Review

Oleic and Undecylenic Acids as Renewable Feedstocks in the Synthesis of Polyols and Polyurethanes

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Abstract: Nowadays, the utilization of raw materials derived from renewable feedstock is in the spotlight of the chemical industry, as vegetable oils are one of the most important platform chemicals due to their universal availability, inherent biodegradability and low price. Taking into account that polyurethanes are one of the most important industrial products exhibiting versatile properties suitable for use in many fields, our research is focused on exploiting fatty acids in the preparation of biobased polyols and polyurethanes. This review is organized as a function of the nature of the final polyurethane systems; hence we describe the preparation of linear thermoplastic and crosslinked polyurethanes derived from oleic and undecylenic acids-based diols and polyols, respectively.
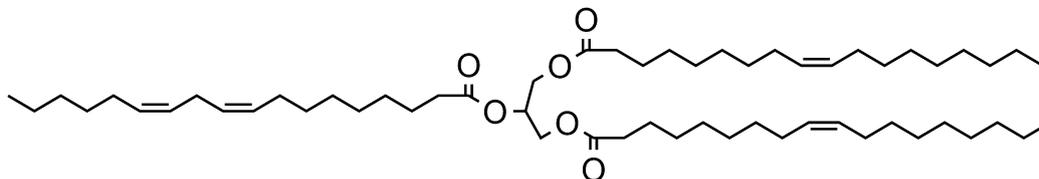
Keywords: vegetable oil; polyol; polyurethane; renewable resources; oleic acid; undecylenic acid

1. Introduction

Renewable resources are recently gaining a lot of attention as a substitute petroleum for producing polymers [1]. This is not only in consideration of the future shortage of petroleum supplies, but also due to a sense of environmental protection. Vegetable oils are one of the cheapest and most abundant

biological resources available in large quantities and are predominantly mixtures of triglyceride molecules, which have the three-armed star structure shown in Figure 1. Triglycerides are made up of three fatty acids joined at a glycerol junction. Most of the common oils contain fatty acids that vary from 12 to 22 carbons in length, with 0 to 3 double bonds per fatty acid.

Figure 1. Schematic representation of the triglyceride molecule structure.

The use of vegetable oils as a starting material offers numerous advantages: for example, low toxicity, inherent biodegradability, and high purity [2,3], thus they are considered to be one of the most important classes of renewable resources for the production of biobased polymers [4–8].
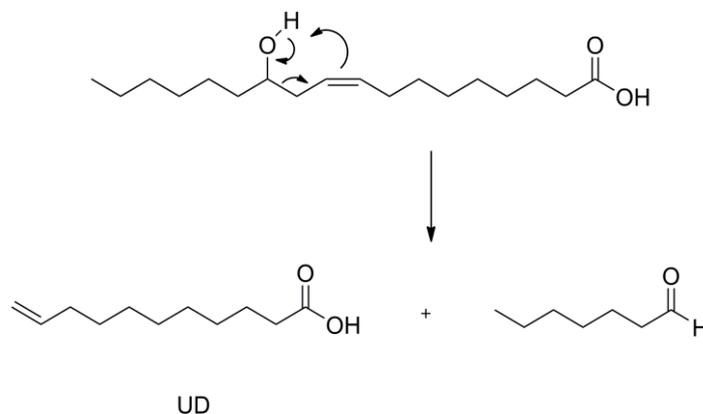
Polyurethanes (PUs) are one of the most important and versatile classes of polymers and can vary from thermoplastic to thermosetting materials. The industrial production of PUs is normally accomplished through the polyaddition reaction between organic isocyanates and compounds containing active hydroxyl groups, such as polyols. Usually, both isocyanate and polyol are petroleum based. Due to uncertainty about the future cost of petroleum, as well as the desire to move toward more environmentally friendly feedstocks, many recent efforts have focused on replacing all or part of the conventional petroleum-based polyols with those made from vegetable oils. Combined with isocyanates, vegetable oil-based polyols produce PUs that can compete in many ways with PUs derived from petrochemical polyols [9]. Moreover, due to the hydrophobic nature of triglycerides, vegetable oil-based polyols produce PUs that have excellent chemical and physical properties, such as enhanced hydrolytic and thermal stability [9].

The preparation of polyols from vegetable oils for general polyurethane use has been the subject of many studies. For natural oils and derivatives to be used as raw materials for polyol production, multiple hydroxyl functionality is required. Traditionally, plant oil-based polyols have been prepared starting from triglyceride molecules. These polyols have been successfully prepared using different methods; most common is the epoxidation of carbon-carbon double bonds and further oxirane ring-opening with alcohols or other nucleophiles [10–16]. Other methodologies involve the transesterification with multifunctional alcohols [17–21] and the combination of hydroformylation or ozonolysis and subsequent reduction of carbonyl groups [22–30]. Unfortunately, limited attention has been paid to the preparation of diols and polyols from fatty acids, which can be easily isolated from oils [31,32].

