

Plant Oils as Platform Chemicals for Polyurethane Synthesis: Current State-of-the-Art

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Plant oils are already one of the most important platform chemicals for the chemical industry due to its universal availability, inherent biodegradability, and low price. Nowadays, plant oils are already a commercial source of multifunctional monomers and oligomers for polyurethane synthesis, and the design of novel biobased polyols derived from them is an active area of research. By taking advantage of the wide variety of possibilities for chemical modification of plant oils, there is a broad palette of strategies to functionalize its structure with hydroxyl groups. The purpose of this review is to comprehensively overview recent developments on the preparation of biobased polyols from plant oils, covering from the general epoxidation and ring-opening approach to novel routes based on thiol-ene click chemistry as well as to highlight the properties of polyurethanes obtained from them.

1. Introduction

In an age of increasing oil prices, global warming, and other environmental problems (e.g., waste), the field of polymers derived from nonpetrochemical feedstock has recently attracted a great deal of interest.¹ Vegetable oils are considered to be one of the cheapest and most abundant biological sources available.² The use of vegetable oils as platform chemicals for polymer synthesis has numerous advantages, including inherent biodegradability and limited toxicity. However, it is important to keep in mind that vegetable oils are not exempt from possible unsuitability for health and safety reasons such as ricin or erucic acid contamination. In this context, increasing efforts have been focused on the use of vegetable oils as platform chemicals for polymer synthesis, and nowadays there is a broad palette of chemical pathways for the preparation of thermosets and thermoplastic polymers based on plant oils.^{3,4}

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.⁵ Polyurethanes are among the most important polymeric materials, which exhibit versatile properties suitable for use in many fields, such as footwear, machinery industry, coatings and paints, rigid insulations, elastic fibers, and medical devices.⁶ It is important to point out that the history of the polyurethane technology is strongly linked to renewable resources. For example, glycerol, the most important starting point for the synthesis of polyether polyols from alkylene oxides, can be produced by the hydrolysis of natural oils. Tetrahydrofuran, used as a precursor of polytetramethyleneglycol-based polyols, which are ideal for making polyurethane elastomers, was produced in the early stages of this technology from furfural, which results from the acid hydrolysis of the pentosanes present in many agricultural waste products. Additionally, naturally hydroxylated castor oil, extracted from castor beans, played an important role in the infancy of the polyurethane industry before synthetic polyols were

Chart 1. Schematic Representation of Triglyceride Molecule Structure

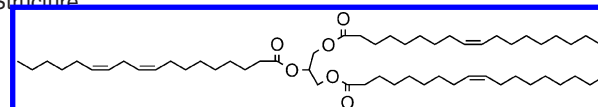


Table 1. Typical Composition of Industrially Important Plant Oils in %^a

$R(x,y) =$	10:0	12:0	14:0	16:0	18:0	18:1	18:2	18:3	20:0
new rapeseed			0.5	4	1	60	20	9	2
sunflower				7	5	19	68		
palm kernel	5	50	15	7	2	15	1		
linseed				5	4	22	15	52	
soybean				11	4	23	53	8	
canola				4	2	64	19	9	
high-oleic sunflower				4	5	83	7		

^a $R(x,y)$ = composition of the fatty acids; x = chain length in carbon atoms; y = number of double bonds. Important note: numbers do not add to 100%.

available. Nevertheless, nowadays commercial polyols are mostly produced from petroleum-based monomers.

Polyurethanes prepared from vegetable oils exhibit a number of excellent properties that are attributable to its hydrophobicity.⁵ Natural plant oils such as soybean oil, sunflower oil, palm oil, rapeseed oil, cottonseed oil, and linseed oil are predominantly made up of triglyceride molecules (triesters of glycerol with long-chain fatty acids, see Chart 1) with varying composition of fatty acids depending on the plant, the crop, the season, and the growing conditions.⁷ Most of the common oils contain fatty acids that vary from 14 to 22 carbons in length, with 0–3 double bonds per fatty acid (Table 1). The annual global production of the major vegetable oils in 2007/08 amounted to 128 million tons (Mt), increasing in 2008/09 to 132 Mt and to 137 Mt in 2009/10.⁸ About one-quarter of the global oil production comes from soybean, followed by palm oil, rapeseed, and sunflower. These commodity oils also make available fatty acids in such purity that may be used for chemical conversions and for the synthesis of chemically pure compounds such as oleic acid from

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sunflower, linoleic acid from soybean, linolenic acid from linseed, erucic acid from rapeseed, and ricinoleic acid from castor oil.

With the exception of castor oil, vegetable oils must be functionalized with hydroxyl groups to be used as polyols for polyurethane synthesis. Triglycerides and fatty acids contain several active sites amenable to chemical reaction, being double bonds and ester groups the most important. These active sites open up various strategies to tailor new biosourced target molecules exhibiting the architectural features and chemical functionality of the currently available polyurethane precursors of petrochemical origin, polyether and polyester polyols. Polyether polyols with terminal hydroxyl groups are the most important polyols for polyurethanes and are produced by the addition of propylene oxide and ethylene oxide to polyfunctional initiators, that is, propylene glycol. On the other hand, polyester polyols are produced by polycondensation of di- and trifunctional polyols with dicarboxylic acids or their anhydrides. Polyols commonly used are ethylene glycol, 1,2-propanediol, 1,4-butanediol, 1,6-hexanediol, neopentylglycol, diethylene glycol, glycerol, and trimethylolpropane. Common dicarboxylic acids or anhydrides are succinic acid, glutaric acid, phthalic anhydride, isophthalic acid, and terephthalic acid.⁹ In the search for green routes to the key polyurethane intermediates, fats and oils offer important alternatives for the production of diols, polyols, and other oxo chemicals, thus, enabling to substitute petrochemicals. On the other hand, the development of nonisocyanate chemistries is one of the major challenges in the field.^{10,11} It is well-known that the conventional method of producing polyurethane products is based on the reaction between polyols and isocyanate chemicals. From an environmental viewpoint, this method is not advantageous because it uses highly reactive and toxic isocyanates, which are commonly produced from an even more dangerous component, phosgene.

The following discussion covers the recent advances made in the functionalization of triglyceride molecules with hydroxyl groups, grouping the contributions of the literature as a function of the triglyceride-active sites involved in the chemical transformation. Moreover, environmentally friendly routes for the production of polyurethanes, using plant-derived diols and diisocyanates or using nonisocyanate chemistries, as well as the main challenges and opportunities for the near future in this field are discussed.

