Synthesis and Characterization of Polyurethanes from Epoxidized Methyl Oleate Based Polyether Polyols as Renewable Resources

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ABSTRACT: Oligomeric polyether polyols were obtained through the acid-catalyzed ring-opening polymerization of epoxidized methyl oleate and the subsequent partial reduction of ester groups to give primary alcohols. The oligomers were characterized with titration, spectroscopic techniques (Fourier transform infrared and nuclear magnetic resonance), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, size exclusion chromatography, and differential scanning calorimetry. Depending on the degree of reduction, polyols of different hydroxyl content values were obtained and were reacted with 4,4′-methylenebis(phenyl isocyanate) to yield polyurethanes. These materials, which were characterized by differential scanning calorimetry, thermogravimetric analysis, and dynamic mechanical thermal analysis, could behave as hard rubbers or rigid plastics. © 2005 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 44: 634–645, 2006

Keywords: polyether; polyurethanes; renewable

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 for fossil, depleting feedstocks.[1] The encouragement of the environmentally sound and sustainable use of renewable natural resources is an important aim of Agenda 21.[2] 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 they offer

to chemistry a large number of possibilities for applications that can be rarely met by petrochemistry. Vegetable oils containing unsaturated fatty acids can be used in polymerizations to make biobased polymers.[3–5] Numerous fatty acids are now available in a purity that makes them attractive for synthesis and as raw materials for the chemical industry.[6]

There have been many studies on the synthesis and characterization of a wide variety of polymers based on vegetable oils.[7,8] 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. Various chemical pathways for the functionalization of triglycerides and fatty acids have been studied.[9] Epoxidation is one of the most impor-
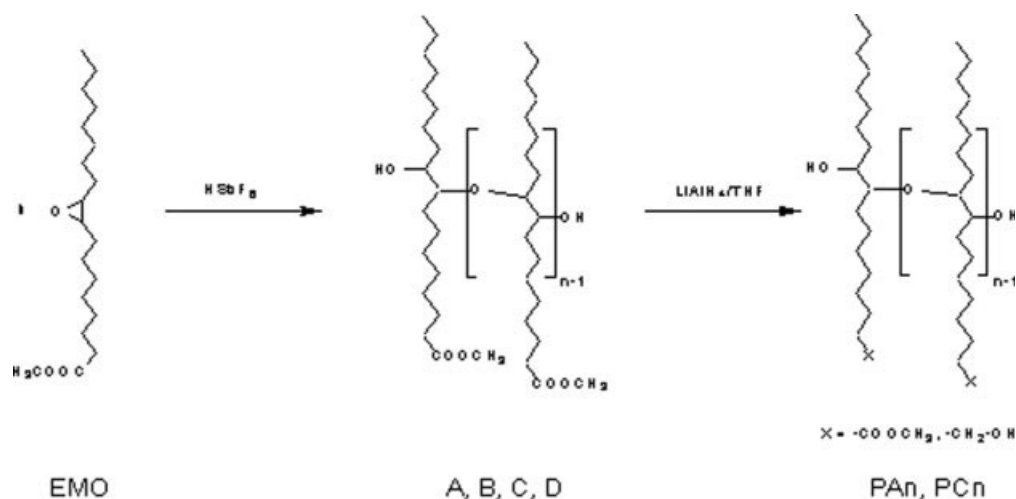
Scheme 1

tant functionalization reactions of the C—C double bond. The chemistry of the Prileshajev epoxidation of unsaturated fatty compounds is well known.[10] A short-chain peroxy acid, preferably peracetic acid, is prepared from hydrogen peroxide and the corresponding acid either in a separate step or *in situ*.[11] For chemical synthesis on the laboratory scale, better results can be achieved with preformed peroxy acids such as *m*-chloroperbenzoic acid. Other methods for the epoxidation include the use of dioxiranes,[12] the generation of peracids from aldehydes and molecular oxygen,[13] and the use of alkyl hydroperoxides with transition-metal catalysts.[14] Recently, a convenient method for the chemoenzymatic self-epoxidation of unsaturated fatty acids was developed.[15] Unsaturated fatty compounds are preferably epoxidized on an industrial scale by the *in situ* performic acid procedure.[16] Epoxidized fatty acids are monomers suited for ring-opening polymerizations.[17]

The preparation of polyols from fatty acids and oils for general polyurethane use has been the subject of many studies,[18–20] but limited attention has been paid to the preparation of polyether polyols from this kind of compound. Polyether polyols are important building blocks for polyurethane applications with molecular weights of 200–10000 g/mol.[21] 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.

Industrial polyether polyols, mainly from ethylene oxide and propylene oxide, are produced

for applications in polyurethane foams. Longer chain oxiranes or functionalized epoxides show lower reactivity because of a higher sterical hindrance and side reactions, and high-molecular-weight polymers cannot be obtained with anionic or cationic catalysts.[22] Coordinative ring-opening polymerization has been described for functionalized epoxides as phenyl glycidyl ether derivatives[23] or ω-epoxy alkanoates.[24] As has been mentioned previously, polyether polyols of about 200–1200 g/mol are used to obtain rigid polyurethanes. These low-molecular-weight polyethers can be synthesized by cationic ring-opening polymerization, which requires an acid catalyst. Several classes of cationic initiators have been developed, such as photosensitive onium salt initiators, which are inactive under ambient conditions and can release the acid initiator by UV radiation or heat[17] and have been applied to epoxidized fatty compounds.[25–27]

In this article, we report the synthesis and characterization of polyether polyols from epoxidized methyl oleate (EMO; Scheme 1). Polyols (PA*n* and PC*n*; Scheme 1) were prepared through the combination of the cationic polymerization of EMO oligomers (A–D, Scheme 1) and the controlled reduction of the carboxylate groups to hydroxyl moieties with lithium aluminum hydride (LiAlH$_4$) as a reducing agent. Polyols were characterized by chemical methods, spectroscopic techniques [Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR)], matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS), and thermal techniques [differential scanning calorimetry (DSC)]. They were reacted with 4,4′-methylene-

bis(phenyl isocyanate) (MDI) to obtain polyurethanes. The properties of the prepared polyurethanes were studied with DSC, thermogravimetric analysis (TGA), and dynamic mechanical thermal analysis (DMTA).