In this context, our research is focused in the preparation of diols and polyols from oleic acid (OL) and undecylenic acid (UD). OL is a C18 fatty acid containing a carbon-carbon double bond at the ninth position that can be found in several natural oils such as olive oil (71%), canola oil (61%), sunflower oil (42%) and palm oil (39%). Modern genetic engineering techniques are already able to develop natural oils with much higher content of an individual fatty acid. For example, "high oleic" sunflower oil with an oleic acid content of more than 90% is available. UD is a C11 fatty

acid-derivative with a terminal carbon-carbon double bond. It can be easily obtained from castor oil. Up to 90% of the fatty acid fraction in castor oil is ricinoleic acid. UD can be obtained by heating ricinoleic acid under vacuum pyrolysis. Several mechanisms, including a McLafferty-type rearrangement (Figure 2) and a free-radical mechanism [33], have been proposed for the transformation of ricinoleic acid into UD and heptaldehyde.

Figure 2. McLafferty-type rearrangement of ricinoleic acid to undecylenic acid (UD) and heptaldehyde.

In sustainable materials, PUs are currently prepared from renewable polyols while the second partner, isocyanate, is mainly made from petroleum resources [9]. The functionality of the polyol determines the properties of the final polyurethane polymers. Polyols with functionality 2 (diols) lead to linear thermoplastic PUs, whereas polyols with three or more hydroxyl groups are required to prepare polyurethane networks. Taking these premises into account, we present our research in this field organized in two polyurethane systems: linear thermoplastic and crosslinked polyurethanes derived from OL and UD-based diols and polyols, respectively.
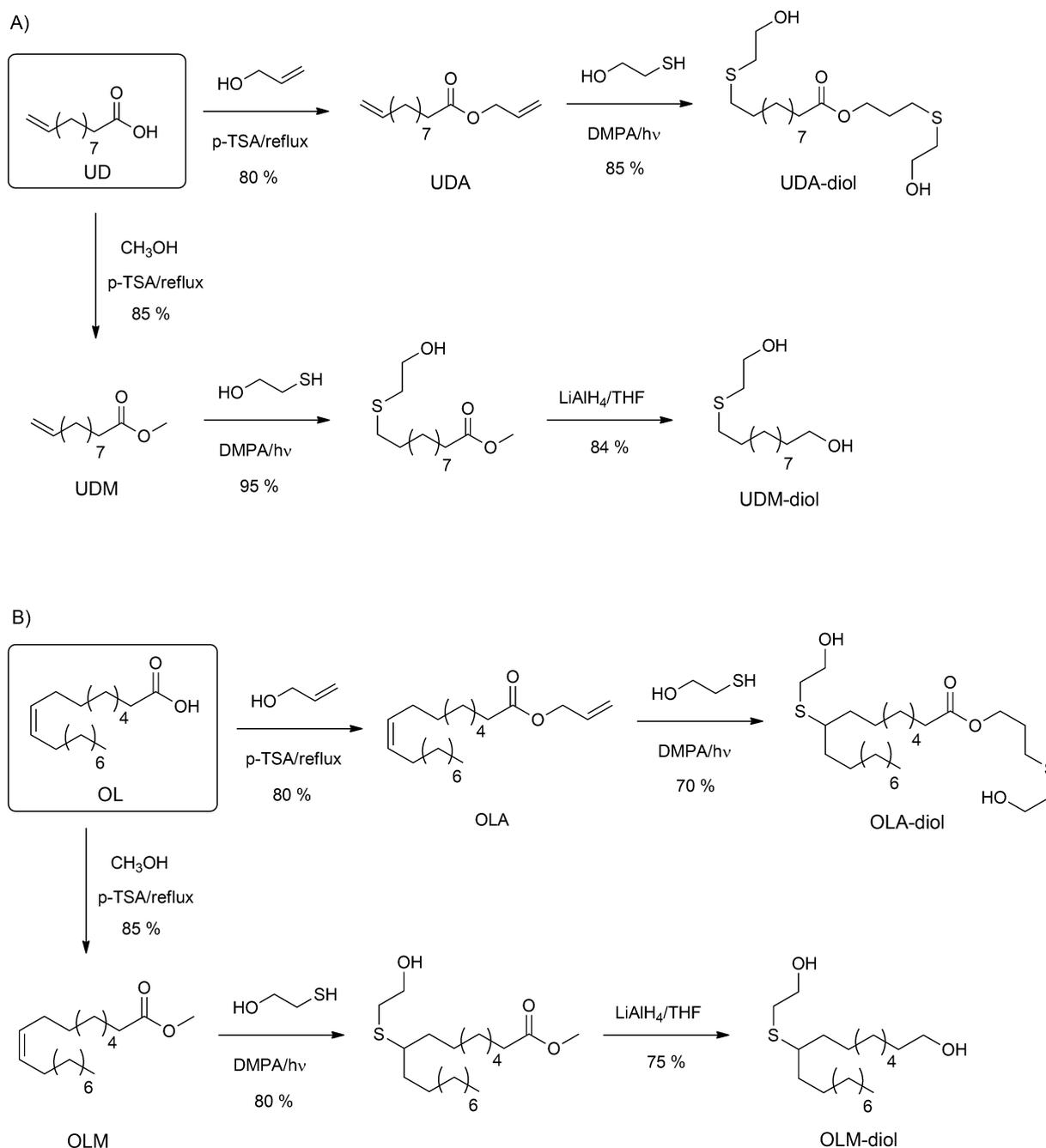
2. Linear Thermoplastic Polyurethanes Derived from OL and UD-Based Diols