2. Synthesis of Vegetable Oil-Based Polyols through Reactions Involving the Ester Groups

Transesterification of natural triglycerides with multifunctional alcohols is a well-known methodology for the preparation of polyols from vegetable oils. Transesterification of natural and modified plant oils such as palm oil,^{12–14} rapeseed oil,^{15,16} olive oil,¹⁵ soybean oil,^{17–19} hydroformylated and ozonolyzed oils^{20,21} with polyols such as glycerol, pentaerythritol, neopentylglycol, trimethylolpropane or by transamidation with alkanolamines^{16,22} have been used to prepare biobased polyols. On the other hand, transesterification of castor oil with multifunctional alcohols is also a useful methodology to solve some disadvantages derived from the direct utilization of castor oil as polyol: low functionality, low hydroxyl number, and low reactivity related to the presence of secondary hydroxyl groups.^{23,24} In the transesterification of vegetable oils with alcohols, triglyceride and polyol react in the presence of a catalyst, producing a mixture of fatty acid alkyl esters.^{25,26} Catalysts may be strong acids, inorganic bases, or sodium and potassium methoxide, but a range of

organic bases were found effective. The overall process is a sequence of consecutive and reversible reactions in which di- and monoglycerides are formed as intermediates. Several aspects, including the type of catalyst, alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content), and free fatty acid content, have an influence on the course of the transesterification.^{27,28}

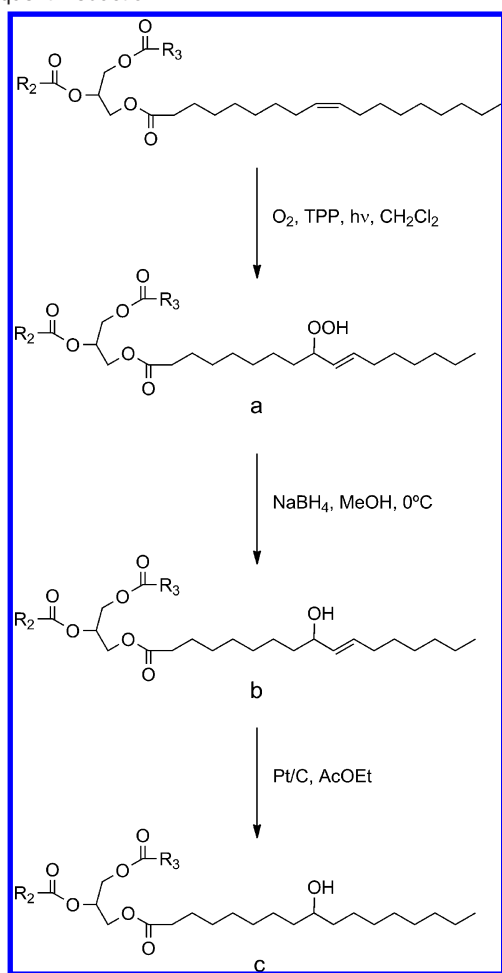
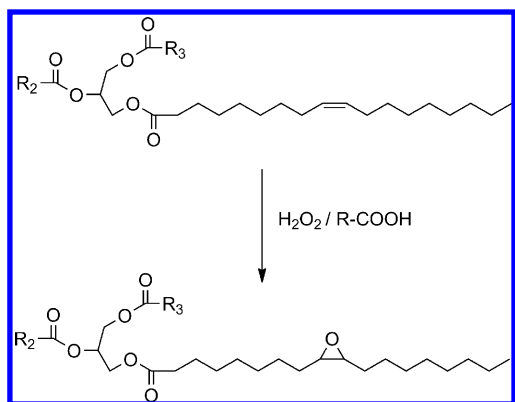
3. Synthesis of Vegetable Oil-Based Polyols through Reactions Involving C–C Double Bonds

The functionalization of triglycerides with hydroxyl moieties through reactions involving the C–C double bonds is the most used methodology for the preparation of plant oil-derived polyols. Air oxidation of plant oils is the most inexpensive and simple reaction in terms of reactants (air and vegetable oil) as a method for the production of high hydroxyl number plant-oil polyols. Air oxidation involves free radical intermediates due to the abstraction of allylic hydrogens and the subsequent formation of a delocalized free radical. These free radicals react with oxygen and other triglycerides to form polyols and a host of other products.²⁹ Kurth reported the utilization of oxidized soybean oil as a polyol in the production of polyurethane materials.^{30,31} More recently Keles and Hazer reported the synthesis of segmented polyurethanes based on polymeric soybean oil polyol prepared by air oxidation in the presence of metal catalysts.³² The air oxidation of soybean oil in the absence of catalyst and subsequent polyol formation was also explored, leading to soy-based polyols with hydroxyl numbers ranging from 7 to 110 mg KOH/g.³³

In this line, our group recently reported the synthesis of a secondary-alcohol-containing triglyceride derivative from high oleic sunflower oil (>90% oleic acid) using an environmentally friendly chemical procedure (Scheme 1).³⁴ High oleic sunflower oil was photochemically oxidized in situ with singlet oxygen generated with a high pressure sodium-vapor lamp and tetraphenylporphyrin (TPP) as sensitizer in an oxygen-saturated medium. In this way, a mixture of isomeric allylic hydroperoxides (a, Scheme 1) was obtained and further reduced to unsaturated hydroxylated oil (b, Scheme 1) using sodium borohydride. The resulting allylic alcohol triglyceride derivative was also transformed to the saturated analogues (c, Scheme 1) by hydrogenation at room temperature using 5% charcoal supported platinum as catalyst. The performance of both polyols as precursors of cross-linked polyurethanes is currently under study in our laboratories.

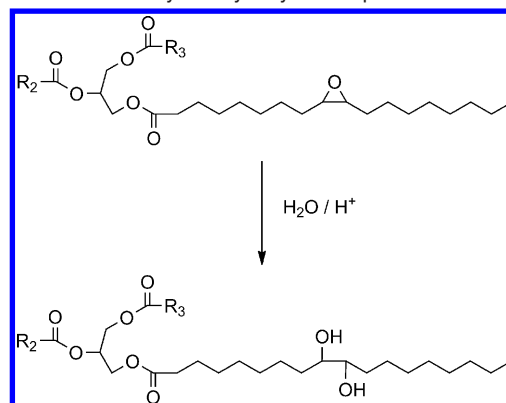
The epoxidation reaction, which makes triglycerides capable of reacting via ring-opening, is the conventional methodology for the functionalization of C–C double bonds with hydroxyl groups. The chemistry of the Prileshajev epoxidation of unsaturated fatty compounds is well-known.³⁵ A short-chain peroxy acid, usually peracetic acid, is prepared from hydrogen peroxide and the corresponding acid either in a separate step or in situ (Scheme 2).

For chemical synthesis on the laboratory scale, better results can be achieved with preformed peroxy acids such as *m*-chloroperbenzoic acid. Other epoxidation methods include the use of dioxiranes,³⁶ the generation of peracids from aldehydes and molecular oxygen,³⁷ and the use of hydrogen peroxide and methyltrioctyl-ammonium(diperoxotungsto)phosphate as a catalyst.³⁸ A method for the chemoenzymatic self-epoxidation of unsaturated fatty acids was also developed.³⁹ This method is of considerable interest because it abolishes the undesirable ring-opening of the epoxide. The unsaturated acid or ester is initially

Scheme 1. Functionalization of High Oleic Sunflower Oil with Secondary Hydroxyl Groups via Photoperoxidation and Subsequent Reduction**Scheme 2.** Functionalization of Triglyceride Molecules via Epoxidation

converted into an unsaturated percarboxylic acid by a lipase-catalyzed reaction with H_2O_2 and is then self-epoxidized in an essentially intermolecular reaction. A method for the enzymatic epoxidation of unsaturated fatty acids was reported by Uyama et al.⁴⁰