EXPERIMENTAL

Materials

The methyl oleate used in this study was supplied by Cognis (Düsseldorf, Germany). EMO was synthesized with a literature procedure.[28] The following chemicals were obtained from the sources indicated: formic acid (Scharlau), hydrogen peroxide, 50% (w/v; Aldrich), fluoroantimonic acid ($HSbF_6$; Aldrich), $LiAlH_4$ [1.0 M in tetrahydrofuran (THF); Aldrich], and MDI. They were used as received. THF was distilled from sodium immediately before use. Other solvents were purified by standard procedures.

Oligomerization of EMO

$HSbF_6$ (0.05 g; 0.5 wt %) was added to 10 g of EMO. The mixture was stirred at room temperature for 1 h. The reaction was quenched by the addition of 1.5 mL of water followed by 100 mL of diethyl ether. The organic solution was washed with a sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and filtered. Finally, the solvent was evaporated off *in vacuo*, and this yielded oligomer A as a viscous oil. A similar procedure was followed to obtain oligomers B–D with the addition of 10, 20, and 50 mol % water to the oligomerization mixture

^{1}H NMR [CDCl$_3$/tetramethylsilane (TMS), δ, ppm]: 3.63 (s, —OCH$_3$), 3.62–3.16 (m, polyether backbone), 2.27 (t, —CH$_2$COO—), 1.70–1.10 (m, —CH$_2$— aliphatic backbone), 0.85 (t, CH$_3$)

Representative Procedure for the Reduction of Oligomers A and C

Oligomer A (6 g, 3.2 mmol) was dissolved in 60 mL of anhydrous THF under nitrogen. A 1 M solution (6 mL) of $LiAlH_4$ in THF (6 mmol of $LiAlH_4$) was added slowly with stirring. After the $LiAlH_4$ addition was complete, the mixture was stirred vigorously at room temperature. After 30 min, excess $LiAlH_4$ was decomposed by the addition of 20 mL of ethyl acetate dropwise, then a saturated 10% H_2SO_4 solution (aqueous) was added, the phases were separated, and the aqueous layer was extracted with ethyl acetate. The combined organic phase was washed with a saturated aqueous NaCl solution, dried over anhydrous magnesium sulfate, and filtered, and the solvent was removed *in vacuo* at 50 °C.

^{1}H NMR (CDCl$_3$/TMS, δ, ppm): 3.63 (s, —OCH$_3$), 3.55 (t, —CH$_2$OH), 3.62–3.16 (m, polyether backbone), 2.27 (t, —CH$_2$COO—), 1.70–1.10 (m, —CH$_2$— aliphatic backbone), 0.85 (t, CH$_3$)

Representative Procedure for the Synthesis of Polyurethanes (PUAn and PUCn)

Polyurethanes were synthesized by the reaction of the polyols with MDI with a 2% molar excess of isocyanate (MDI). The samples were prepared through the mixing of a proper amount of polyol and MDI at 60 °C. Curing was carried out at 60 °C for 2 h and 110 °C overnight.

Characterization

NMR spectra were recorded on a Bruker AM 300 spectrometer. The samples were dissolved in deuterochloroform, and ^{1}H NMR and ^{13}C NMR spectra were obtained at room temperature with TMS as an internal standard. 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.

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. 2,5-Dihydroxybenzoic acid (DHB) was used as a matrix, and silver trifluoroacetate was used as a dopant. Size exclusion chromatography (SEC) analysis was carried out with a Waters 510 pump system equipped with a Shimadzu RID-6A refractive-index detector. THF was used as an eluent at a flow rate of 1.0 mL/min. The calibration curves for SEC analysis were obtained with polystyrene standards.

Calorimetric studies were carried out with a Mettler DSC822e thermal analyzer with N$_2$ as the purge gas. A heating rate of 20 °C/min was used. Thermal stability studies were carried out with a Mettler TGA/SDTA851e/LF/1100 with N$_2$ as the purge gas at a scanning rate of 10 °C/min.

Table 1. General Properties of the Oligomers Obtained by the Cationic Ring-Opening Polymerization of EMO[a]

Oligomer	Water (mol %)	HV (mg of KOH/g)	EW (g/equiv)[b]	M_n (SEC; g/mol)	M_w/M_n (GPC)	Functionality[c]
A	—	52	1079	1235	1.59	1.1
B	10	74	758	1076	1.48	1.4
C	20	89	630	1025	1.47	1.6
D	50	108	519	961	1.45	1.8

[a] Polymerization conditions: 0.5 wt % HSbF$_6$, 1 h, and room temperature.
[b] Equivalent weight calculated from the HV.
[c] Obtained by the division of the experimental molecular weight (M_n) by the EW.

The mechanical properties were measured with a TA DMA 2928 dynamic mechanical thermal analyzer. Specimens 1.2 mm thick, 5 mm wide, and 10 mm long were tested in a three-point-bending configuration. The various thermal transitions were studied between −100 and 140 °C at a heating rate of 5 °C/min and at a fixed frequency of 1 Hz.

General Procedure for the Unilever Method Hydroxyl Value Determination[29]

For an expected hydroxyl value (see ref. 29), an accurately measured volume of acetic acid anhydride was added to a known amount of a sample weighed into a round-bottom flask. After mixing, the flask was placed in an oil bath at 95–100 °C. After 1 h, the flask was cooled, and 1 mL of distilled water was added. After shaking, heating was continued for 10 min to convert acetic acid anhydride into acetic acid. After the mixture was cooled again, 5 mL of 95% ethanol was added, and the contents were titrated with a 0.5 M ethanolic potassium hydroxide solution with phenolphthalein as an indicator. A blank determination was carried out with a similar procedure.

