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Polymer 48 (2007) 3990–3998

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Step-growth polymerization of 10,11-epoxyundecanoic acid. Synthesis and properties of a new hydroxy-functionalized thermoplastic polyester

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Received 28 March 2007; received in revised form 2 May 2007; accepted 5 May 2007

Abstract

Oxidation of undecylenic acid, a derivative of castor oil, affords 10,11-epoxyundecanoic acid (**5**). In the presence of a quaternary ammonium or phosphonium bromide as an initiator, monomer **5** undergoes an AB polymerization *via* nucleophilic ring-opening of the epoxide group with the carboxylic acid moiety to yield high-polymeric hydroxy-functionalized aliphatic polyester (**6**). Polymer **6** is a crystalline thermoplastic ($T_m = 97$ °C) that exhibits yield stress, break stress and elongation (9.7 MPa, 24.1 MPa and 450%) very similar to those of linear low density polyethylene. However, in contrast to the behavior of the polyolefin and owing to the pendent hydroxyl moieties of **6**, films of the polyester adhere strongly to metallic substrates and have moderately good barrier to oxygen. In addition to physical properties of **6**, the effect of the initiator utilized in the polymerization of **5** on the molecular weight and polydispersity of product **6** is discussed.

Keywords: Thermoplastic; Polymerization; Polyester

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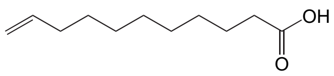
1. Introduction

As part of our continuing efforts to develop industrially useful materials from common seed oils and related oleochemicals, we are exploring new applications for 10-undecylenic acid (**1**), a commercially available derivative of castor oil and an intermediate in the production of nylon 11 [1]. Recently, we demonstrated that **1**, when esterified with glycerin followed by oxidation with peracetic acid, yields triglyceride **2** containing sterically accessible terminal epoxy functionalities which are far more labile to ring-opening, nucleophilic attack than the ‘‘internal’’ epoxy groups of conventional, well-known epoxidized soybean and linseed oils [2]. Consequently, **2** cures readily at elevated temperatures with aromatic amines to produce high-modulus, remarkably ductile network polymers [2] applicable to structural end uses or with aliphatic amines at 25 °C in formulations which afford UV- and corrosion-resistant coatings for steel and aluminum substrates [3].



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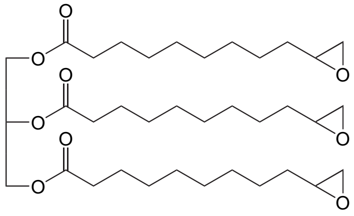

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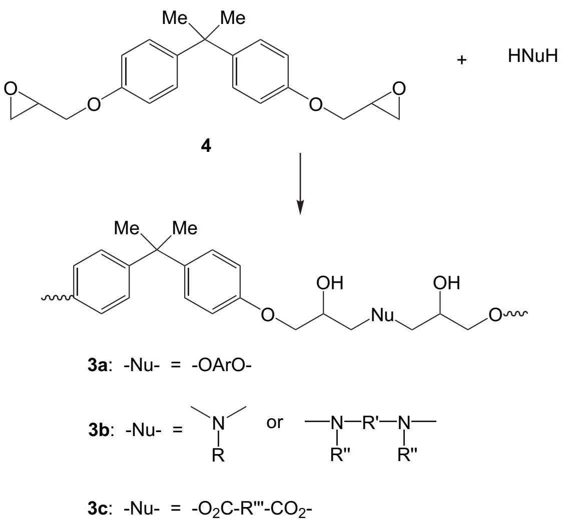
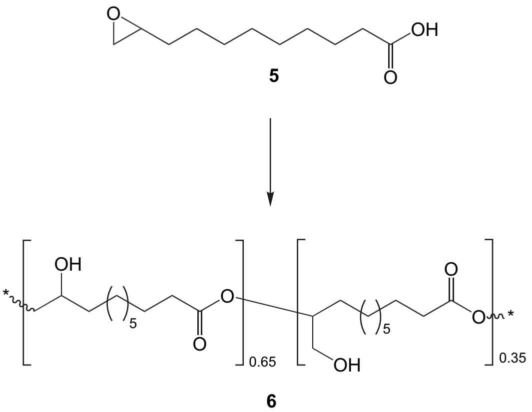
doi:10.1016/j.polymer.2007.05.031

During our studies of thermosetting resins based on **2**, it occurred to us that reactions of nucleophiles with the relatively reactive terminal epoxy moiety of the 10,11-epoxyundecenoyl residue, if contained in a monomer of appropriate functionality, could be utilized to produce linear polymers rather than the network materials derived from trisepoxide **2**. Such a possibility was supported by well-established condensations of the epoxy groups in diglycidyl ethers with dinucleophilic species, which can be used to form high-molecular-weight thermoplastics while liberating a pendent hydroxyl moiety on the backbone of the resulting polymer [4]; we have synthesized a number of epoxy-based polymers of general structure **3** by polymerizations of bisphenol A-diglycidyl ether (**4**) and similar diepoxides with a wide variety of bisphenols [5], difunctional amines [6], disulfonamides [7] and diacids [4], collectively represented by HNuH in Scheme 1. The acid–epoxy reaction was of particular interest, because it suggested that 10,11-epoxyundecanoic acid (**5**), formed by oxidation of **1**, could undergo a straightforward AB polymerization to a high-molecular-weight hydroxy-functionalized polyester. An earlier attempt at AB self-condensation of **5** in the presence of strong base gave only a crosslinked gel when pushed to a degree of polymerization beyond 7 [8], but we believed that conditions used to prepare poly(hydroxyl ester ethers) (**3c**) [4,9] would convert **5** to the high-polymeric material that we were seeking. As it turns out, such is indeed the case, the present paper describes the successful polymerization of monomer **5** and the basic structural characteristics and properties of the intriguing crystalline thermoplastic polyester (**6**; Scheme 2) that result.



