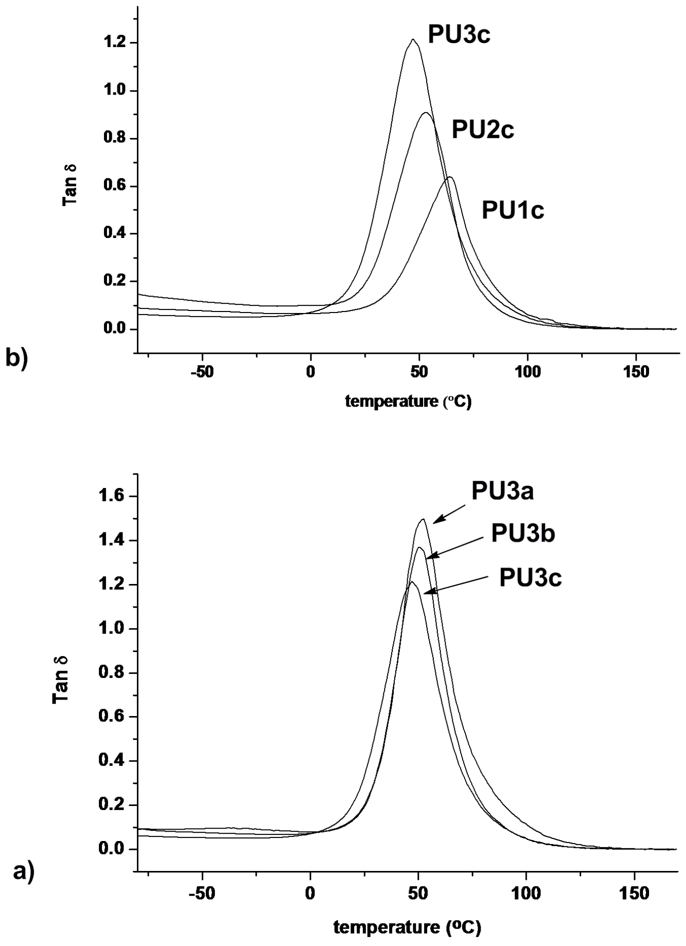


Figure 7. Variation of Tan δ peak of PUs with a) the molecular weight of the parent polyol (PU3a, PU3b and PU3c) and b) with the hydroxyl content of the parent polyol (PU1c, PU2c, and PU3c).

In the case of PU3 series, which are practically amorphous, a slight decrease of the maxima is observed (Figure 7a). The variation of the Tan δ peak when comparing PU1, PU2 and PU3 series (Figure 7b) is also consistent with the decrease in the crystalline content as the functionality of the parent polyol increases. These results seem to indicate that mechanical properties of the PUs are mostly governed by its crystalline content which is directly related to the molecular weight of the parent polyol, instead of the amount of urethane links introduced.

Figure 8 shows the stress-strain curves and Table 4 summarizes the mechanical properties of obtained PUs. Young's modulus and tensile strength at break increase as the molecular weight of the parent polyol increases for all series. As expected, an enhancement of the modulus and tensile strength can be observed when increasing the semicrystalline nature of the PUs. What is most notable is the high modulus of PU1c which is consistent with its high crystalline degree and its maximum T_g and Tan δ values determined by DSC and DMTA.

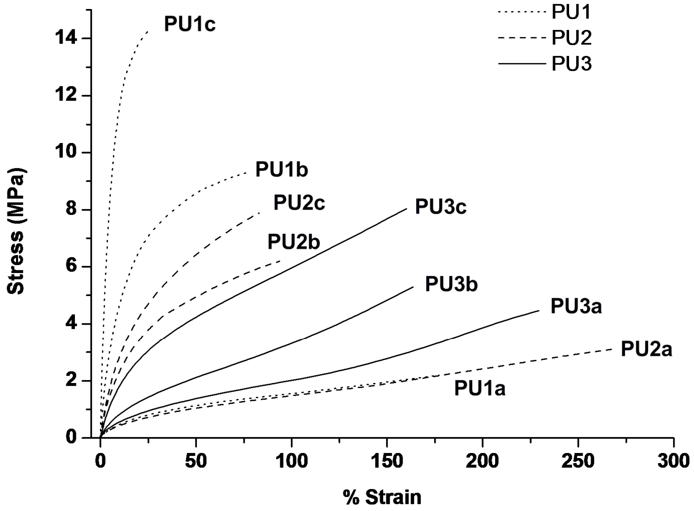


Figure 8. Stress-strain plots of all PUs.