RESULTS AND DISCUSSION

Oligomerization of EMO

EMO was prepared by the reaction of methyl oleate with formic acid and hydrogen peroxide. Precipitation with acetone was applied to purify the product. Gas chromatography analysis showed that EMO was obtained in a purity of 96%.

EMO was cationically oligomerized. We tested several acids as catalysts: HSbF$_6$, hexafluorophosphoric acid (HPF$_6$), and trifluoromethanesulfonic acid (HSO$_3$CF$_3$). Among these, only HSbF$_6$ pre-

dominantly produced oligoether species, as could be observed from MALDI-TOF MS analysis. The oligomerization was carried out with different amounts of HSbF$_6$ at room temperature (0.1, 0.5, 1.0, and 1.5 wt %). NMR analysis of the oligomer obtained with 0.1 wt % initiator revealed the presence of nonreacted epoxide, whereas higher amounts of the initiator gave complete oligomerization. Therefore, the cationic polymerization of EMO was carried out in the presence of 0.5 wt % HSbF$_6$ at room temperature for 1 h. The catalyst was completely soluble in EMO at room temperature, and the oligomerization was performed homogeneously in the absence of a solvent, thus being an advantageous process from an environmental viewpoint.[1] The oligomerization reaction was monitored by FTIR spectroscopy, which showed a decrease in the absorption centered at 836 cm^{-1}, corresponding to an oxirane ring, and a slight increase in the absorption at 1075 cm^{-1} (C—O—C ether) and in the broad band around 3500 cm^{-1} (O—H hydroxyl group). This indicated that oxirane ring opening took place to form ether linkages and hydroxyl-terminated polymer.

The cationic oligomerization of EMO resulted in a clear, yellow, viscous oil, and the results are summarized in Table 1 (oligomer A). The ^{1}H NMR spectrum of oligomer A is given in Figure 1. ^{1}H NMR showed that no epoxy groups (2.8 ppm) remained after the polymerization, in accordance with FTIR results, thus showing that the epoxy group of the methyl ester is reactive enough to polymerize under the set conditions. A new broad peak due to the oligoether backbone was observed between 3.1 and 3.6 ppm. Signals in the ^{1}H NMR spectrum at 3.6 (—OCH$_3$), 2.3 (—CH$_2$—COO—), 1.1–1.7 (—CH$_2$— aliphatic backbone), and 0.8 ppm (—CH$_3$) confirmed the oligomer structure. Traces of ketones, formed by the acid-catalyzed isomerization of the oxirane ring, were observed in the product of oligomeri-
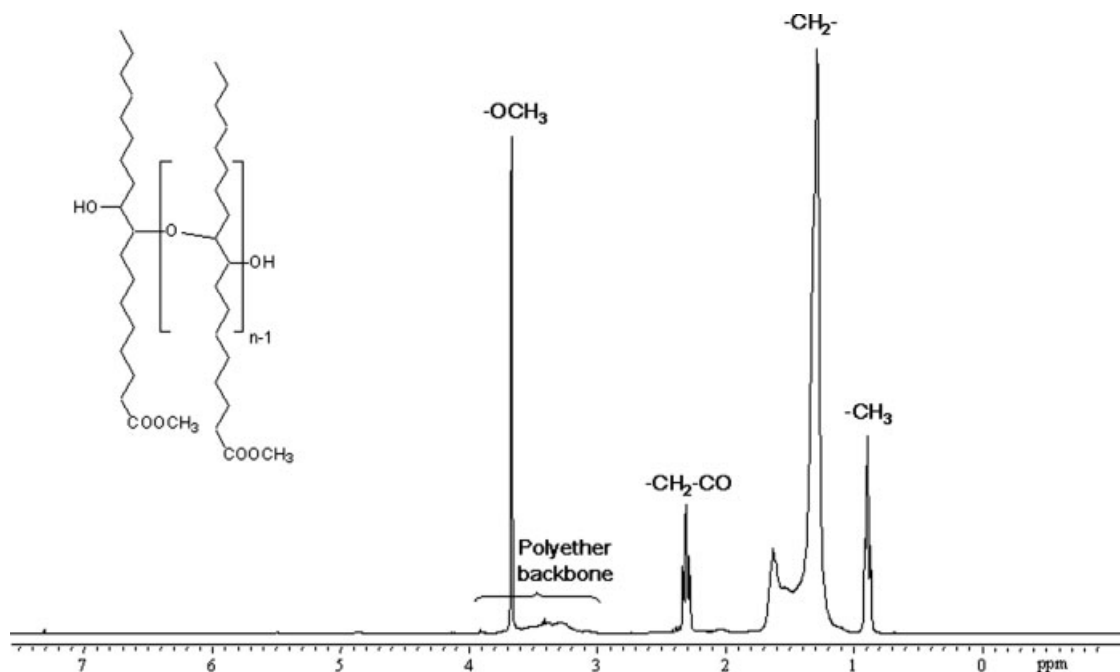
Figure 1. ^{1}H NMR spectrum (CDCl$_3$, 300 MHz) of oligomer A.

zation initiated by HSbF$_6$ by ^{1}H NMR at 2.4 ppm. In contrast, we observed the formation of higher amounts of corresponding ketones when using HSO$_3$CF$_3$ as an initiator.