Scheme 1. Polymerization of diglycidyl ether **4** with dinucleophilic monomers.



Scheme 2. Synthesis of poly[10-hydroxyundecanoate]-*co*-[(10-(hydroxymethyl)-decanoate] (**6**).

2. Experimental

2.1. Materials and methods

10-Undecylenic acid (**1**), peracetic acid (in acetic acid), tetraphenylphosphonium bromide (TPPB), tetrabutylammonium bromide (TBAB), Dowanol™ PMA (propylene glycol monomethyl ether acetate, ≥99.5%), tetrahydrofuran (THF) and other reagents and solvents were obtained from the Aldrich Chemical Company and other commercial sources were generally used as received. Dowanol PMA was stored over 4 Å molecular sieves prior to use. All reactions were conducted with oven-dried glassware under a nitrogen pad or slow nitrogen flow.

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker model AC250 instrument operating at 250 MHz; resonances are reported relative to tetramethylsilane (TMS). Infrared (IR) analysis of polyester **6** was performed with a Bio-Rad model FTS-40 spectrometer; the spectrum of **6** (Fig. 3) was obtained for a thin film of the resin cast on a sodium chloride plate from THF. Gel permeation chromatography was performed with an Agilent model 1100 high-pressure liquid chromatograph equipped with two Polymer Labs PLGel Mixed C columns in series and using THF as the mobile phase with a flow rate of 1 mL/min. Samples were allowed to dissolve in THF (10 mg/mL) containing butylated hydroxytoluene (100 ppm) as a flow marker for molecular weight calibration and injected (100 μL) onto the columns. Relative molecular weights of **6** were calculated relative to those of polystyrene calibration standards.

The glass transition temperature (T_g) of polymer **6** (−8 °C; Table 2), taken as the peak of tan δ, was determined using dynamic mechanical analysis at a frequency of 1.0 rad/s and a heating rate of 2 °C/min over a temperature range of −150 to 150 °C using a Rheometrics model RMS 800 instrument. Endothermic melting transitions of samples of **6** were obtained using a TA Instruments model DSC 2920 differential scanning calorimeter at a heating rate of 10 °C/min (Table 2).

2.2. Synthesis of 10,11-epoxyundecanoic acid (5)

A 0.40 M solution of sodium acetate in acetic acid containing 32 wt% of peracetic acid (231 mL, 1.1 mol of peracetic acid) was added slowly *via* an addition funnel to a chilled (−12 °C), continuously stirred solution of **1** (184.3 g, 1.0 mol) in chloroform (1.6 L) stirred in a jacketed reactor. The rate of addition was adjusted so that the temperature of the reaction mixture remained below 20 °C, after which stirring was continued at 40 °C for 12 h. The resulting solution was again chilled to −12 °C, and excess peracetic acid was neutralized by slow addition of a chilled aqueous 0.80 M solution of sodium sulfite; the temperature of the mixture was maintained below 20 °C during the addition, which was continued until peroxide was no longer detectable with peroxide test paper. The organic layer was separated and washed with water until pH test paper indicated that the washings were neutral. The solution then was dried over sodium sulfate for 24 h, filtered and the solvent was removed *via* rotary evaporator, the water bath of which was kept below 50 °C. The resulting crude **5** was dissolved in warm (40 °C) ligroin (about 1 L) and the resulting solution was allowed to cool to room temperature. The precipitate was collected by filtration and dried *in vacuo* at 25 °C to give **5** as a white crystalline solid (160.09 g, 80%) having a mp of 48 °C (peak temperature by DSC) and the ^{1}H NMR spectrum of the product in chloroform-d_1 is shown in Fig. 1a. This **5** (70 g) was purified further with a Biotage FLASH 75i model flash chromatograph equipped with