Click chemistry concept, introduced by Sharpless and colleagues in 2001, describes chemistry tailored to generate substances quickly and reliably by joining small units together [34]. Recently, the addition of thiols to double bonds, defined as thiol-ene click coupling, has emerged as a powerful tool for synthetic purposes [35,36]. In particular, we believe that thiol-ene click chemistry of fatty acids obtained from plant oils is a promising addition to ease the preparation of fatty acid-derived diols.

Four monomers: UDA-diol, UDM-diol, OLA-diol and OLM-diol (Figure 3), suitable for linear polyurethane synthesis, were prepared from renewable resources. UDM-diol and OLM-diol (Figure 3A and B) were obtained in high yields, applying photoinitiated thiol-ene coupling with 2-mercaptoethanol (ME) to methyl esters of oleic and undecylenic acids (OLM and UDM respectively), and the subsequent reduction [37]. As expected, the addition of ME to UDM reached 100% in a few minutes; whereas the addition to OLM required longer reaction times (90 min to reach 99%). This difference in reactivity is due to ene susceptibility to thiyl attack and subsequent hydrogen abstraction [38]. A similar procedure was applied to their allyl ester derivatives (UDA and OLA), leading to two diols containing ester groups (UDA-diol and OLA diol). It is worth mentioning

that fatty acid allyl ester derivatives are 100% renewable monomers as they can easily be prepared by esterification of the corresponding fatty acid with allyl alcohol, which can be obtained from glycerol, the main byproduct in the triglyceride transesterification process for biodiesel manufacture [39].
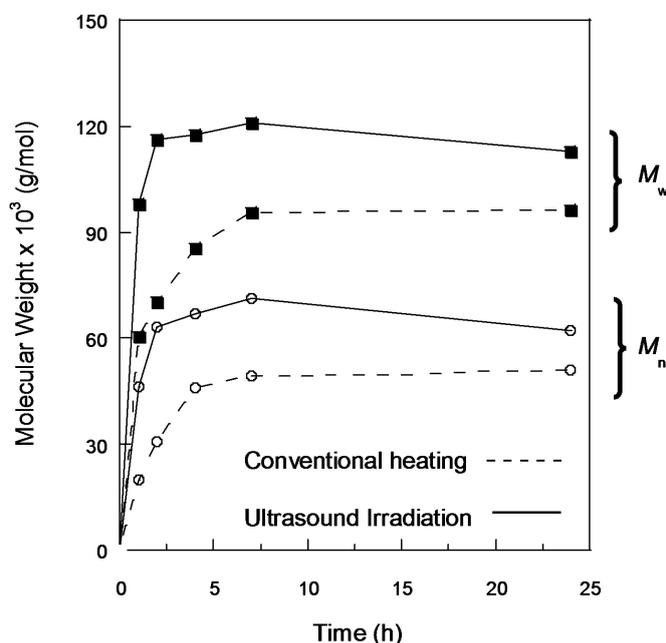
Figure 3. Synthetic procedure for the preparation of UD- and OL-derived diols using thio-lene click coupling as a key step [37].

Linear polyurethanes with molecular weight of about 50,000 Da were obtained in high yields by polymerization in DMF solution of the above mentioned diols with 4,4'-methylenebis(phenylisocyanate) (MDI), applying conventional heating (60 °C). High intensity ultrasound irradiation was also utilized for comparison to the preparation of the polyurethane derived from UDA-diol. In this case, the sonochemical reaction proceeded faster in the early stages and led to higher molecular weight

polyurethane (Figure 4). All synthesized polyurethanes showed excellent hydrolytic and chemical resistance (no weight loss and decrease in the molecular weight were observed after six months in a sodium phosphate buffer solution at pH 7.4 and 60 °C) due to its high hydrophobicity. This hydrophobic character can be exploited in moisture-sensitive environments and long-term applications.