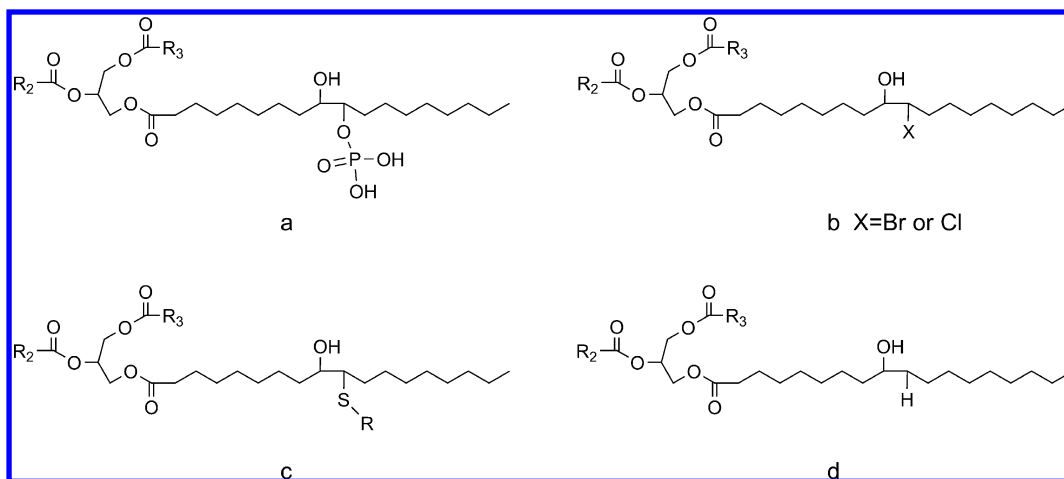
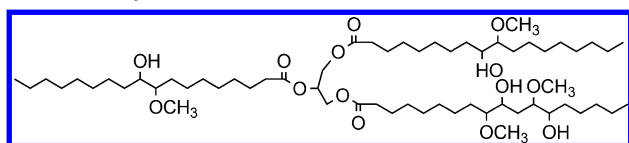
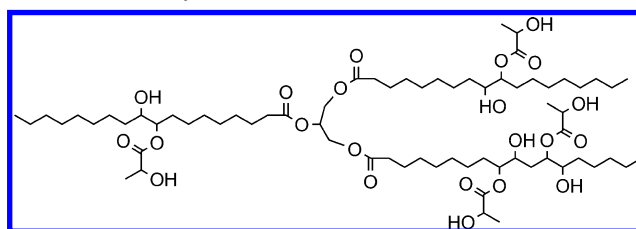
Among the known applications of epoxidized vegetable oils as plasticizers for polyvinyl chloride,⁴¹ reactive diluents,⁴² IPNs,⁴³ epoxy resins monomers,^{44–48} and toughening materials for commercial epoxy resins,^{49,50} they are also important intermediates for polyol production after the oxirane ring-opening with nucleophilic compounds. Hydrolysis of epoxy

Scheme 3. Acid-Catalyzed Hydrolysis of Epoxidized Plant Oils

rings in the presence of different acids such as formic acid,^{51,52} acetic acid,^{53,54} and perchloric acid⁵⁵ produces compounds with multiple 1,2-diol structures, depending on the oxirane content and the extent of hydrolysis (Scheme 3). Epoxidized vegetable oils and several amines, such as ethylene diamine, have also been combined to prepare polyols having amine and secondary hydroxyl functionality.^{56–58}

Ring-opening of epoxidized oils with water in the presence of phosphoric,⁵⁹ hydrobromic, or hydrochloric acids⁶⁰ is particularly interesting because depending on the reaction conditions the catalyst may be chemically incorporated into the polyol (Chart 2a,b). Besides eliminating the need for its removal from the reaction mixture, the presence of phosphorus and halogen atoms in the polyol structure will add value to the product for many end-use applications, such as in flame-retardant polyurethanes. Ring-opening of epoxidized soybean oil approach was also used to prepare hydroxy thio-ether derivatives (Chart 2c).⁶¹ Unfortunately, the performance of these products as polyols for polyurethane formulations was not investigated. Alternatively, epoxidized vegetable oils have also been transformed into polyols via reduction by catalytic hydrogenation⁶⁰ or with sodium cyanoborohydride and boron trifluoride (Chart 2d).⁵⁵ Soybean oil-based polyols containing secondary hydroxyl groups prepared by catalytic hydrogenation were used as precursors of highly viscous biobased hyperbranched polyols.⁶²

Among the variety of chemical transformations of epoxidized vegetable oils, ring-opening with mono- and polyfunctional alcohols received high industrial attention in the 1980s.^{63–68} More recently, the extensive research carried out by Petrovic and co-workers, developing and investigating the structure and properties of polyols produced via alcoholysis reaction of epoxidized plant oils is notorious.^{60,69–75} Special attention has been paid to soybean oil-based polyols due to its very low price and abundance. The oxirane ring-opening by alcoholysis reaction of epoxidized vegetable oils is a slow reaction that requires an acid catalyst.^{55,76} Although several alcohols such as ethanol, *n*-propanol, *n*-butanol, and *n*-pentanol, or branched isomers may be used, methanol is preferred due to its lower cost and the favorable results obtained. The epoxy groups of epoxidized soybean oil were methoxylated in the presence of fluoroboric acid as a catalyst at moderate temperature (40–50 °C). The resulting soybean oil-based polyols had molecular weight of about 1000 g/mol, an OH number of approximately 200 mg of KOH/g and a functionality of 3.5–4 OH groups/molecule, and its approximate structure is shown in Chart 3.⁶⁰ Size exclusion chromatography (SEC) of these polyols indicated the presence 15–18% oligomers formed by epoxy ring-opening during the hydroxylation stage. The problem with this process is that the

Chart 2. Schematic Representation of Vegetable Oil-Based Polyols Prepared by Ring-Opening of Epoxide Groups with Water in the Presence of Phosphoric Acid (a) Hydrobromic or Hydrochloric Acids (b), Thiols (c), and Hydrogenation (d)**Chart 3.** Schematic Representation of Methoxylated Soybean Oil-Based Polyol Structure**Chart 4.** Schematic Representation of Epoxidized Soybean Oil/Lactic Acid Polyol Structure

fluoroboric acid is expensive, highly reactive, hazardous to handle and highly exothermic, must be quenched, and its byproducts present disposal problems. To solve this problem, these oleochemical oil-based polyols can be prepared from an epoxidized oil and alcohol using recyclable and reusable activated or acid-leached clay⁷⁷ or even in one-pot reaction taking advantage of the acid used for epoxidation step.⁷⁸