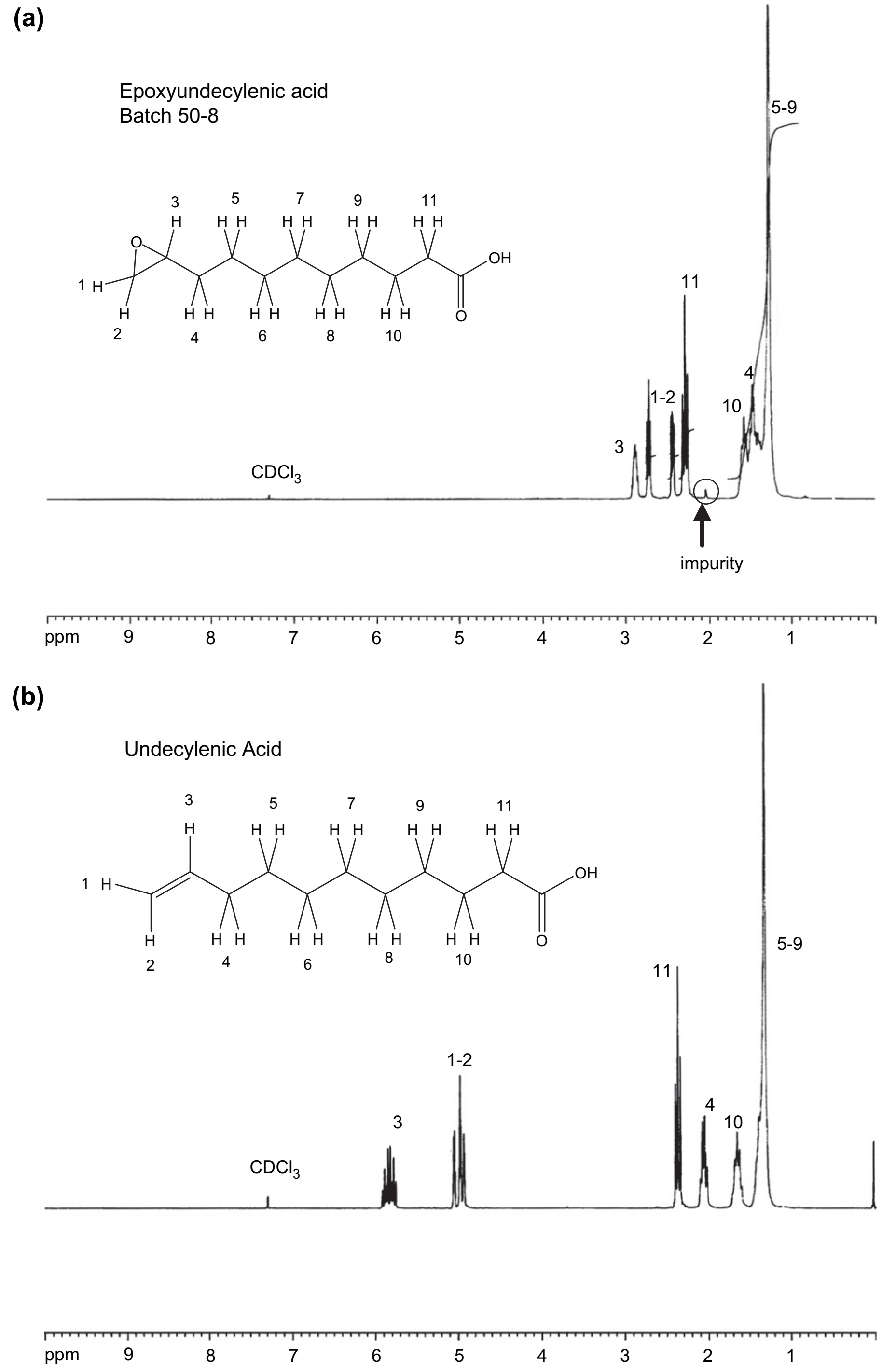


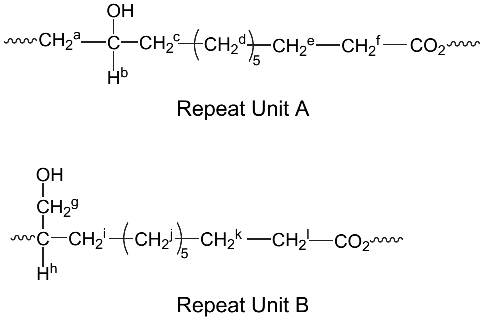
Fig. 1. (a) Proton NMR spectrum of **5** prior to chromatographic purification. (b) Proton NMR spectrum of **1**.

a KP-Sil, 36–63 nm, 60 Å disposable silica gel column and sample injection module. The dry silica column was washed with one column volume (about 1 L) of ethyl acetate and then with a solution of ethyl acetate (45%)/hexane (55%) (2 L), and **5** (60 g) in the mixed solvent (250 mL) was injected onto the column. Fractions collected after elution of 1 L of the mixed solvent were combined and the solvent was removed by rotary evaporation at 30 °C to give white, crystalline **5** (15 g) having an epoxy equivalent weight of 201.5 (calculated: 200.21) measured according to ASTM method D1652. Monomer **5** was refrigerated prior to use.

*2.3. Synthesis of poly[10-hydroxyundecanoate]-co-[(10-(hydroxymethyl)decanoate] (**6**)*

In a series of experiments, monomer **5** in Dowanol PMA (65% solids) was allowed to polymerize in the presence of 0.6–1.8 mol% TPPB or TBAB at 140 °C for 0.25–6 h. During these reactions, aliquots were periodically removed, diluted with THF and injected onto a GPC column; with both initiators, mp (determined relative to polystyrene standards) reached a plateau (55–60,000 with TPPB) after 2–2.5 h. Based on these data, the following procedure was adopted for preparation of the polyester: A mechanically stirred solution of **5** (20.00 g, 0.1 mol) and TPPB (0.75 g, 1.8 mmol) in Dowanol PMA (10.5 ml) in a reaction flask equipped with a condenser and thermocouple was heated slowly under a pad of nitrogen to 140 °C (care was taken during heating to insure that the reaction temperature did not exceed 140 °C) and maintained at that temperature for 2.5 h, after which the reaction solution was diluted with additional Dowanol PMA (20 mL) and allowed to cool to room temperature. The resulting solution was then added to vigorously stirred (blender) ice water to precipitate white solid, which was collected by filtration and dried *in vacuo* (50 °C) to give white fibrous **6a** (19.60 g, 98%). The material was then allowed to stir overnight in acetone (about 750 mL) and collected by filtration; drying *in vacuo* gave **6a** (see Table 2 for numerical designations of **6**) as a white fibrous solid (17.60 g, 88%) having the IR spectrum as shown in Fig. 3, the ^{1}H NMR spectrum tabulated in Table 1 and M_w, M_n and M_w/M_n listed in Table 2.