MALDI-TOF MS was used to analyze the oligomer distribution. Figure 2 shows the MALDI-TOF MS spectrum of oligomer A, which is dominated by a series of peaks ranging from a mass of 750 Da to a mass of 2630 Da, corresponding to linear hydroxyl-terminated oligomers doped with Ag$^+$ ions of type H—[O— C$_{19}$H$_{36}$O$_2$]$_n$—OH—Ag$^+$ (mass = 312n + 18 + Ag$^+$); n values varying from 2 to 8
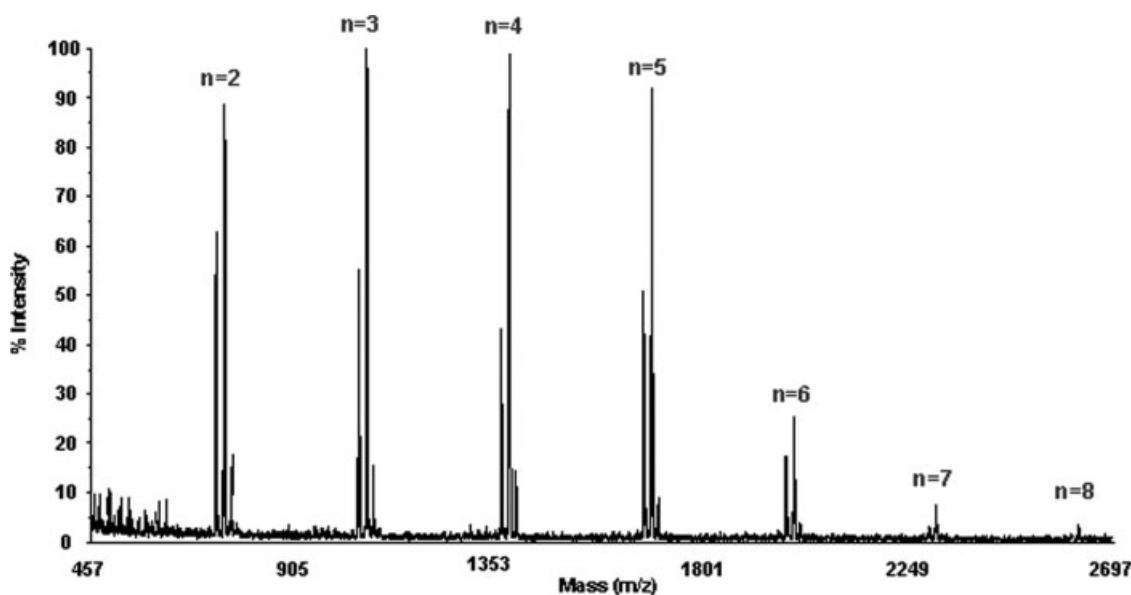
Figure 2. MALDI-TOF MS spectrum of oligomer A doped with silver trifluoroacetate, showing the ion series H—[O—C$_{19}$H$_{36}$O$_2$]$_n$—OH—Ag$^+$ (mass = 312n + 18 + Ag$^+$), [O—C$_{19}$H$_{36}$O$_2$]$_n$Ag$^+$ (mass = 312n + Ag$^+$), and CH$_3$—[O—C$_{19}$H$_{36}$O$_2$]$_n$ —OH—Ag$^+$ (mass = 312n + 32 + Ag$^+$; see Schemes 1 and 2).
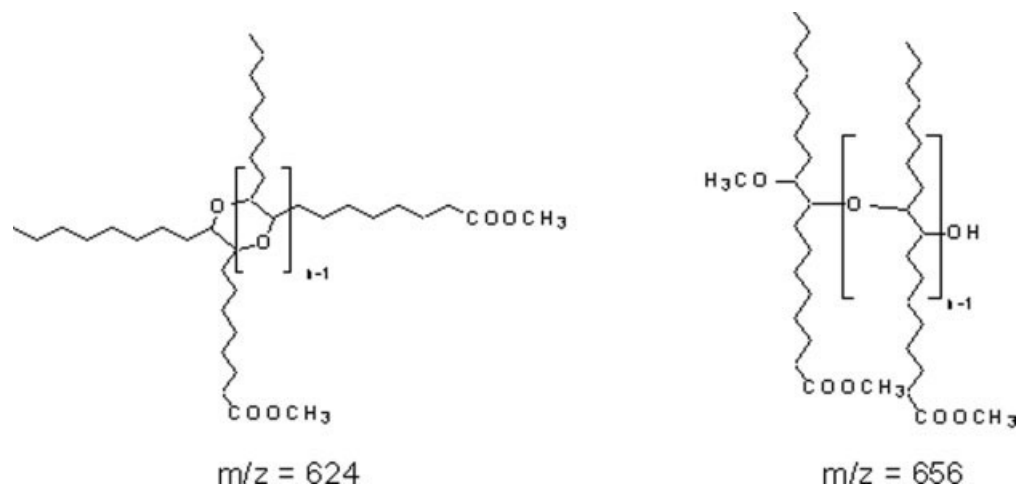
Scheme 2

were detected (Scheme 1). The three most intense peaks belonging to this series correspond to oligomers with n values of 3–5. The spectrum also displays other peaks of lower intensity with masses of $312n + Ag^+$, corresponding to cyclic structures formed by back-biting (Scheme 2), and peaks with the general formula $CH_3—[O—C_{19}H_{36}O_2]_n—OH—Ag^+$ (mass $= 312n + 32 + Ag^+$), corresponding to oligomers terminated by OH on one end and OCH_3 on the other (Scheme 2). These last peaks can appear in the spectrum because of the presence of traces of methanol, generated by the transesterification of ester groups or as impurities in the monomer, which reacted during polymerization and formed chain ends. Therefore, MALDI-TOF MS confirmed the presence of a mixture of linear and cyclic oligomers.

As is well known, the cationic polymerization of epoxides produces macrocycles and hydroxy-terminated open chain oligomers. For disubstituted epoxides under photoinitiated cationic polymerization, Warwel[27] reported obtaining macrocycles, linear oligomers, and ketones formed by the rearrangement of the monomer. By the addition of water, macrocyclization was completely suppressed, and linear oligomers of different molecular weights were obtained; this showed that the nucleophilic attack of water competes with the intramolecular attack, and the proportion of linear species increases.