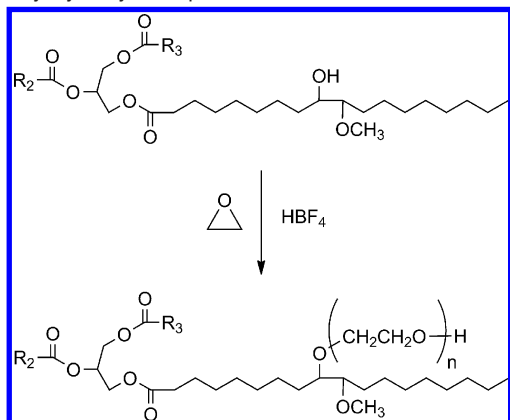
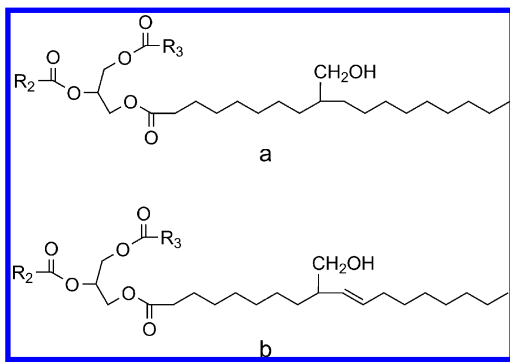
Such polyols possess secondary hydroxyl groups located in the middle of the fatty acid chains (9th or 10th and 12th or 13th carbon atoms), whereas the portion of fatty acids between hydroxyl group and the chain end form pendant groups. Thus, when cross-linking reaction with isocyanates is complete, a portion of the chains (e.g., from the 10th to the 18th carbon) is not included in the network, reducing polymer rigidity. In addition, soybean oil comprises about 15% saturated fatty acids, which are also dangling chains. Besides soybean oil, a broad palette of polyols have been synthesized from various vegetable oils and derivatives with different degree of unsaturation (i.e., sunflower, midoleic sunflower, canola, corn, linseed, peanut, sunflower, triolein, and metathesized triolein) using this two-step process. As expected, polyol functionality was found to be related to the oil double bond content, for example, functionality of polyol resulting from highly unsaturated linseed oil was as high as 5.2.⁶⁹

Methoxy-containing soybean oil polyols have been widely used to produce polyurethanes that can compete in many aspects with polyurethanes obtained from petrochemical polyols.^{79–82} The thermal and oxidative stabilities of methoxylated soybean oil-based polyurethanes are higher than those of conventional polypropylene oxide-based polyurethanes.⁷¹ On the other hand, respirometry data for soybean oil-based polyurethanes revealed that biodegradation of these materials is slow.⁸³ Methoxy-containing soybean oil polyols were also used as soft segments in the preparation of segmented polyurethanes,⁸⁴ waterborne polyurethanes,^{85–87} and waterborne polyurethane/acrylic hybrid latexes.⁸⁸ From these results it is envisioned that plant oil-based

polyols have greatly promising applications. Unfortunately, general plant oil-based polyurethanes show low glass transition temperatures around 30 °C that will limit the stiffness of the material under warm conditions.⁶⁹

As mentioned above, acids are normally added as catalysts to accelerate the ring-opening of epoxidized oils with alcohols. Acid has to be removed after the reaction or remain in the polyol after neutralization with bases and can give rise to cloudy effects and shrinkage where the polyol is used in polyurethane composition. In the absence of catalysts, epoxidized oils can be directly ring-opened with carboxylic acids, in which case high viscous reaction mixtures modified by hydroxyl and acetoxy groups are formed.^{89–93} Recently, Wang et al. investigated the coupling of epoxidized soybean oil and lactic acid via ring-opening reaction in order to increase hydroxyl groups into triglyceride molecule (Chart 4).⁹⁴ Polyurethanes prepared from these polyols exhibited much higher T_g (31–96 °C) than previously reported soybean oil polyols.⁶⁹

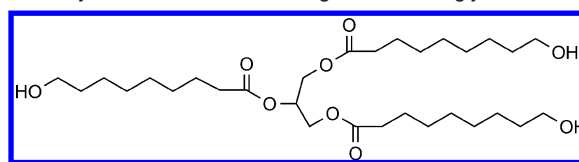
The reactivity of polyols toward isocyanates is a very important practical characteristic in polyurethane fabrication. It is well-known that reactivity of primary OH groups is 3–3.3 times higher than that of secondary OH groups in the uncatalyzed reactions with isocyanates. Epoxidation and further oxirane ring-opening or hydrogenation leads to polyols with secondary OH groups. Three different ways of preparing vegetable oil-based polyols with primary OH groups have been successfully developed. The first one is based on the addition of ethylene oxide, a relatively inexpensive and accessible petrochemical monomer, to vegetable oil polyols with secondary hydroxyl groups prepared by ring-opening reaction of epoxidized soybean oil with methanol (Scheme 4).⁹⁵ This methodology uses low alkoxylation temperature (35–45 °C), low pressure (0.1–0.2 MPa) and HBF_4 as catalyst. The new soybean oil polyols

Scheme 4. Ethoxylation of Methoxylated Soybean Oil Polyol with Secondary Hydroxyl Groups**Chart 5.** Schematic Representation of Hydroformylated (a) and Hydroxymethylated (b) Triglyceride Polyol Structures

showed higher reactivity toward isocyanates in polyurethane formation. This methodology has also been applied to other hydroxylated plant oils such as blown soybean oil containing a hydroxyl value of about 100–180 mg KOH/g.⁹⁶

The second strategy is the transformation of unsaturated triglycerides to polyols having primary OH groups in two steps, hydroformylation, using either rhodium or cobalt as a catalyst, and subsequent reduction of aldehyde groups (Chart 5a). After the pioneer work of Frankel and co-workers with several vegetable oils and fatty acids,^{97–99} Petrovic et al. reported the preparation of polyols and the corresponding polyurethanes from hydroformylation of soybean oil.^{100,101} In the first step, the C–C double bonds were transformed to aldehyde groups (at a high yield) by the hydroformylation reaction with syngas (a mixture of hydrogen/carbon monoxide at 1:1) at 70–130 °C in the presence of rhodium or cobalt catalysts. In the second step, the resulting aldehyde groups were hydrogenated to a polyol comprising only primary OH groups, with hydroxyl value between 160 and 230 mg KOH/g, depending on the hydroformylation catalyst used. As expected from vegetable oil composition, polyols prepared following this procedure are a heterogeneous mixture of different functional species being 4-functional polyols the most frequent species as in the original soybean oil. It is worth mentioning that reacting soybean oil with paraformaldehyde in the presence of a Lewis acid catalyst also yields a hydroxymethylated soybean oil derivative (Chart 5b).^{102,103}

The third approach is the ozonolysis of vegetable oils producing aldehyde functionalities that can be reduced to primary alcohols (Chart 6). Ozonolysis has been successfully

Chart 6. Schematic Representation of Triol Structure Prepared by Ozonolysis and Reduction of Vegetable Oil Triglycerides

applied to soybean oil,^{104–107} castor oil,¹⁰⁵ canola oil,^{106,108} and triolein¹⁰⁶ and leads to trifunctional polyols, unless some sort of oligomerization reaction is applied to increase the molecular weight. It should be noticed that polyols produced by ozonolysis do not contain dangling chains, except for a small percentage of saturated fatty acid chains. Polyurethanes derived from these polyols displayed excellent mechanical properties and higher T_g compared to polyurethanes from epoxidized and hydroformylated polyols of the same functionality, presumably due to the absence (or lower content) of dangling chains.^{106,109,110} Hydroformylated soybean oil polyols have been used in the preparation of highly viscous hyperbranched polyols containing primary hydroxyl groups, whereas canola oil polyols synthesized following the same procedure were used in IPNs of polyurethane and poly(methyl methacrylate).^{111,112} Recently, Benecke and co-workers reported a novel process for the economical production of high quality biobased polyols, containing a mixture of primary and secondary hydroxyl groups, by the ozonolysis of mixtures of vegetable oils, for example, soybean oil and glycerin. High performance coatings and both rigid and flexible foams have been prepared from these polyols.^{113,114}