Table 1
Proton NMR chemical shifts (ppm) of polyester **6** in tetrahydrofuran-d_8 relative to TMS



Absorption, ppm	Protons	Integration
4.91–4.78 (m)	h	0.35H
3.96–3.90 (d)	a	1.30H
3.87–3.80 (d)	g	0.70H
3.52–3.41 (t)	b	0.65H
2.37–2.20 (m)	f + l	2.00H
1.71–1.40 (m)	c + e + i + k	4.00H
1.37 (bs)	d + j	10.00H

Table 2
Fundamental properties of polyester **6**

Initiator	$M_w \times 10^{-3}$ [a]	$M_n \times 10^{-3}$ [a]	M_w/M_n	T_g[b], °C	T_m[c], °C	ΔH[c], J/g
TPPB (**6a**)	122.1	32.9	3.7	−8	97 (107[d])	32.4 (57.4[d])
TBAB (**6b**)	173.9	13.3	13.1	−8	90	

[a] Determined by gel permeation chromatography relative to polystyrene standards (see Section 2).

[b] Determined by dynamic mechanical analysis; value shown is tan δ (see Section 2).

[c] Determined by differential scanning calorimetry (see Section 2).

[d] After annealing at 75 °C for 48 h.

*2.4. Physical property evaluation of polymer **6***

For some experiments (see Table 3), tensile specimens of **6** were fabricated by compression molding dry **6** at 107 °C and 65.5 MPa in a 0.4-mm mold using an electrically heated, hydraulic press. The samples were allowed to cool to room temperature and removed from the mold; cutting, conditioning and tensile testing of the specimens were conducted according to ASTM method D882; in comparative tensile testing of linear low density polyethylene (LLDPE; Dowlex™ 2045), tensile samples were prepared by compression molding pellets of the resin at 200 °C and 27.6 MPa. T-peel specimens (Table 4) were prepared by pressing films of **6** (prepared as described above) between cold rolled steel or aluminum T2024 substrates (0.8 mm thick), previously wiped with methyl ethyl ketone, at 110 °C and 3.4 MPa using the molding press described above; peel strengths of the resulting assemblies were determined at 25 °C using an Instron tensile tester at a cross head speed of 254 mm/min (ASTM method D1002). Lap shear samples (Table 4) were fabricated by molding films of **6** between 1.6-mm thick cold rolled steel and aluminum substrates with a 12.7 mm overlap under the conditions noted above for the T-peel specimens; shear strengths were

Table 3
Tensile properties of polyesters TPPB-initiated **6** and LLDPE[a]

Polymer	Yield stress, MPa	Break stress, MPa	Elongation, %	Modulus, MPa
6a	9.7	24.1	450	197.9
6a[b]	12.4	31.0	430	227.6
6b	10.7	15.6	580	226.8
LLDPE[c]	11.0	24.8	400	191.0

[a] Determined for compression-molded films (0.4 mm) using ASTM method D 882; see Section 2.

[b] Specimens were annealed at 75 °C for 48 h prior to testing; for the annealed polymer, $M_w = 84.2 \times 10^3$; $M_n = 21.8 \times 10^3$; and PDI = 3.9.

[c] Dowlex™ 2045: density = 0.920 g/mL; melt index = 1.0 g/10 min.

Table 4
Adhesive properties of polyesters **6b**, **3b-1** and LLDPE[a]

Polymer	Substrate	Peel strength, N/mm	Lap shear strength, MPa
6b	Steel	1.6	9.4[b]
6b	Aluminum	1.4	9.4[b]
3b-1	Steel	1.3	
3b-1	Aluminum	1.6	22.1[b]
LLDPE[c]	Aluminum		1.7[d]

[a] Values shown were determined for polymer films compression laminated to the substrates (see Section 2) and taken from Ref. [6] (**3b-1**).
[b] Cohesive failure.
[c] Dowlex™ 2517: density = 0.917 g/mL; melt index = 25 g/10 min.
[d] Adhesive failure.

determined using an Instron tensile tester at a cross head speed of 2.54 mm/min (ASTM method D1876). Lap shear strength LLDPE (Dowlex™ 2517; see Table 4), using films that were compression-molded as described above, was determined using aluminum substrates assembled as above at 200 °C and 27.6 MPa.

The oxygen transmission rate (O_2TR) and water vapor transmission rate (WVTR) of films of **6**, prepared as described above, were determined under the conditions noted in the footnotes of Table 5.

3. Results and discussion

3.1. Synthesis of 10,11-epoxyundecanoic acid (5)

10,11-Epoxyundecanoic acid (**5**) was prepared in 80% yield by reaction of **1** with a 10% molar excess of peracetic acid in acetic acid/chloroform at 40 °C. The ^{1}H NMR spectrum of monomer **5** (after recrystallization from ligroin; Fig. 1a) displays multiplets at about 3.0, 2.8 and 2.5 ppm, corresponding to absorptions of the three protons bonded directly to the epoxy ring, along with the complete absence of the vinylic proton signals near 5.8 and 5.0 ppm in the spectrum of starting compound **1** (Fig. 1b). While the spectrum of **5** in Fig. 1 is generally consistent with the structure shown, the NMR trace contains a weak but clearly discernable peak at 2.1 ppm (circled in the figure), indicating the presence of an impurity that potentially could disrupt the 1:1 epoxy/acid stoichiometry of the AB monomer and limit the molecular weight attainable during its polymerization or possibly complicate the polymerization in other ways. In addition, purity of the monomer was suspected because its epoxy equivalent weight (eew), determined by titration of epoxy functionality (ASTM method D1652), is considerably higher (205.1) than that calculated (200.2) for the structure shown. Consequently, for the purposes of the current study, recrystallized **5** was further purified by flash chromatography (see Section 2), which lowered the eew of the product to 201.2; an NMR spectrum of the chromatographed product showed complete loss of the absorption at 2.1 ppm.