Figure 4. Polyaddition of UDA-diol with 4,4'-methylenebis(phenylisocyanate) (MDI). Evolution of M_n and M_w *versus* time under conventional heating and ultrasound irradiation.

To further explore the potential of thiol-ene coupling in the functionalization of plant oil derivatives, we developed an efficient and versatile "onepot" method for the rapid preparation of well defined telechelic diols from UDA via two sequential thiol-ene click processes: step-growth photopolymerization and post-polymerization end group modification (Figure 5) [40]. A major problem for the preparation of telechelic polymers, and particularly for the transformation of end-groups, is the incompleteness of the reactions. Thus, it is essential to develop synthetic methodologies involving high efficiency reactions such as thiol-ene coupling.

UDA and a 3,6-dioxa-1,8-octanedithiol were "clicked" to prepare alkene-functionalized linear polymers with variable molecular weight by thiol-ene click step-growth polymerization. Thereafter, the modification at the polymer terminus has been done using ME to prepare new biobased telechelic diols with a targeted molecular weight ranging from 1,000–3,000 g/mol. An exhaustive ^{1}H NMR and MALDI-TOF MS analysis demonstrated the high end-group fidelity of this methodology, as an interesting procedure for the accelerated preparation of telechelics derived from divinyl monomers. Figure 6 shows the complete chain ends modification with ME. It can be seen that the series corresponding to alkene-terminated oligomers completely disappears and a new series, corresponding to the hydroxyl-containing oligomers, appears 157 mass units above the former series. This value corresponds to two-times the molar mass of ME and confirms the click joining of two ME at both polymer end groups. UDA-based thelechelic diols, prepared using this methodology, were reacted with MDI and 1,3-propanediol as a chain extender, to obtain multiblock poly(ester urethane) with phase

separated morphology. We are currently studying thermal, mechanical, biodegradation and cytotoxicity properties of UDA-based telechelic diol thermoplastic polyurethanes. The above presented results envision that thiol-ene click chemistry is a promising route for designing novel bio-inspired monomers and shaping structural and functional polymers.

Figure 5. Synthetic procedure for the preparation of telechelics from UDA, 3,6-dioxa-1,8-octanedithiol and 2-mercaptoethanol (ME) through two consecutive thiol-ene click reactions [40].
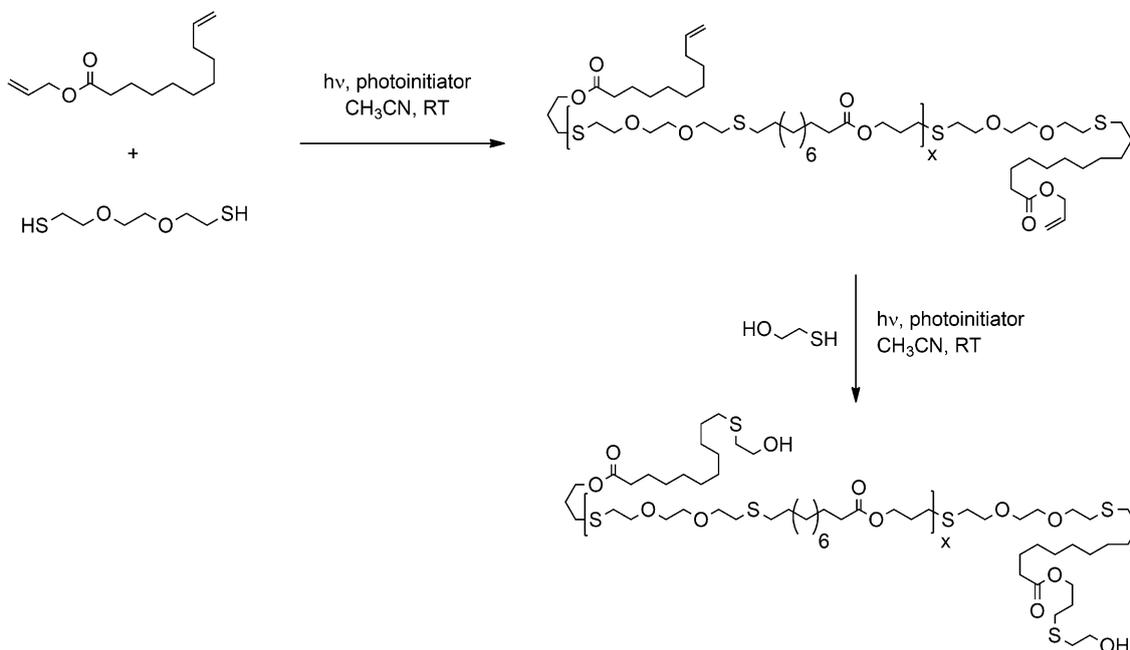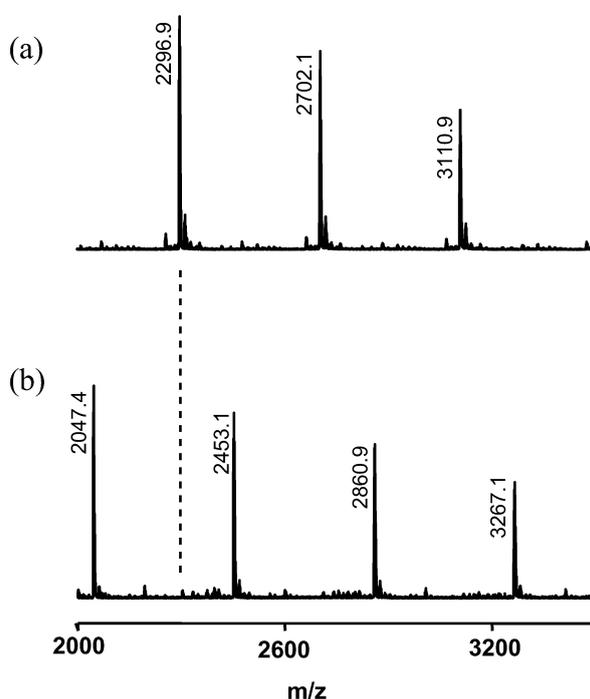