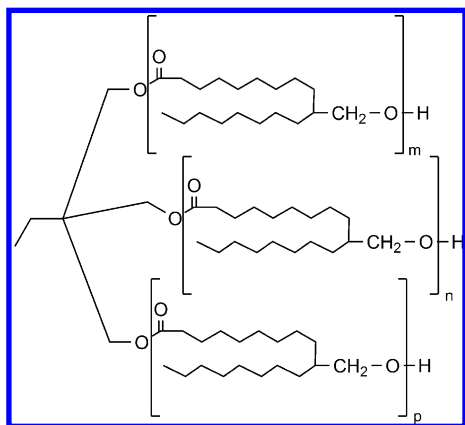
4. Synthesis of Vegetable Oil-Based Polyols by Polymerization of C–C Double Bonds and Subsequent Hydrolysis of Ester Groups

Soybean oil-based polyols prepared by any of the methodologies described above are potentially low-cost raw materials in polyurethane manufacturing. However, the performance of these polyols is sometimes limited by their low molecular weights, low alcohol reactivity due to the presence of secondary moieties, and limited control on crystalline behavior due to nonfunctional branches.

Triglyceride molecules contain C–C double bonds capable of being polymerized through a free radical or cationic mechanism.¹¹⁵ Thus, heat polymerization or heat bodying is an easy and economical method to create soy-based oligomers as starting materials that can be subsequently functionalized with hydroxyl moieties. In a study reported by Suppes et al., bodied soybean oil was partially enzyme-hydrolyzed to give oligomeric polyols with hydroxy number of about 50 mg KOH/g.¹¹⁶ An important characteristic of these products is that contain primary hydroxyl groups due to the 1,3-regiospecific lipase hydrolysis. To prepare soy-based polyols with increased amount of primary hydroxyl moieties and a tunable hydroxyl equivalent weight, transesterification of bodied soybean oil with glycerol is also an effective procedure.¹¹⁷ Unfortunately, the suitability of these polyols for polyurethane synthesis was not tested.

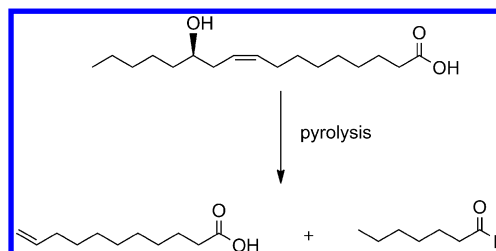
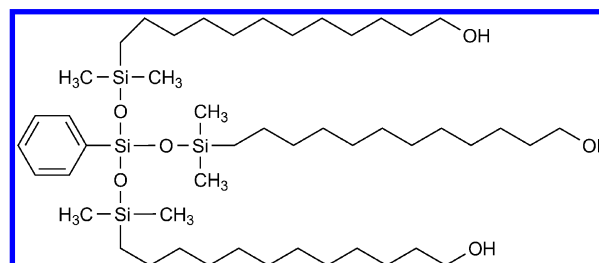
5. Synthesis of Fatty Acid-Based Polyols

Fatty acids which can be easily isolated from oils are also attractive platform chemicals for polyurethane industry since they can be used as building blocks for the synthesis of polyols. Polyols with functionality higher than 2 (polyols for polyure-

Chart 7. Schematic Representation of Triol Structure Prepared by Polycondensation of Hydroformylated Oleic Acid and Trimethylolpropane

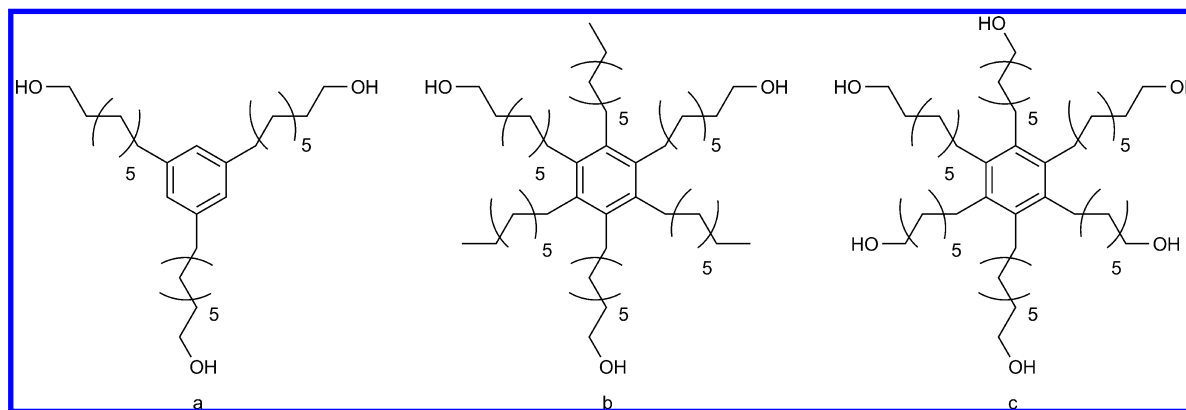
thane networks) can be prepared by polycondensation of hydroxyl containing fatty acid with multifunctional alcohols. More recently, Petrovic et al. used this methodology for the preparation of polyester triols of M_w ranging from 1000 to 4000 g/mol from methyl ricinoleate,¹¹⁸ hydroformylated oleic acid,¹¹⁹ and trimethylolpropane as initiator (Chart 7). In the case of methyl ricinoleate, it was found that some dehydration and cyclization occurred during the polymerization, producing a mixture of different species. The efficiency of transesterification was higher in the case of hydroformylated oleic acid due to the presence of primary hydroxyl groups, but side reactions could not be completely suppressed. Polyurethanes made from these polyols showed low glass transition temperatures being interesting raw materials for elastomers and flexible foam applications.

Another effective way to prepare polyester polyols from fatty acids was reported by Wang et al.¹²⁰ In this case, oleic acid was first chemoenzymatically epoxidized using H_2O_2 /Novozyme 432 and then polymerized to prepare poly(oleic acid) containing pendant secondary hydroxyl groups. Linear poly(oleic acid) was cross-linked with 1,6-hexamethylenediisocyanate and MDI producing a series of soft to rigid polyurethane films. Methyl oleate has also been used as a precursor for the preparation of polyether polyols, important building blocks for polyurethanes applications that are usually produced by the anionic ring-opening polymerization of petroleum-derived alkylene oxides, from renewable resources. In this case, polyether polyols with molecular weights up to 1200 g/mol were obtained by acid catalyzed, ring-opening polymerization of epoxidized methyl oleate and subsequent partial reduction of ester groups giving primary alcohols.¹²¹ Depending on the degree of reduction, polyols of different hydroxyl values were obtained, which were reacted with MDI and methyl-2,6-diisocyanatohexanoate (L-lysine diisocyanate, LDI) to yield polyurethanes.^{121,122} Very recently, we applied the same two-steps methodology using tetraisobutylaluminumoxane (TIBAO) and Vandenberg catalyst ($C_2H_5)_3Al/H_2O$ as ionic-coordinative catalysts.¹²³ In this case, polyether polyols with a higher molecular weight (up to 9000 g/mol) were obtained. These materials were found to consist of a complex mixture of cyclic and linear chains with different chain ends that were related to the catalyst nature and the occurrence of two main polymerization mechanisms, the cationic and the ionic coordinative. A series of segmented and nonsegmented cross-linked polyurethane 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.¹²⁴