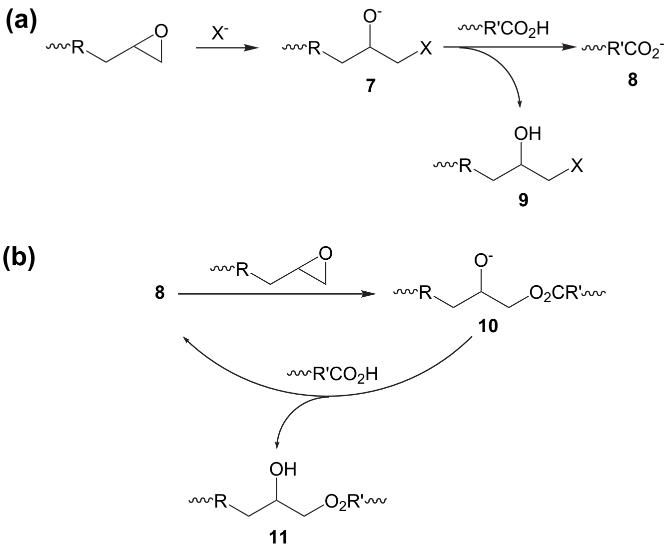
Table 5
Barrier properties of **6b**, **3c-1**, **3c-2**, **3b-1** and LLDPE

Polymer	T_g, °C	T_m, °C	O_2TR, BU	WVTR, g mil/100 in.^{2} 24 h
6b	−8	97	14.0[a]	13.0[b]
3c-1	10	72	10.0[c]	
LLDPE[d]			>150[e]	1.1[f]

[a] Determined for compression-molded films of **6** at 25 °C and 60% relative humidity according to ASTM method D 3985-81; BU = cc mil/100 in.^{2} 24 h atm (O_2) (to convert to barrers, divide by 166.8).
[b] Determined for compression-molded films at 37 °C and 100% relative humidity according to ASTM method F-1249-90.
[c] Value taken from Ref. [4].
[d] Dowlex 3010: density = 0.921 g/mL; melt index = 5.5 g/10 min.
[e] See Ref. [18].
[f] Value shown was taken from a product selection guide from The Dow Chemical Company: "621 Ways to Succeed", 1993–1994.

3.2. Synthesis and structure of polyester 6

Earlier work in our laboratories demonstrated that in accordance with Scheme 1, both bisphenols or diacids polymerize readily with diepoxides to produce poly(hydroxy ethers) (**3a**) or poly(hydroxy ester ethers) (**3c**) at 100–180 °C in etheric solvents containing a quaternary ammonium or phosphonium halide (Q^+X^-) [4,10], the role of which can be rationalized by a mechanism detailed earlier [4,11] and summarized here in Scheme 3. Briefly, the polymerization is initiated by attack of halide on an epoxy functionality to form haloalkoxide **7**, which subsequently deprotonates a carboxylic acid group to form a nucleophilic carboxylate (**8**) and a neutral halohydrin (**9**; Scheme 3a). Condensation of **8** with an unreacted epoxy moiety then yields ester-alkoxide intermediate **10**, which propagates the polymerization (until the epoxy and acid functionalities are completely consumed) by proton transfer from available carboxylic acid moieties to regenerate reactive carboxylates **8**, available for further condensation with epoxy end groups, while forming the hydroxy ester linkage (**11**) that constitutes the polymer's backbone (Scheme 3b). Halohydrin



Scheme 3. Rationalization for reactions of acids with epoxides mediated with quaternary halides.

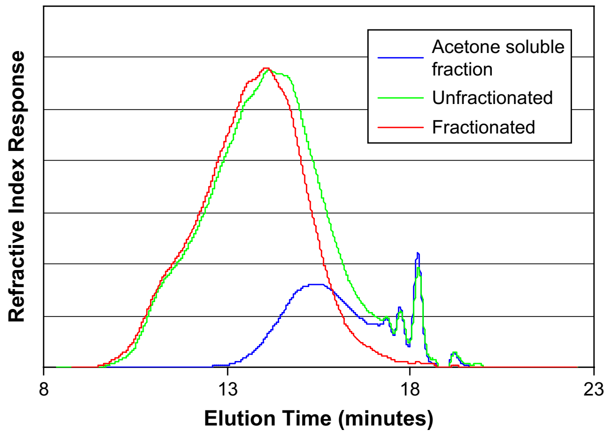


Fig. 2. Gel permeation chromatogram of polymer **6**, prepared by polymerization of monomer **5** with $Bu_4N^+Br^-$, before and after fractionation with acetone overlaid on a chromatogram of the acetone soluble fraction.

end groups (**9**) apparently do not act as inert chain caps that would otherwise limit molecular weight growth by unbalancing the stoichiometry of this step-growth process; rather, **9** remains as an active participant in the polymerization either through direct halide displacement by carboxylate or by recyclization to epoxy end groups that participate normally during the propagation step of Scheme 3b [4,11].