Figure 6. Expanded MALDI-TOF MS spectra of (a) alkenyl-terminated oligomer and (b) the corresponding diol, recorded during the preparation of telechelic diols from UDA.
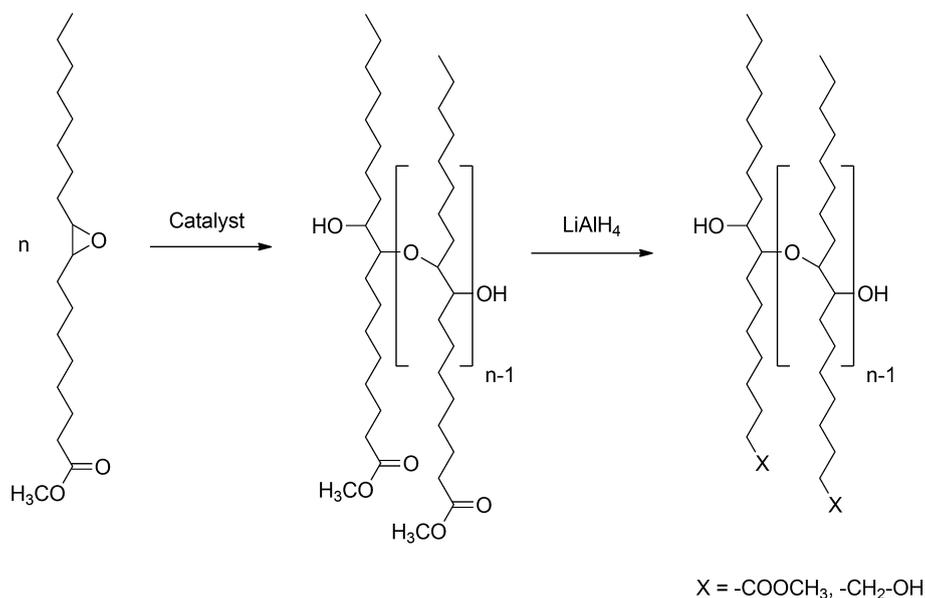
3. Polyurethane Networks Derived from OL and UD-Based Polyols

Polyether polyols are important building blocks for polyurethane applications with molecular weights of 200 to 1,0000 g/mol. Polyols with molecular weights of about 3,000 g/mol or more are used to produce flexible PUs, and polyols of about 200 to 1,200 g/mol are used for rigid PUs. Polyether polyols are usually produced by the anionic ring-opening polymerization of petroleum-derived alkylene oxides, such as ethylene oxide or propylene oxide.

We reported the synthesis and characterization of polyether polyols from epoxidized methyl oleate (EMO). Polyols were prepared through combining the polymerization of EMO and the controlled partial reduction of the carboxylate groups to hydroxyl moieties (Figure 7). Two different polymerization initiators, cationic and ionic-coordinative, were used in order to modulate the molecular weight of the final products.

> **Figure 7.** Synthetic procedure for the preparation of epoxidized methyl oleate (EMO)-derived polyether polyols through catalyzed polymerization of EMO and further partial reduction of ester groups.

$$X = \text{-COOCH}_3, \text{-CH}_2\text{-OH}$$

Low molecular weight polyols (up to 1,200 Da) were prepared from EMO through cationic polymerization in the presence of 0.5%wt. $HSbF_6$ at room temperature and the further partial reduction of the carboxylate groups to hydroxyl moieties using lithium aluminum hydride as a reducing agent [41]. The catalyst was completely soluble in EMO at room temperature, and the oligomerization was performed homogeneously in the absence of solvent, making it an advantageous process from an environmental viewpoint. In this way, polyols with a broad range of functionalities were obtained, ranging from clear liquids to white waxy solids at room temperature.