Scheme 5. Undecylenic Acid, an Industrial Platform Chemical Produced from Castor Oil**Chart 8.** Chemical Structure of Silicon-Containing Triol Prepared from Undecylenic Acid via Hydrosilylation

In this field, some papers have appeared in recent years about the synthesis of polyols from undecylenic acid and derivatives. Undecylenic acid, also known as 10-undecenoic acid, is a C11 fatty acid with a terminal carbon-carbon double bond that, owing to its bifunctional nature, has many possibilities to develop sustainable applications.¹²⁵ Undecylenic acid can be easily obtained from castor oil or ricinoleic acid by pyrolysis under vacuum (Scheme 5). Hydrosilylation of methyl 10-undecenoate with a trifunctional silane followed by a reduction of carboxylate groups was used to prepare a novel silicon-containing fatty acid OH-terminated derivative with primary hydroxyl groups (Chart 8). Silicon-containing triol was obtained in 89% yield and the titrimetrically determined hydroxyl value of the product was 194 mg KOH/g versus a theoretical value of 200 mg KOH/g.¹²⁶ This polyol, together with epoxidized methyl oleate-based polyether polyol¹²¹ and MDI, was used to prepare hybrid biobased-polyurethanes with flame retardant properties. Undecylenic acid was also used as starting material in the preparation of polyester polyols with high weight content on renewable feedstock.¹²⁷ An α,ω -diene monomer containing hydroxyl groups was prepared from undecylenic acid and 1,3-dichloro-2-propanol. The acyclic diene metathesis copolymerization (ADMET) of this monomer with a plant-derived phosphorus-containing α,ω -diene¹²⁸ afforded a series of phosphorus-containing linear polyesters with pendant hydroxyl groups. The performance of these products in polyurethane synthesis was not evaluated, but thermosetting materials were prepared via acrylation of hydroxyl moieties and subsequent radical cross-linking.

Methyl 10-undecynoate and methyl 9-octadecynoate, which can be obtained from undecylenic acid and oleic acid by bromination, dehydrobromination, and esterification, were also used to prepare aromatic biobased triols in two steps: transition-metal-catalyzed cyclotrimerization and subsequent reduction of ester groups.¹²⁹ The chemical structure of these two aromatic triols is shown in Chart 9a and b. 1,3,5-(9-Hydroxynonyl)benzene (Chart 9a) was obtained regioselectively (NMR analysis confirmed that only 1,3,5-trisubstituted benzene derivative was obtained) in a 70% yield. In the case of methyl 9-octadecynoate, the cyclotrimerization under the reported conditions (Pd/C as a

Chart 9. Chemical Structure of Aromatic Polyols Synthesized via Cyclotrimerization of Fatty Acid Derivatives

catalyst in normal atmosphere with refluxing THF and commercial grade trimethylsilylchloride) afforded a mixture of both symmetric and nonsymmetric trimer derivatives (70% yield; see Chart 9b for chemical structure of symmetric trimer). This methodology was later applied to 9-octadecynoic acid,¹³⁰ behenic acid,¹³⁰ and unsaturated α,ω -dicarboxylic acid synthesized from oleic acid by metathesis,¹³⁷ yielding hexasubstituted benzene derivatives. Chemical structure of hexol synthesized from α,ω -dicarboxylic acid derived from oleic acid is shown in Chart 9c.¹³⁷ All these products showed to be suitable for the preparation of polyurethane networks^{130,131,137} and segmented polyurethane networks.¹²⁹

To the best of our knowledge, limited attention has been paid to the preparation of long-chain or oligomeric diols with functionality 2 (requirement for thermoplastic polyurethane formulations) using fatty acids as starting materials. Dimerization of oleic and linoleic acids, producing a complex mixture known as dimer acid, and consecutive reduction of carboxylate groups is a classical procedure for the synthesis of long-chain diol known as dimer diol. This methodology was originally introduced in the 1950s by General Mills Chemicals and Emery (now Cognis Corp.).^{132,133} Dimer diol, dimer diol oligoethers (manufactured by acid-catalyzed dehydration of dimer diol), and dimer diol oligocarbonates (synthesized by transesterification with dimethyl carbonate) are commercially available. Due to their improved stability toward hydrolysis and oxidation, dimerdiol polyethers (and dimerdiol polycarbonates) are used as soft segments in the preparation of thermoplastic polyurethanes. Polyurethanes prepared from these oleochemical building blocks are used to prepare saponification-resistant thermoplastic polyurethane sealings, which allow contact to aggressive aqueous media due to its hydrophobic character.¹³⁴

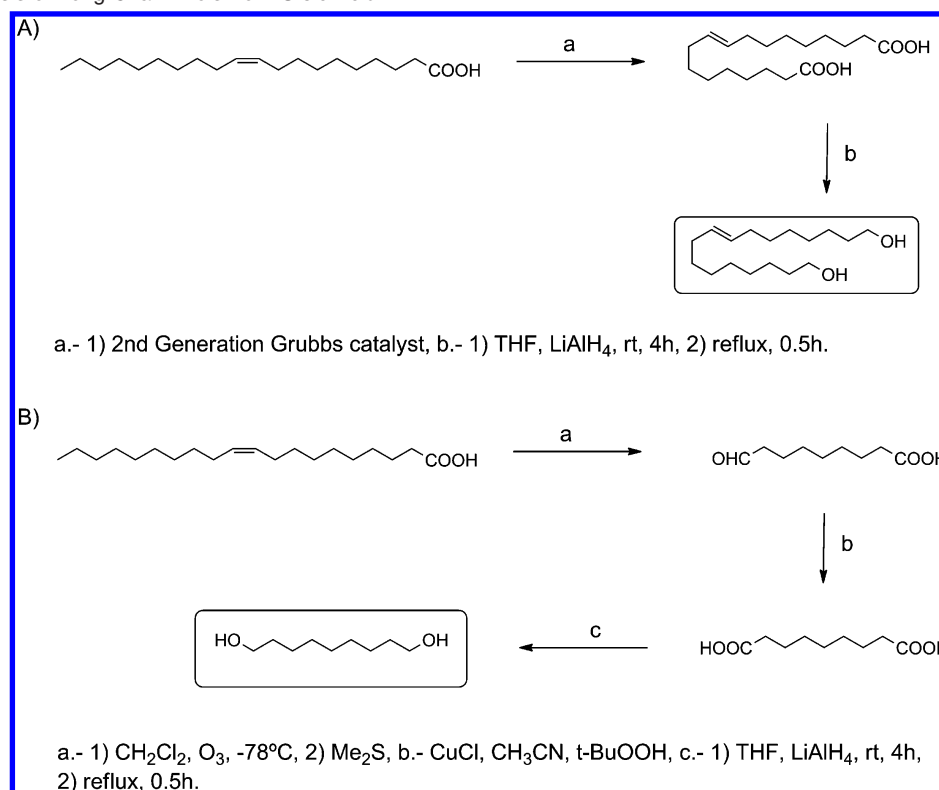
A metathesis reaction is also a prominent tool for the preparation of fatty acid-derived monomers, including dimer fatty acids and derivatives.^{135,136} By taking advantage of this methodology, 1,18-octadec-9-endiol, a long chain diol from oleic acid, was synthesized using second generation Grubbs catalyst.^{137,138} The corresponding *trans*-unsaturated dicarboxylic acid was reduced to corresponding diol by using LiAlH_4 . Following this procedure, highly pure 1,18-octadec-9-endiol (99% by gas chromatography-flame ionization detector (GC-FID)) was obtained in an overall yield of 58%. Alternatively, 1,9-nonanediol was synthesized by cleaving oleic acid via ozonolysis followed by oxidation to azelaic acid and reduction of carboxylate groups.¹³⁸ This procedure afforded the above-mentioned diol (99% purity determined by GC-FID) in a higher overall yield of 72%. Both synthetic procedures are described in Scheme 6.