During the beginning phases of our exploration of the polymerization of Scheme 2, we focused on tetrabutylammonium bromide (TBAB) as the initiator for the polymerization of **5**, since TBAB had previously proven useful for the synthesis of high-molecular-weight **3c** [4,9]; later we found that tetraphenylphosphonium bromide (TPPB) affords polyester **6** with both higher molecular weight and significantly narrower molecular weight distribution (M_w/M_n) than is the case with TBAB (see discussion below). Consequently, this paper will describe certain characteristics of **6** formed with both initiators, initial surveys of which were conducted by maintaining identical samples of monomer **5** at 140 °C in propylene glycol monomethyl ether acetate (65% solids) containing either TPPB or TBAB (0.6–1.8 mol%) for 1–6 h. For both initiators, peak molecular weight (T_p, relative to polystyrene calibration standards) of unisolated **6**, monitored by GPC, reached a plateau (55×10^3 for TPPB) after 2–2.5 h, indicating that linear chain growth was complete within that period. Thus, in preparative experiments performed under essentially the same conditions, polyester **6** was isolated in greater than 95% yield by precipitation from cold water after reaction for 2.5 h. Gel permeation chromatograms of **6** revealed that the crude product contains at least three oligomeric components with the long elution times illustrated in Fig. 2. We found that fractionation of the polymer with acetone completely removes these low-molecular-weight constituents (Fig. 2); as a result, samples of **6** destined for the property evaluations described below were thoroughly washed with acetone. We made no attempt to identify the oligomeric components separated from **6**, but the formation of macrocycles in these highly concentrated AB polymerizations is not unreasonable.

That **6** is a hydroxy-functionalized polyester and it was confirmed by its infrared (IR) spectrum which displays classical O–H and ester C=O stretching absorptions at 3421 and 1733 cm^{-1}, respectively (Fig. 3). However, the ^1H NMR spectrum of the material, which is tabulated completely in Table 1, indicates that **6** is formally a copolymer. While 65 mol% of the repeat units in **6** are the 10-hydroxyundecanoate linkages (repeat unit A, Table 1) expected from the attack by carboxylate on the terminal carbon of **5** (Scheme 3), about 35 mol% of the backbone is composed of repeat

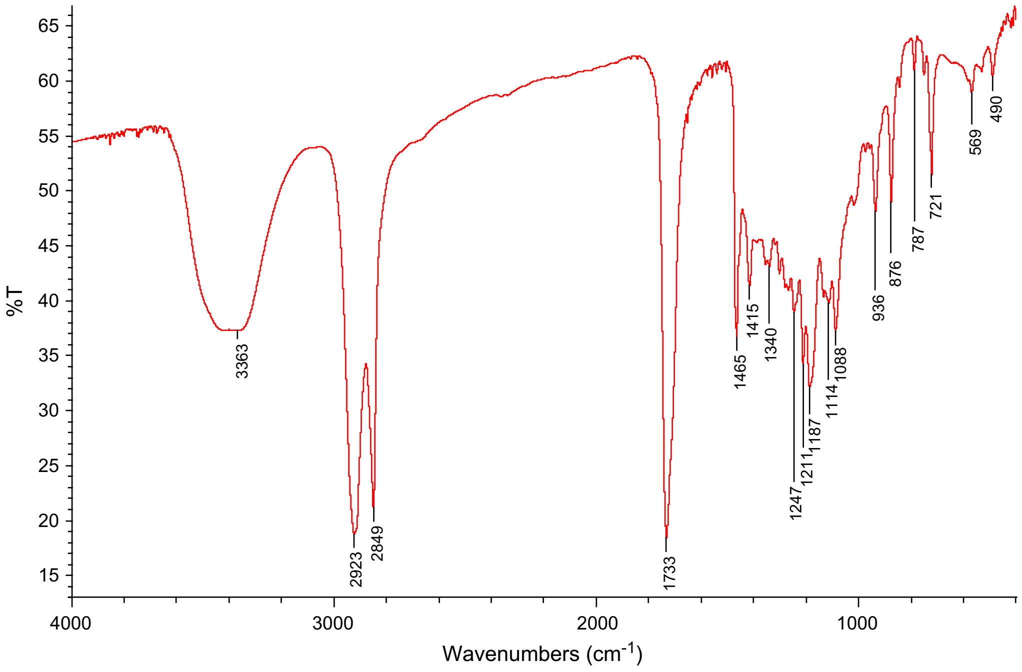
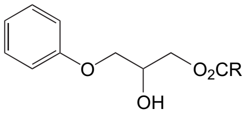


Fig. 3. Infrared spectrum of polyester **6**.

unit B, 10-(hydroxymethyl)decanoate. Thus, the spectrum clearly distinguishes the methine protons of each repeat unit (H^b and H^h; Table 1) by exhibiting multiplets at 3.52–3.41 and 4.91–4.78 ppm with an integration ratio dictating the composition of **6** shown in Scheme 2; integration ratios of H^b and H^h and of other protons shown in Table 1 were determined relative to those of H^f and H^l which were collectively assigned a value of 2.0. In addition, the chemical shift and integration of a doublet at 3.87–3.80 ppm nicely correspond to the methylene protons (H^g) of the pendent methylol group of repeat unit B. In fact, the presence of this structural feature in **6** was not surprising; although not explicitly indicated in the general structure of poly(hydroxyl ester ethers) (**3c**) shown in Scheme 1, about 20–25 mol% of the hydroxyl ester linkages in **3c** contain the methylol side group (**13**); the remainder have the conventional hydroxy ester structure, **14**. Linkage **13** probably arises from intramolecular transesterification of the ester-alkoxide intermediate **10** (introduced in Scheme 3b) as shown in Scheme 4 [4,9]. Methylol side chains are peculiar to epoxy-based polyesters and are completely absent in **3a** and in poly(hydroxy amino ethers) (**3b**) [4–7], lending credence to Scheme 4 by making it unlikely that the appearance of two types of hydroxyl ester linkages in **3c** or **6** simply is due to an inability of a nucleophilic carboxylate to discriminate between the two carbons of the epoxide ring [12].