Polyols of industrial importance are usually required to have a low viscosity and a high hydroxyl content value (HV). To increase the proportion of linear oligomeric structures, to reduce their molecular weight, and to increase their hydroxyl content, water was added to the oligo-

merization system. The oligomerization of EMO was carried out in the presence of 10, 20, and 50 mol % water to give oligomers B, C, and D (Table 1). MALDI-TOF spectra show that the highest intensity signals correspond to a lower molecular weight ($n = 2$ or 3). Moreover, from MALDI-TOF analysis, a decrease in the signal intensity corresponding to the cyclic oligomers was observed, and for the product obtained with 50%, this signal was almost negligible. These results are in accordance with the ones previously described.[27]

^{1}H NMR spectra of oligomers B–D did not show significant differences between them and sample A obtained in the absence of water. FTIR spectra showed a significant increase in the hydroxyl absorption at 3500 cm^{-1}, which indicates that the presence of water causes an increase in the HV.

The HV of the oligomers was determined according to the Unilever method.[29] This method uses a solution of acetic anhydride in pyridine, and the HV is defined as the number of potassium hydroxides required to neutralize the amount of acetic acid capable of combining by acetylation with 1 g of the sample. The results are summarized in Table 1; as can be seen, the HV increases as the water content in the polymerization system increases, and SEC analysis has shown that the molecular weight decreases as the HV increases, according to the MALDI-TOF results. The compounds obtained so far are polyether diols with secondary alcohol functionality and side products containing only one or no hydroxyl group. These products are not suited for synthesizing polyurethanes. In addition, pri-

Table 2. General Properties of the Obtained Polyols

Polyol	Starting Oligomer	mmol of LiAlH$_4$/g of Oligomer	HV (mg of KOH/g)	EW (g/equiv)[a]	M_n (SEC)	Functionality[b]
PA1	A	0.5	94	597	1220	2.0
PA2	A	1.0	184	305	1187	3.8
PA3	A	1.5	260	216	1149	5.3
PC1	C	0.5	127	442	1010	2.3
PC2	C	1.0	216	260	980	3.7
PC3	C	1.5	298	188	935	4.9

[a] Equivalent weight calculated from the HV.
[b] Obtained by the division of the experimental molecular weight (M_n) by the EW.

mary hydroxyl groups are more reactive and much better suited for the synthesis of polyurethanes. Therefore, to obtain a broad range of polyol structures that may have different properties and may impart different properties to the final product when converted to polyurethanes, we carried out a partial reduction of the carboxylate groups to yield primary hydroxyl moieties.