Classical polycondensation reactions have also been used for the preparation of oligomeric diols. Xu et al. reported the synthesis of polyester diol ($M_n = 2580 \text{ g/mol}$) from methyl ricinoleate and diethylene glycol by polycondensation at high temperatures (Chart 10).¹³⁹ Following this procedure, higher experimental molecular weight than the theoretical was obtained due to the loss of diol and methyl ricinoleate during the vacuum process at high temperatures. This product was used as soft segment in the preparation of segmented polyurethanes. Diricinoleate diols have also been used to prepare polyurethane coatings having a low viscosity suitable for spray coating applications.¹⁴⁰

The contribution of chemists to sustainable development not only involves the use of renewable raw materials but also the application of environmentally friendly and high efficient processes. In this line, chemical couplings defined as click chemistry reactions,¹⁴¹ have emerged as green methodologies and have opened new perspectives for the synthesis and modification of polymeric materials with targeted properties.^{142,143} Our group recently reported the application of thiol-ene chemistry to the preparation of biobased oligomeric diols from undecylenic acid.¹⁴⁴ This methodology is based on two one-pot photoinitiated thiol-ene click processes: step-growth polymerization using a divinyl monomer and a dithiol (3,6-dioxal-1,8-octanedithiol) and subsequent end-groups postpolymerization modification with 2-mercaptoethanol (Scheme 7). We applied this approach to a potentially 100% biomass-derived monomer, allyl ester of 10-undecenoic acid (UDA), to prepare a series of well-defined telechelics with molecular weight ranging from 1000–3000 g/mol and hydroxyl groups at the polymer terminus were prepared. UDA-based thelecheleic diol prepared using this methodology was reacted with 4,4'-methylenebis(phenylisocyanate) and 1,3-propanediol as the chain extender to obtain thermoplastic multiblock poly(ester urethane)s. A very recent paper from Meier and Türling studies thiol-ene additions of methyl 10-undecenoate with the goal of preparing a set of renewable monomers suitable for polyester synthesis.¹⁴⁵ This work demonstrates that thiol chemistry offers yet another efficient and sustainable entry to renewable raw materials derived from plant oils.

6. Alternative Environmentally Friendly Routes to Polyurethanes from Vegetable Oils

The above presented literature revision revealed a number of publications on the synthesis of biobased polyurethanes. Unfortunately, in almost all of them, petroleum-based isocya-

Scheme 6. Synthesis of Long Chain Diols from Oleic Acid**Chart 10.** Schematic Representation of Polyricinoleate Diol Prepared by Polycondensation

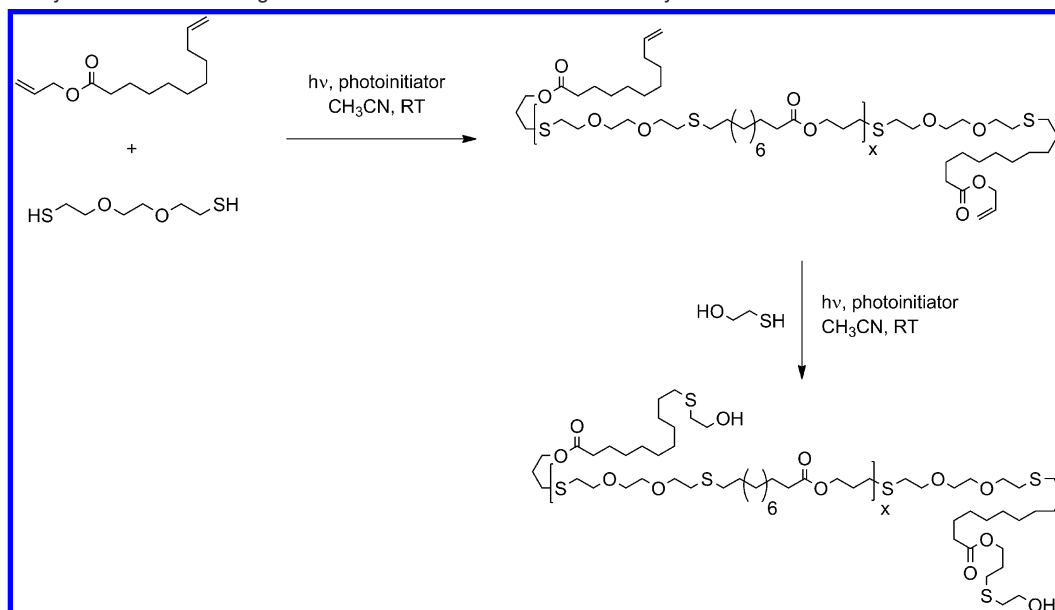
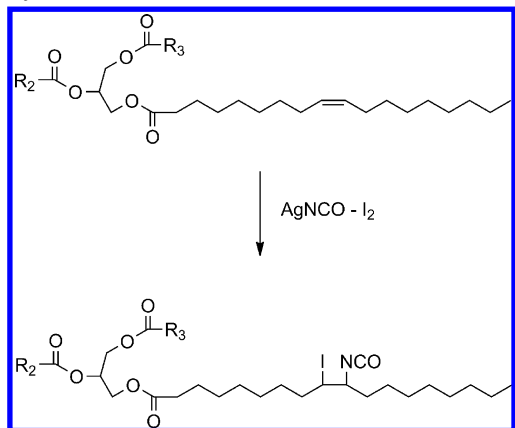
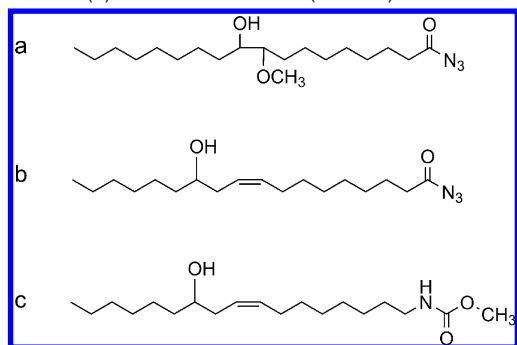
anates were used. Thus, it is a challenge to synthesize suitable diisocyanates derived from vegetable oils, making possible to produce polyurethanes completely from renewable resources, or ideally to avoid isocyanate chemicals, due to its high reactivity and toxicity, developing nonisocyanate routes toward polyurethanes.