Table 4. Mechanical properties of the polyurethanes

	DMTA		
Sample	Young's M. (MPa)	Stress(MPa)	Strain(%)
PU1a	5.5	2.2	177
PU1b	85	9.3	76
PU1c	254	14.3	25
PU2a	6.0	3.1	268
PU2b	41	6.2	94
PU2c	46	7.9	83
PU3a	7.6	4.5	229
PU3b	12.9	5.3	163
PU3c	28.8	8.0	160

Conclusions

The transformation of saturated and insaturated fatty acids in oxazoline monomers is a straightforward and convenient methodology to produce polymers with controlled molecular weight, composition and end group functionality using CROP. The side chain unsaturated groups can be effectively and quantitatively functionalized under mild conditions using the thiol-ene addition of mercaptoethanol to produce renewable polyoxazoline-polyols. These polyols have preset characteristics that can be used to prepare PUs with tailored properties ranging from hard-rigid to soft-elastic materials.

Acknowledgements

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Conclusions

Conclusions

In the course of this thesis, new thermosetting polyurethanes from vegetable oils have been developed, showing that it is possible to exploit renewable resources to manufacture original and useful materials. The conclusions of this work are stated below:

- Polyether-polyols of high molecular weight were synthesized by the ionic-coordinative ring opening polymerization of epoxidized methyl oleate followed by partial reduction of the ester groups to primary alcohols.

- Lineal polyether-polyols of controlled molecular weight containing primary and secondary hydroxyl groups were obtained by acyclic diene metathesis (ADMET) polymerization of 1,3-di-10-undecenoxy-2-propanol with 10-undecenol as chain stopper.

- Branched polyester-polyols of controlled molecular weight were obtained by acyclic triene metathesis (ATMET) polymerization of glyceryl triundec-10-enoate with different amounts of 10-undecenol as chain stopper.

- Copoly-2-oxazolines of controlled molecular weight were developed by cationic ring opening copolymerization of fatty acid based 2-oxazolines.

- The thiol-ene click coupling has proven to be an efficient tool to functionalize the terminal carbon double bond of the side chain of polyoxazolines, taking place with quantitative yields and under mild conditions.

- Poly(ether-urethane) networks were obtained from the epoxidized methyl oleate based polyether-polyols and 4,4’-methylene-bis(phenylisocyanate) or L-lysine diisocyanate. Segmented poly(ether-urethane) networks were obtained from the epoxidized methyl oleate based polyether-polyols, 1,3-propanediol and 4,4’-methylene-bis(phenylisocyanate) or L-lysine diisocyanate. The segmented polyurethanes were phase segregated to varying degrees depending on the hard segment content.

- Amorphous and semicrystalline poly(ether-urethane) and poly(ester-urethane) networks were obtained from the linear polyether or branched polyester polyols obtained by metathesis and 4,4'-methylene-bis(phenylisocyanate). The semicrystalline polyurethane thermosets showed good shape memory properties.

- Poly(2-oxazoline-urethane) networks were obtained from the poly-2-oxazoline-polyols and 4,4'-methylene-bis(phenylisocyanate). The mechanical properties were found to depend on the molecular weight and the hydroxyl content of the starting polyol.

Apendixes

Apendix A: List of abbreviations

ADMET	Acyclic diene metathesis
ATMET	Acyclic triene metathesis
BEO	Benzyl 9,10-epoxyoleoylether
DCE	Dichloroethane
DMTA	Dynamic mechanical thermal analysis
DP	Degree of polymerization
DSC	Differential scanning calorimetry
E’	Storage modulus
E”	Loss modulus
EMO	Epoxidized methyloleate
EO	4,5-Epoxyoctane
FTIR	Fourier transform infrared spectroscopi
gHSQC	Gradient-selected heteronuclear single quantum correlation
GC/MS	Gas chromatography couple with mass spectrometry
GPC	Gel permeation chromatography
ΔH_m	Melting enthalpy
LDI	l-Lysine diisocyanate
MALDI-TOF-MS	Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry
MAO	Methyl aluminoxane