### Partial Reduction of Ester Groups of Oligomers A and C

Oligomers A and C were used as starting materials for the partial reduction of the ester groups to synthesize polyols having primary hydroxyl moieties. The reduction of these oligomers was carried out with different amounts of LiAlH$_4$ as a reducing agent, giving polyols PA1, PA2, and PA3 (Table 2). Figure 3 shows the ^{1}H NMR spectra of oligomer A and the corresponding polyols. A new signal appears at $\delta = 3.6$ ppm due to the protons of the CH_2—OH moiety. As the reduction degree increases, the intensity of this signal increases, whereas the intensity of the peak at $\delta = 2.3$ ppm decreases. The same trend can be observed for polyol C.
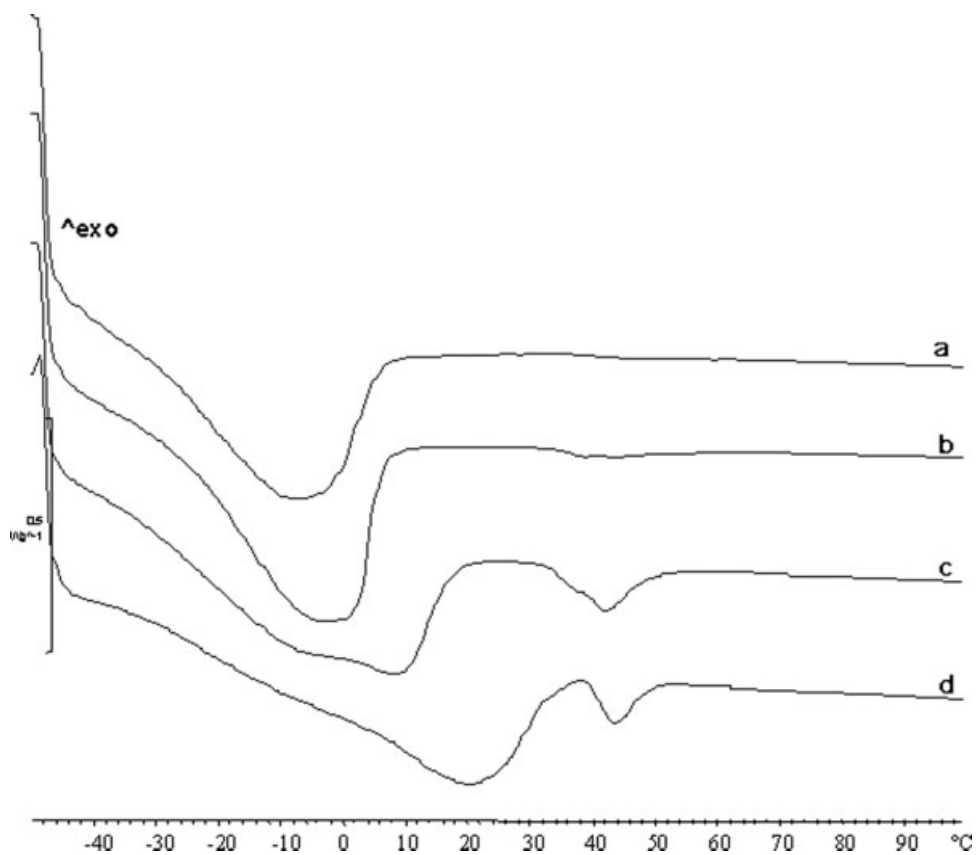
The FTIR spectra of the polyols are presented in Figure 4. In comparison with the spectrum of A, there was an increase in the hydroxyl group
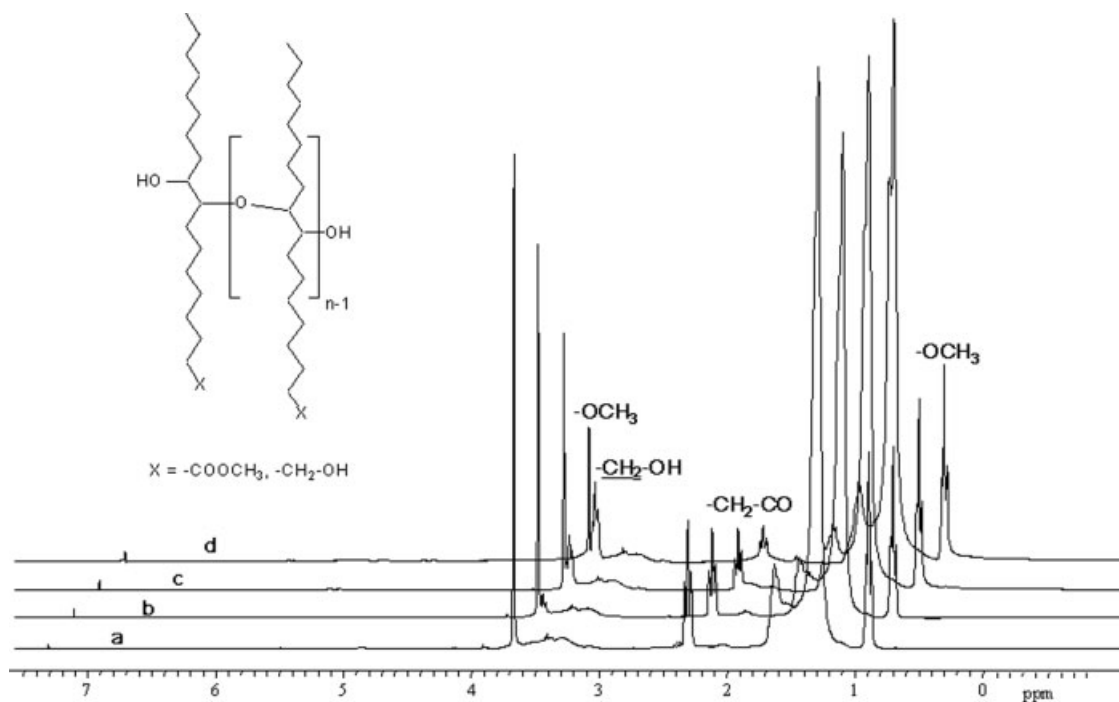
Figure 3. ^{1}H NMR spectra (CDCl$_3$, 300 MHz) of (a) oligomer A, (b) polyol PA1, (c) polyol PA2, and (d) polyol PA3.
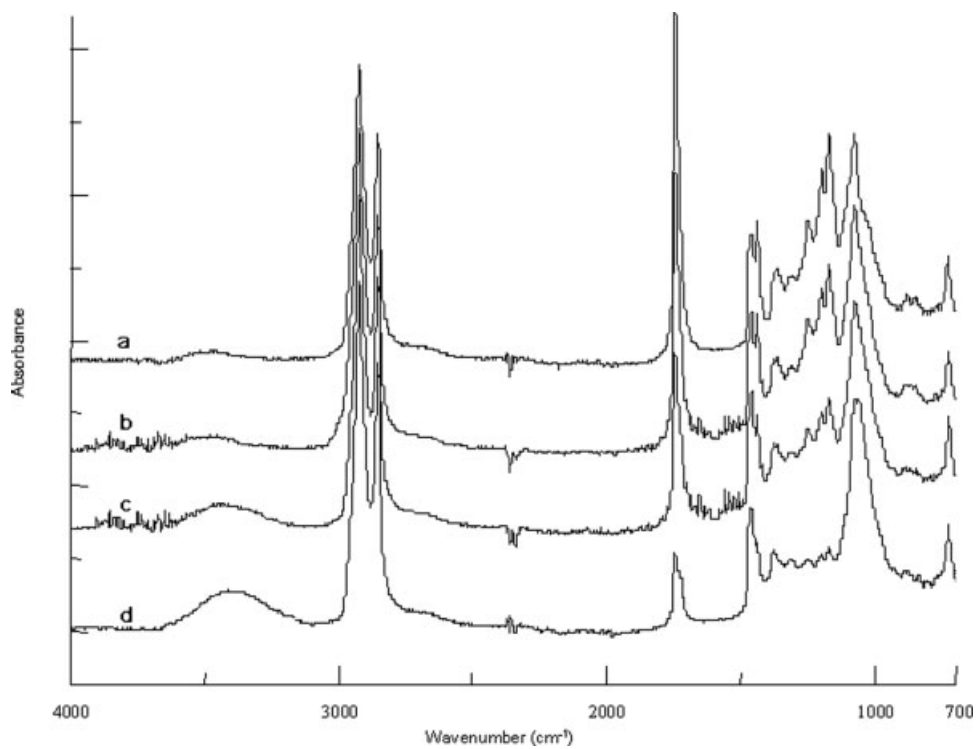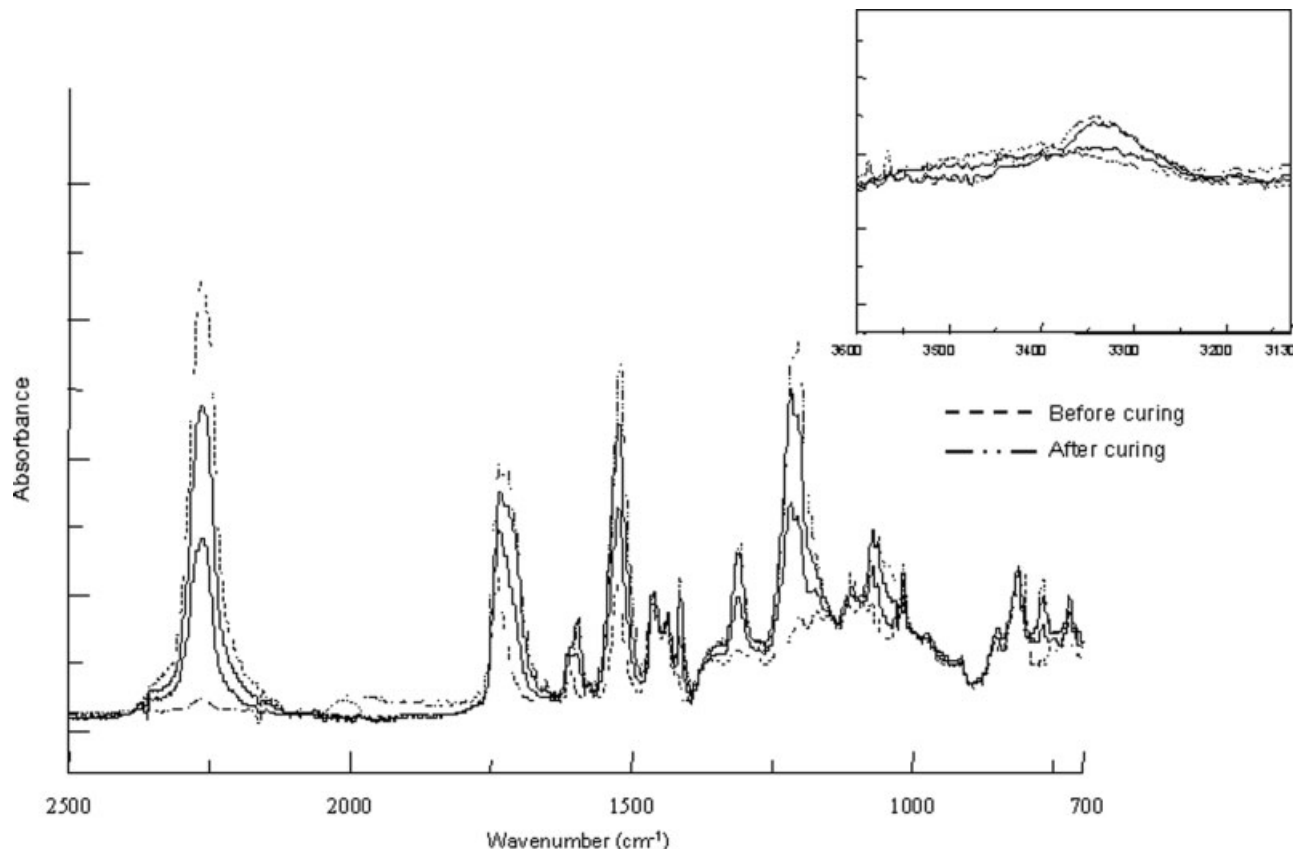
Figure 4.   FTIR spectra of (a) oligomer A, (b) polyol PA1, (c) polyol PA2, and (d) polyol PA3.