When ionic-coordinative catalysts such as tetraisobutyldialuminoxane (TIBAO) and Vandenberg catalyst $(C_2H_5)_3Al/H_2O$ were used, polyols with higher molecular weight (up to 9,000 Da) than the above mentioned cationic catalyst were obtained [42]. These materials were found to consist of a complex mixture of cyclic and linear chains with different chain ends which related to the catalyst

nature and the occurrence of two main polymerization mechanisms, the cationic and the ionic-coordinative.

A series of segmented and non-segmented crosslinked PUs were synthesized from the above mentioned polyols using MDI or L-lysine diisocyanate (LDI) as coupling agents and 1,3-propanediol as a chain extender [41,43]. Segmented PUs are elastomeric block copolymers that generally exhibit a phase-segregated morphology made up of soft rubbery segments and hard glassy or semicrystalline segments. As expected, mechanical properties of the segmented PUs improved as the concentration of hard segment was increased, whereas non-segmented polyurethanes behave as soft rubbers showing low Tg values that increase with polyol functionality.
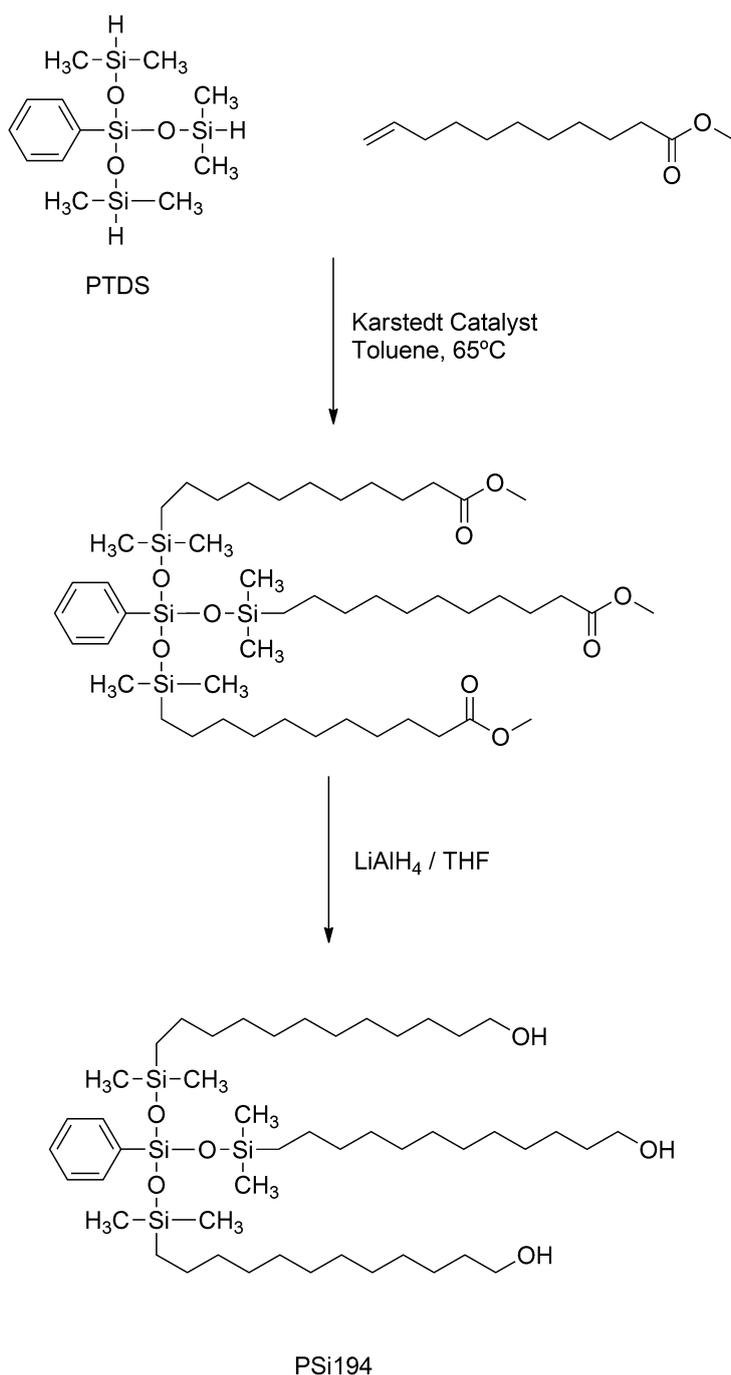
Starting from a low molecular weight EMO-based polyether polyol, we synthesized two different polyurethane systems: PUs entirely from renewable resources with potential applications in the biomedical field, and silicon-containing PUs with improved flame retardant properties.