Besides the commercially available fatty-acid based diisocyanate known as dimer diisocyanate supplied by Henkel Corporation Co. or General Mills Co. there is limited literature available concerning the synthesis of isocyanate compounds based on plant oils. Kusefoglul and Çayli reported two synthetic routes for the functionalization of soybean oil with isocyanate moieties. In the first one, triglyceride was brominated at the allylic positions with *N*-bromosuccinimide and then reacted with AgNCO to convert it to isocyanate-containing triglyceride.¹⁴⁶ The average number of isocyanate groups per triglyceride was found to be 2.1. The second methodology produced iodine isocyanate adduct of soybean oil containing 3.1 isocyanate groups per triglyceride in one-step by the reaction of iodine isocyanate and soybean oil at room temperature (Scheme 8).¹⁴⁷ Both plant-based isocyanates were suitable for polyurethane preparation.

On the other hand, Narine et al. reported the synthesis of 1,7-heptamethylene diisocyanate from oleic acid in three steps.¹⁴⁸ First, azealic acid was prepared by ozonolysis of oleic acid to the corresponding aldehyde product (step a, Scheme 6B), followed by oxidation to the dicarboxylic acid (step b, Scheme 6B). Finally, diisocyanate compound was prepared via a two-

step Curtius rearrangement. 1,7-Heptamethylene diisocyanate (97% purity determined by GC-FID) was obtained in an overall yield of 49%. The feasibility of utilizing this new diisocyanate for the production of cross-linked polyurethanes was demonstrated by reacting it with commercial petroleum-derived polyols and canola oil-derived polyols. Unsaturated α,ω -dicarboxylic acid synthesized from oleic acid by metathesis¹³⁷ was also used to prepare a novel long chain unsaturated diisocyanate using a similar procedure.¹⁴⁹ A longer fatty acid derivative is expected to avoid explosivity problems derived from azide intermediates involved in this procedures. However, 1,16-diisocyanatohexadec-8-ene was obtained in only 57% overall yield (98% purity determined by GC-FID).

Concerning nonisocyanate methods for the preparation of polyurethanes derived from plant oils, two methodologies have been applied: the reaction of cyclic carbonates with amines and the self-condensation approach of an AB-type monomer. Wilkes et al. investigated the polyurethane synthesis based on carbonated soybean oil and aliphatic diamines.^{150,151} Epoxidized soybean oil was effectively converted to carbonated soybean oil containing five-membered cyclic carbonates by reaction with carbon dioxide in the presence of tetrabutylammonium bromide as catalyst at 110 °C in high yield. Carbonated oil was reacted with di- and tri-primary amines to give the corresponding nonisocyanate polyurethane networks. Later, Petrovic et al. demonstrated that the amidation reaction competes with urethane linkage formation.¹⁵² Alternatively, Cramail et al. recently reported an elegant route to biobased polyurethanes from fatty acids via an AB-type self-condensation approach.¹⁵³ Four novel AB-type self-condensable monomers, 10-hydroxy-9-methoxyoctadecanoyl azide, 10-hydroxy-10-methoxyoctadecanoyl azide, 12-hydroxy-9-*cis*-octadecenoyl azide, and methyl-*N*-11-hydroxy-9-*cis*-heptadecen carbamate, were synthesized from methyl oleate and ricinoleic acid using simple reaction steps (Chart 11). Self-polycondensation of an AB-type monomer makes the

Scheme 7. Undecylenic Acid-Based Oligomeric Diols via Thiol-ene Click Chemistry**Scheme 8.** Synthesis of Iodine-Containing Plant Oil-Based Polyisocyanates**Chart 11.** AB-Type Self-Condensable Monomers Derived from Methyl Oleate (a) and Ricinoleic Acid (b and c)

advantage of built-in stoichiometric control for attaining high molar mass. The above presented methodologies establish that the production of polyurethanes mostly from lipid feedstock is possible.

7. Summary and Outlook

Plant oils as well as fatty acid have been used in polyurethane technology for a long period of time. In contrast to petrochemical resources, the availability of these renewable natural raw

materials is practically unlimited. The extensive use of plant oils as renewable feedstock in the preparation of polyols and the corresponding polyurethanes is reflected in a large number of papers published in the last years. Most of these publications are focused to develop new polyol structures applying conventional reactions. Thus, a variety of new structures suitable for polyurethane synthesis are available nowadays: (a) polyether polyols accessible via ring-opening polymerization of epoxy fatty acids and subsequent reduction of ester groups, (b) polyester polyols, that can be obtained from ω -hydroxy fatty esters via polycondensation or by ring-opening of epoxidized oils with a variety of nucleophiles, (c) diols of different chain lengths, accessible from fatty acids via metathesis or ozonolysis reactions followed by reduction of ester groups, (d) aromatic polyols prepared using transition-metal catalyzed cyclotrimerization of alkyne fatty acid derivatives as a key step, and (e) silicon-containing polyols prepared through hydrosilylation coupling. It is obvious that most products obtainable from these renewable raw materials may at present not be able to compete with the products of the petrochemical industry, but this will change as oil becomes scarcer and oil prices rise, as they are regarded as more sustainable than conventional materials based on fossil fuels. However, a few points deserve consideration. New structures will continually be developed in the future, but in our opinion it is necessary to take a step back and improve some of the synthetic strategies reviewed above. The contribution of this technology to sustainable development must go further than simply exploit renewable feedstock. Some of the synthetic procedures mentioned within this review have limitations; it is sometimes necessary to employ toxic reagents and higher than catalytic amounts of expensive transition-metal catalysts, and most of the procedures employ organic solvents, excess reagents, and extended reaction times, and usually tedious purification steps are required. If the synthesis of a particular plant-derived polyol is a tedious, inefficient, and expensive process, a significant portion of the benefit provided by polyurethane technology is lost. Therefore, there is no doubt that future research in this field should move to more efficient chemical routes. Thus, the application of atom-economical transformations exemplified by click chemistry reactions will facilitate the synthesis of biobased products in a more sustainable way. An

example of such an advance was recently reported by us¹⁴⁴ and Meier¹⁴⁵ demonstrating the power of thiol-ene click chemistry in the field of oleochemistry as a “green” tool. In this line, much work is also expected in developing new synthetic routes for the preparation of polyurethanes entirely from vegetable oil sources using biobased isocyanates.^{146–149} Even more promising are nonisocyanate routes to polyurethanes being the recent work reported by Cramail and co-workers as a promising starting point.¹⁵³ On the other hand, in spite of the prolific scientific production in the field, little is known about the relationship between the structure and properties of the polyurethanes derived from them. Thus, further studies are now required to elucidate this point in order to identify the range of applications of plant oil-derived polyurethanes. In summary, the abundant evidence for the suitability of plant oils and derivatives in polyurethane technology holds the promise for a dramatic increase in the use of vegetable oil-based polyols in the years to come.

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