Figure 5.   DSC curves of (a) oligomer A, (b) polyol PA1, (c) polyol PA2, and (d) polyol PA3.

Figure 6. FTIR spectra of the crosslinking of polyether polyol PA2 with MDI to give polyurethane PUA2 at different curing times (0, 30, and 60 min at 60 and 110 °C overnight).

peak (3500 cm^{-1}), whereas a decrease in the aliphatic ester carbonyl peak (1750 cm^{-1}) was observed. We determined the HV of the polyols according to the Unilever method (Table 2). As the amount of LiAlH$_4$ increases, the hydroxyl value increases, as expected.

In this way, polyols with a broad range of functionalities have been obtained, and they range from clear liquids to white, waxy solids at room temperature. DSC traces for A and its polyol derivatives are collected in Figure 5. As can be seen, A exhibits a broad melting peak centered at

**Table 3.** Thermal Properties of the Polyurethanes

| Polyurethane | Starting Polyol | T_g (°C) | | TGA (N$_2$ Atmosphere) | |
		$1/2\Delta C_p$[a]	$\tan \delta_{max}$[b]	$T_{5\% loss}$[c]	Yield$_{800 °C}$ (%)[d]
PUA1	PA1	−15	—	307	2
PUA2	PA2	39	63	310	3
PUA3	PA3	80	93	316	5
PUC1	PC1	0	—	309	2
PUC2	PC2	37	62	303	4
PUC3	PC3	52	76	313	4