In the first case, we prepared novel segmented biobased PUs using the one-shot technique from EMO-based polyether polyol, LDI, and 1,3-propanediol (PDO) as a chain extender [44]. Water uptake and *in vitro* degradation studies were carried out, and the morphologies of the degraded PUs were observed by scanning electronic microscopy (SEM). The hard segment content was found to be the main factor that controls the amount of absorbed water. As the hard segment content increases, a more hydrophilic character in the final network due to the presence of a higher amount of urethane groups can be expected, thus increasing the water uptake. The *in vitro* degradation experiments of the synthesized PUs were carried out by immersion of the samples in phosphate buffer solution (pH 7.4, 0.1 M) at 37 °C, and the degradation rate was evaluated by the weight loss of the polymers over predetermined time intervals. After 72 days of degradation, the weight losses of all the PUs were below 12%. The visual examination of the surface of the degraded PUs was carried out using SEM. For all samples, the surface appeared spotted with round pits where material had been removed, and over the weeks more extensive cracks and numerous pores were progressively observed, indicating a larger extent of degradation over time. Moreover, with increasing hard segment content, the erosion was more serious. The spotted surface is due to the presence of areas with marked differences in hydrolytic stability.

The flammability of PUs, as for all synthetic polymers, is a shortcoming in some applications. As a second polyurethane system, we reported the preparation of silicon-containing biobased PUs combining EMO-based polyether polyol, a biobased silicon-containing polyol (PSi194) and MDI as a crosslinking agent (Figure 8) [45]. The concept of sustainable development requires fire retardant technologies to be developed which have minimum impact on health and the environment throughout the life cycle of the fire retardant material. These considerations mean that the search is now on for new environmentally friendly flame retardant polymeric materials. Phosphorus- and silicon-containing polymers are well recognized for their flame retardant properties and they are increasingly becoming more popular than their halogen counterparts, as they generally give off non-toxic combustion products [46]. Previous studies have shown that the addition of relatively small amounts of silicon compounds to various polymeric materials has a flame retardant effect. This is partly because these compounds dilute the more combustible organic components, and partly because the silicaceus residues can form a barrier to an advanced flame [47]. PSi194 was synthesized by hydrosilylation of UDM with a trifunctional hydrosilylating agent, phenyltris(dimethylsiloxy)silane (PTDS), and the
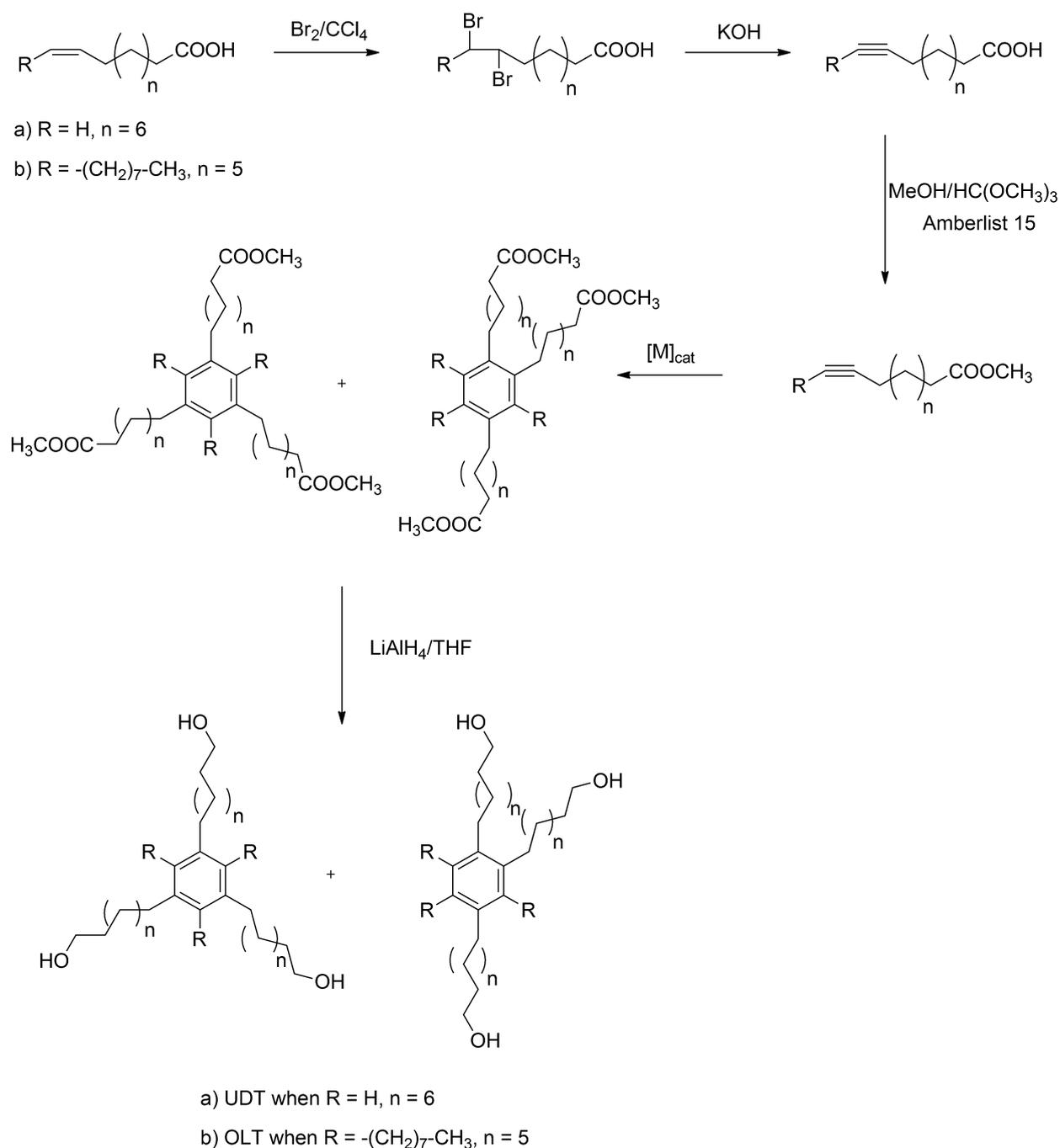
subsequent reduction of carboxylate groups to obtain primary hydroxyl groups (Figure 8). A series of five different PUs with silicon content between 1.7 and 9.0% was prepared by varying the Polyol/PSi194 molar ratio. Silicon has proven to be one of the first choices as a flame retardant element and Limiting Oxygen Index (LOI) increased with the PSi194 ratio and reached a maximum value for neat PSi194 polyurethane. The significance of this result is that PUs with LOI values higher than 21 no longer burn in ambient air if there is no supplementary oxygen, and are therefore very interesting materials for applications that require fire resistance.