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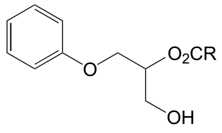

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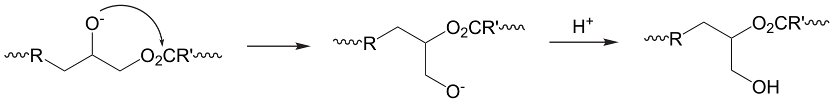
After washing with acetone, polymer **6**, prepared with TPPB and henceforth designated as **6a**, has a weight-average molecular weight (M_w; relative to polystyrene) of roughly 120,000 accompanied by a molecular weight distribution (M_w/M_n) of 3.7 (Table 2). As indicated above, when synthesized using TBAB, the polyester (**6b**) has a considerably higher distribution ($M_w/M_n = 13.1$), and although we were unable to determine M_n for the unfractionated products prepared with either initiator using GPC (owing to baselines obscured by oligomeric components), inspection of Fig. 2 indicates qualitatively that the polymers would clearly be more polydisperse before fractionation. In any case, the values of M_w/M_n for fractionated **6a** and **6b**, along with the slight high-molecular-weight shoulder in chromatograms of the polymer, indicate that even when TPPB initiates the polymerization of **5** at least some branching accompanies linear chain formation [13]. Poly(hydroxy ester ethers) (**3c**) tend to exhibit broader distributions ($M_w/M_n > 5.0$) [9] than do poly(hydroxy ethers) (**3a**) and poly(hydroxy amino ethers) (**3b**) [6], which of course contain no ester groups, suggesting that branching *via* intermolecular transesterification plays a key role in producing the polydispersity observed in **3c**, and one would anticipate that branching could occur similarly in the polymerization of **5**. As discussed in detail elsewhere [6], however, polymers **3a** and **3b** are not entirely free of branching so that side reactions in polymerizations of nucleophilic monomers and epoxides unrelated to transesterification are possible and may also contribute to the branched structures in **3c** and in **6**.

As a practical matter, and regardless of how branching originates in **6**, the molecular weight data listed in Table 2 clearly demonstrate that TPPB is a far more effective initiator for the polymerization of Scheme 2 than is TBAB. Not only is the polydispersity of **6b** over three times that of **6a**, M_n (13,300) of **6b** is less than half that of the polymer formed in the presence of TPPB (**6a**; 32,900) under otherwise identical conditions. Obviously, TBAB promotes or at least permits branching that doesn't occur for polymerizations of **5** initiated with TPPB, and the lower M_n of **6b** indicates that the AB stoichiometry of Scheme 2 may be compromised with this initiator, as well. A careful model study likely will be necessary to determine how the cations of these two initiators act in such a way to make TPPB and TBAB behave so differently. Nevertheless, while questions remain about initiator-related side reactions of Scheme 2, polymerization of **5** in the presence of TPPB is sufficiently well behaved to allow a meaningful evaluation of the general mechanical behavior of polyester **6a**, and samples of **6b**, in spite of its polydispersity, are useful in understanding the influence of pendent hydroxyl groups in **6** on other characteristics of the material.

*3.3. Physical properties of polyester **6***

Notwithstanding any tendency of the pendent hydroxymethyl groups populating the backbone of polyester **6** to subvert interchain packing, the polymer has sufficient structural regularity to allow its facile crystallization from the melt. Table 2 reveals that **6a**, initiated with TPPB, undergoes a glass transition (T_g) at −8 °C and a strong endothermic melting transition with its peak (T_m) at 97 °C ($\Delta H = 32.4$ J/g); annealing the resin at 75 °C elevates its T_m (107 °C) and, based on a significantly increased enthalpy of melting ($\Delta H = 57.4$ J/g), appears to nearly double the crystallinity in the material. Unannealed polymer **6b** prepared using TBAB exhibits $T_m = 90$ °C (Table 2).

The semi-crystalline nature of **6** prompted us to compare the polyester to linear low density polyethylene (LLDPE), another semi-crystalline, low-melting thermoplastic. The quasi



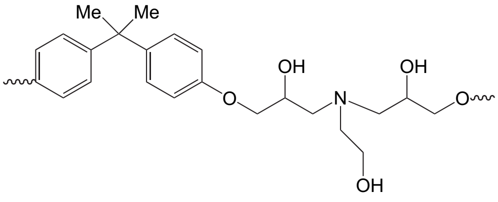
10 **12**

Scheme 4. Intramolecular transesterification during formation of polymer **6**.

olefinic nature of the backbone of **6** coupled with the pendent hydroxy functionality in each repeat unit held out the possibility of a polymer combining the mechanical characteristics of polyethylene combined with the surface energy and gas barrier properties of epoxy-based thermoplastics such as **3**, and this general prediction is, in fact, borne out experimentally. Table 3 shows that compression-molded films (0.4 mm) of **6a** yield at 9.7 MPa and, as expected for a ductile, semi-crystalline polymer, strain harden to break at 24.1 MPa, values are remarkably close to those for high-molecular-weight LLDPE compression-molded under similar conditions (11.0 and 24.8 MPa). Also, samples of both **6a** and LLDPE undergo comparable elongation at break (400–450%) and have nearly identical tensile moduli of around 190 MPa (Table 3). Since annealing **6a** at 75 °C for 48 h raises the level of crystallinity in the material (Table 2), it is not surprising that the same process applied to tensile samples of **6a** produces specimens with a somewhat higher modulus (227.6 MPa) than is the case for unannealed films. Annealing also significantly increases the yield stress and break stress (12.4 and 31.0 MPa) of the polymer despite about a 30% drop of M_n from 32,900 to 21,800 (Table 2 and Table 3, footnote b), which perhaps is due to hydrolysis of a few backbone ester linkages by adventitious moisture. Note that the long annealing time was chosen simply for convenience, and reorganization of the polymer matrix at 75 °C is probably complete in a much shorter time; further study of **6** will include a detailed examination of the effect of heat history on its thermal properties.