[a] Glass-transition temperature obtained by DSC.
[b] Glass-transition temperature obtained by DMTA.
[c] Temperature of 5% of weight loss.
[d] Yield obtained at 800 °C.
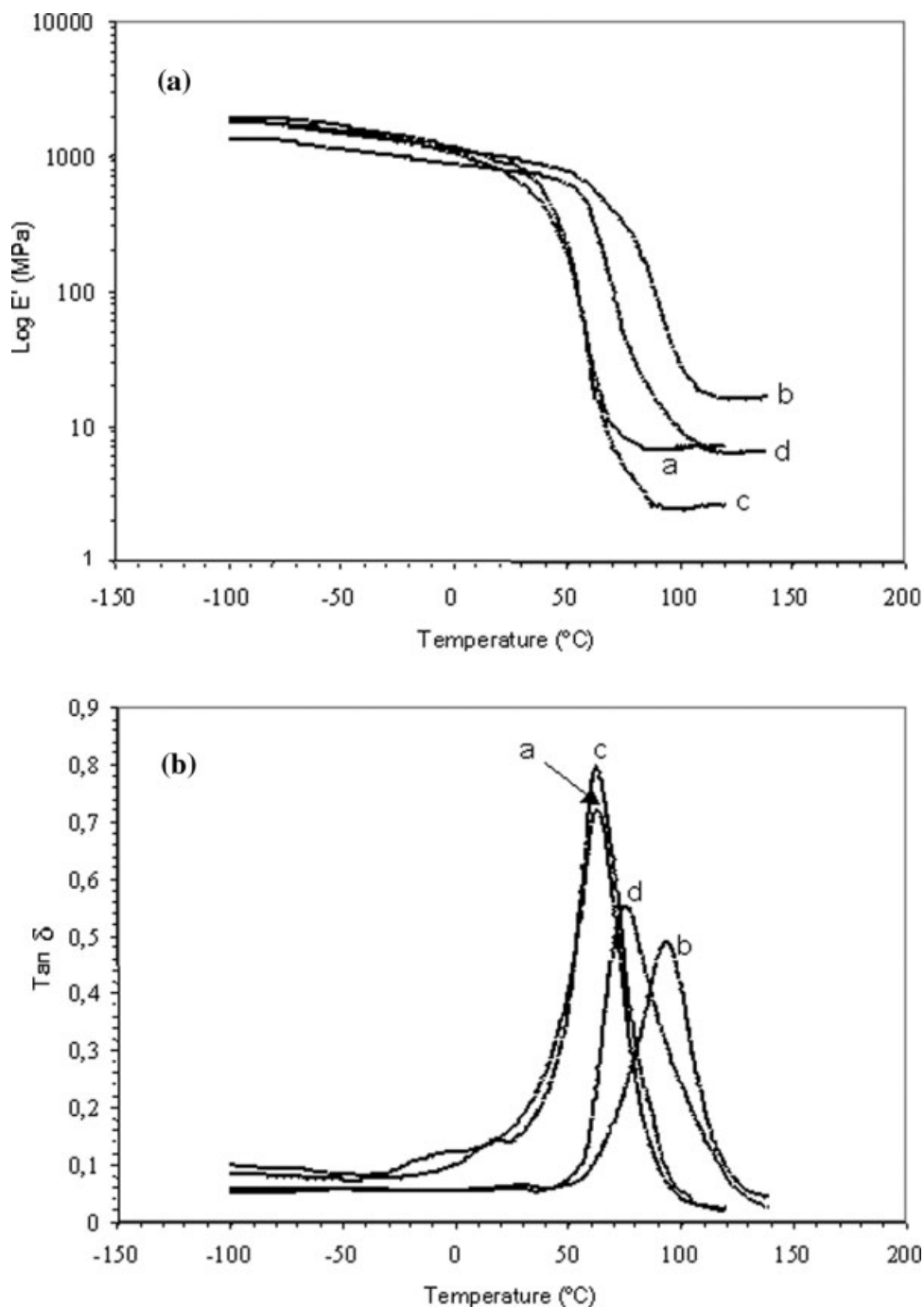
Figure 7. (a) Storage modulus (E')/temperature curves of (a) PUA2, (b) PUA3, (c) PUC2, and (d) PUC3 and (b) tan δ/temperature curves of (a) PUA2, (b) PUA3, (c) PUC2, and (d) PUC3.

-7 °C, which shifts to higher temperatures when the HV increases. Moreover, a second melting endotherm can be observed at 42 °C for PA2 and PA3, with the highest functionality. Multiple peaks in these polyols should be ascribed to different crystalline forms.

Synthesis of Polyurethanes

The six polyols PA1–PA3 and PC1–PC3 were reacted with MDI at 60 °C to give polyurethanes PUA1, PUA2, PUA3, PUC1, PUC2, and PUC3. All the polyols had primary OH groups and

gelled quickly at the mixing temperature. The crosslinking reaction was monitored by FTIR spectroscopy. Figure 6 shows FTIR spectra before and after the curing of polyurethane PUA2. The starting mixture showed a characteristic peak at 2240 cm^{-1} ascribed to —N=C=O stretching of the isocyanate moiety. After the curing, this peak significantly decreased. The crosslinking reaction was also monitored by the appearance of the characteristic absorbances of the urethane link. The band due to the carbonyl stretching vibration of polyurethane occurred at 1723 cm^{-1}, and a combination of N—H deformation and C—N stretching vibrations occurred at 1533 and 1233 cm^{-1}, respectively. The peak appearing at 1309 cm^{-1} was due to —OCONH asymmetric stretching vibrations. Moreover, the broad band centered at 3500 cm^{-1}, corresponding to the O—H stretching, shifted to lower frequencies and showed a maximum at 3350 cm^{-1}, characteristic of N—H stretching.

The thermal behavior of the polyurethanes was investigated with DSC. The glass-transition temperature (T_g) could be observed by this technique. The T_g values determined by DSC are shown in Table 3. The data given show clearly for both series of polyurethanes the expected trend, that T_g was higher when the functionality of the polyol used was higher, which indicates a higher degree of crosslinking.

TGA is the most favored technique for the evaluation of the thermal stability of polymers. Polyurethanes have relatively low thermal stability, mainly because of 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 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 300 °C.

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 the rubbery plateau of each material. Figure 7(a,b) shows the temperature dependence of the storage modulus and loss factor (tan δ) of the polyurethanes. 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 crosslinking among the various polymers. Figure 7(a) shows that the

value of the storage modulus in the rubber plateau decreased as the HV of the starting polyol decreased. DMTA also made it possible to determine the T_g of the crosslinked materials. It was detected as the maximum of tan δ. The T_g values determined by DMTA are shown in Table 3. As expected, the T_g values, like tan δ, are higher than the ½ΔC_p values from DSC and increase as the HV of the starting polyol increases [Fig. 7(b)]. This is caused by the higher crosslinking degree, which increases the stiffness of the network structure. A weak β transition at about 0 °C can be observed. The origin of this peak is not known, but it may be related to the rotational motions of short units in the fatty acid chains.[30]

CONCLUSIONS

Polyether polyols were synthesized by the cationic oxirane ring-opening oligomerization of EMO followed by partial reduction of the ester groups to primary alcohols. The corresponding polyurethane networks were prepared by the reaction of the polyols with MDI. This showed that plant oils as renewable resources can be used to make hard rubbers or rigid plastics.

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