mCPBA	m-Chloroperbenzoic acid
MDI	4,4’-Methylene-bis(phenylisocyanate)
M_n	Number average molecular weight
M_w	weight average molecular weight
NMR	Nuclear magnetic resonace spectrometry
Ox	Oxazoline
PDI	Polydispersity index (M_w/M_n)
PDO	1,3-Propanediol
PBEO	Poly(benzyl 9,10-epoxyoleoylether)
PEMO	Poly(epoxidized methyloleate)
PEO	Poly(4,5-epoxioctane)
POx	Polyoxazoline
PU	Polyurethane
ROP	Ring opening polymerization
SEC	Size exclusion chromatography
SMP	Shape-memory polymer
SPU	Segmented polyurethane
TAI	Trichloroacetylisocyanate
Tan δ	Loss factor
TEA	Triethylaluminum
TFAA	Trifluoroacetic anhydride
$T_{5\% \text{ loss}}$	Temperature of 5% loss
T_g	Glass-transition temperature

TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TIBAO	Tetraisobutyldialuminoxane
TLC	Thin layer chromatography
T_m	Melting temperature
T_{max}	Temperature of maximum weight loss
TMS	Tetramethylsilane
UDTG	10-Undecenyl triglyceride

Apendix B: List of publications

Title: Polymerization of Epoxidized Vegetable Oil Derivatives: Ionic-Coordinative Polymerization of Methylepoxyoleate.
Authors: E. del Río, M. Galià, V. Cádiz, G. Lligadas, J. C. Ronda.
Ref.: J. Polym. Sci., Part A: Polym. Chem., 2010, 48, 4995-5008.

Title: Biobased Polyurethanes from Polyether Polyols Obtained by Ionic-Coordinative Polymerization of Epoxidized Methyl Oleate.
Authors: E. del Río, G. Lligadas, J. C. Ronda, M. Galià, V. Cádiz.
Ref.: J. Polym. Sci., Part A: Polym. Chem., 2010, 48, 5009-5017.

Title: Polyurethanes from Polyols Obtained by ADMET Polymerization of a Castor Oil-Based Diene: Characterization and Shape Memory Properties.
Authors: E. del Río, G. Lligadas, J. C. Ronda, M. Galià, M. A. R. Meier, V. Cádiz.
Ref.: J. Polym. Sci., Part A: Polym. Chem., 2011, 49, 518-525.

Title: Shape memory polyurethanes from branched polyols obtained by ATMET polymerization of glyceryl triundec-10-enoate and 10-undecenol.
Authors: E. del Rio, G. Lligadas, J.C. Ronda, M. Galià, V. Cádiz, M.A.R. Meier
Ref.: Macromol. Chem. Phys., 2011, (Submitted).

Title: Poly-2-oxazoline derived polyurethanes. A versatile synthetic approach to renewable polyurethane thermosets.
Authors: E. del Rio, G. Lligadas, J.C. Ronda, M. Galià, V. Cádiz.
Ref.: J. Polym. Sci., Part A: Polym. Chem., 2011, (Submitted).

Apendix C: Stages and meeting contributions

Authors: E. del Río; J. C. Ronda; M. Galià; V. Cádiz
Oral Communication: Synthesis of polyurethanes from methyl oleate as renewable resource. IV Congress of Young Researchers on Polymers (JIP2008). Peñíscola. June 15-19, 2008.

Authors: J. C. Ronda; E. Del Río; M. Galià; V. Cádiz
Poster presentation: Polyurethanes from epoxidized methyl oleate based polyether polyols. International Workshop on Biomacromolecules. Stockholm. June 1-4, 2008.

Authors: E. del Río; J. C. Ronda; M. Galiá; G. Lligadas; V. Cádiz
Poster presentation: Biobased segmented polyurethanes from methyl oleate based polyether polyols. 2nd Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry. Emden. March 22-24, 2009.

Authors: E. del Río; J. C. Ronda; M. Galiá; V. Cádiz; M. A. R. Meier
Poster presentation: Synthesis of plant oil derivatived polyols via ADMET polymerization. 3rd Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry. Emden. March 14-16, 2010.

Stays abroad

Organization: University of Potsdam
Host center: Institute of Chemistry
Departament: Laboratory for Sustainable Organic Synthesis (Dr. Michael A. R. Meier)
City: Potsdam **Country:** Germany
Lenght: 95 days **Year:** 2009