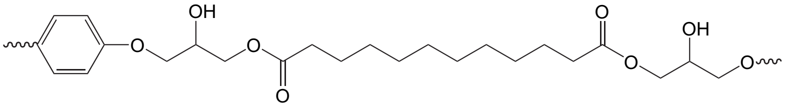
The mechanical characteristics of compression-molded specimens of polydisperse **6b** are generally similar to those of **6a** (Table 3) with the exception of the lower break stress of **6b** (15.6 MPa), a possible consequence of the fact that this polymer has an M_n of less than half that of **6a** or of some morphological difference between **6a** and **6b** that we currently do not understand.

Although **6** and LLDPE can have similar mechanical behavior, surface energy of the polyester with its ester linkages and pendent hydroxyl moieties is predictably higher than that of the less polar polyolefin, an assertion reflected by the adhesive characteristics of the two polymers (Table 4). The lap shear strength of **6** (in this case, **6b**), melt laminated onto cold rolled steel or aluminum substrates, pretreated with methyl ethyl ketone, is 9.4 MPa and the polymer exhibits cohesive failure; in contrast, LLDPE bonds weakly to aluminum (1.7 MPa) and fails adhesively. In another comparison (Table 4), peel strengths of **6b**, again bonded to steel and aluminum, are 1.6 and 1.4 N/mm, and these values are similar to those of an amorphous, hydroxyl-functionalized thermoplastic, poly(hydroxy amino ether) **3b-1**, which adheres tenaciously to metal surfaces [6]. The lap shear strength of **3b-1** (22.1 MPa; aluminum) is over twice that of **6b**, but since both materials fail adhesively, the difference at least in part reflects the inherently higher tensile strength of **3b-1** (break stress = 47.6 MPa) [6]; it is, of course, quite possible that **6a** will prove to have a higher lap shear strength than that shown for **6b**.



3b-1

As a class, epoxy-based thermoplastics **3** are notable for their good-to-excellent barrier (*i.e.*, low permeability) to atmospheric gases, particularly oxygen [4,6,14,15]; a number of **3** have oxygen transmission rates (O_2TR) below 1.0 cc mil/100 in.^{2} 24 h atm (O_2) (barrier units or BU) [4,6,16], values comparable to those of high-barrier food-packaging thermoplastics such as poly(vinylidene chloride) and poly(ethylene-*co*-vinylalcohol) [17] and well below the O_2TR of bottle-grade poly(ethylene terephthalate) (about 5–9 BU) [6]. The permeability (P) of **3** and other resins to oxygen is a product of the solubility (S) and diffusion (D) of the gas in and through the polymer matrix ($P = D \times S$) and is influenced by a complex set of both synergistic and competitive factors arising from polymer structure and morphology that have been discussed in detail elsewhere [4,6,17]. One such factor is the presence of functionalities, such as hydroxyl groups that can contribute to interchain cohesion (or cohesive energy density) and, in turn, barrier performance *via* intermolecular hydrogen bonding [6,17,18]. These interactions appear to contribute moderate barrier properties to polyester **6b** compared with LLDPE; having no opportunity for intermolecular hydrogen bonding, the polyolefin is a poor barrier to oxygen, reflected by an O_2TR of over 150 BU [18]. In contrast, compression-molded films of **6b** have an O_2TR of 14.0 BU (Table 5), performance reasonably consistent with that of structurally somewhat similar poly(hydroxy ester ether) **3c-1** (O_2TR = 10.0 BU; Table 5); both polyesters are crystalline and have T_g below the oxygen permeation test temperature (25 °C), and **3c-1** has only a slightly higher density of hydrogen bonding sites per unit chain length. As one would expect, the greater polarity of **6b** compared with LLDPE results in poorer barrier to moisture; compression-molded films of **6b** exhibit a water vapor transmission rate (WVTR) of 13.0 g mil/100 in.^{2} 24 h which is considerably higher than that of a commercial LLDPE (1.1 g mil/100 in.^{2} 24 h) commonly used as an extrusion-cast coating resin (Table 5).



3c-1 (structure also contains linkage **13**)

4. Conclusions

Derived from castor oil, undecylenic acid (**1**) can be readily oxidized to 10,11-epoxyundecanoic acid (**5**). Polymerization of **5**, *via* an AB process initiated by quaternary ammonium or phosphonium salts, yields hydroxy-functionalized polyester **6** (Scheme 2), a new crystalline thermoplastic that mimics the mechanical characteristics of linear low density polyethylene while exhibiting the adhesion and barrier properties of a group of well-known epoxy-based high polymers (**3**) formed from reactions of dinucleophilic monomers with bisphenol A-diglycidyl ether and other diepoxides (**4**; Scheme 1).

The nature of product **6** is highly dependent on the initiator used for its formation from monomer **5**. Tetraphenylphosphonium bromide affords high-molecular-weight **6a** ($M_n = 32{,}900$) with M_w/M_n of 3.7, while tetrabutylammonium bromide produces highly polydisperse **6b** ($M_w/M_n = 13.1$) with a M_n of only 13,300. Therefore, although a mechanistic rationalization for the polymerization of **5** accounts for the basic construction of the polymer backbone (Scheme 3), further development of **6** will require better understanding of whatever secondary roles initiators play (or do not play) in promoting branching side reactions.

Acknowledgements

The authors wish to thank Mr. Jim Rabon, Mr. Richard Kolonko and Dr. Marlin Walters for preparations of monomer **5**.

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