Figure 8. Synthetic procedure for the preparation of UD-derived silicon-containing triol (PSi194) using hydrosylilation coupling and further reduction of ester groups [45].

The introduction of aromatic biobased comonomers into the polymer structure is mandatory in the search for new viable polymeric materials. Plant oils-based aromatic compounds are not naturally occurring and therefore modern synthetic procedures must be applied. We reported the synthesis and characterization of two biobased triols (UDT and OLT) that were obtained by transition-metal catalyzed cyclotrimerization of methyl 10-undecynoate and methyl 9-octadecynoate, respectively, that can be synthesized from UD and OL via bromination and further elimination to alkyne functionality, and subsequent reduction of carboxylate groups to give primary hydroxyl groups (Figure 9) [48].

Figure 9. Synthetic procedure for the preparation of UDT and OLT aromatic triols using cyclotrimerization as a key step [48].

a) R = H, n = 6

b) R = -(CH$_2$)$_7$-CH$_3$, n = 5

a) UDT when R = H, n = 6

b) OLT when R = -(CH$_2$)$_7$-CH$_3$, n = 5

Segmented PUs were obtained from these triols, 1,4-butanediol as a chain extender, and MDI. Partial crystallinity and phase separation were detected in samples with a hard segment content of about 50% but were not discernible in samples with lower hard segment content. In UDT-based PUs the soft segment exhibits higher polarity and a higher affinity to the hard phase, meaning that phase mixing is more likely than phase separation. Phase separation was higher in OLT based PUs containing 52% hard segment content. Although the presence of hard segments lowers the crosslinking density, samples with higher hard segment content have higher glass transition temperatures, revealing dispersion of hard segments in the soft phase.

4. Summary and Outlook

The exploitation of plant oils and derivatives, as practically unlimited resources, has recently attracted great interest in polyurethane technology. UD and OL, two of the most valuable renewable building blocks from plant oils, were used to prepare a variety of diols and polyols. Efficient synthetic methodologies such as hydrosilylation, cyclotrimerization of alkynes, and the recently emerged thiol-ene click coupling were applied. In our opinion, thiol-ene click chemistry of fatty acids obtained from plant oils is a promising entry to the easy and rapid preparation of new fatty acid-derived diols and polyols, and therefore is a very promising future technology. All the synthesized hydroxyl-containing monomers were used in the preparation of linear thermoplastic and crosslinked PUs systems, depending on its functionality. Polyurethane systems covering a broad range of final applications—from biomedical implants to flame retardant sealants—have been considered. These results show that it is possible to exploit renewable resources to manufacture original and useful materials.

Acknowledgment

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