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Amorphous Phenoxy Thermoplastics with an Extraordinary Barrier to Oxygen

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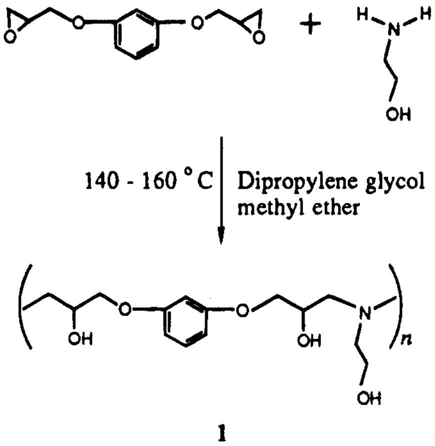
Introduction. Polymers with an excellent barrier to oxygen and other atmospheric gases represent a group of specialty thermoplastics used across a wide range of protective packaging applications.[1,2] Factors contributing to the barrier characteristics of such materials include (a) high intermolecular cohesion that discourages oxygen diffusion through the amorphous regions of a thermoplastic and (b) morphologies in which crystalline domains operate as completely impermeable regions within the polymer matrix.[1,2] Indeed, while some amorphous thermoplastics exhibit a significant barrier to oxygen, exceptionally low oxygen permeability, characterized by oxygen transmission rates (O_2-TR) of less than about 0.1 cc·mil/100 in.^{2}·atm·day (barrier units or BU), has mainly been limited to *crystalline* materials such as poly(vinylidene chloride) copolymers (PVDC), ethylene−vinyl alcohol polymers (EVOH), certain polyamides, and some phenoxy-type thermoplastics.[2−4]

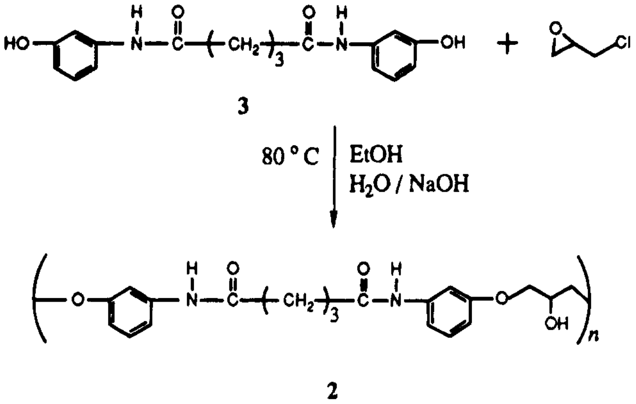
As part of a program[3−6] to explore the barrier properties of various "phenoxy-type" thermoplastics,[7] we have uncovered two completely amorphous materials (species **1** and **2**) with barrier properties (O_2TR of 0.04 and 0.11 BU, respectively) comparable to those of crystalline, high-barrier polymers like PVDC and EVOH. Polymers **1** and **2** are of fundamental interest because they form amorphous matrices with an unusual ability to restrict oxygen permeation. In addition, polymers **1** and **2** offer for the first time the potential to couple extraordinarily high-barrier performance with the broad thermal processing windows and high melt strengths normally associated with amorphous materials.

Synthesis and Characterization. Poly(hydroxy amino ether) **1** was prepared by the reaction of 2-aminoethanol (monoethanolamine) with the diglycidyl ether of resorcinol in dipropylene glycol monomethyl ether solvent (Scheme 1). The primary amino group of monoethanolamine is sufficiently nucleophilic to open the epoxide ring at elevated temperatures, without the aid of a catalyst. As the reaction proceeds, 2-hydroxy-1,3-propylidene linkages form, flanked by oxygen and nitrogen atoms. The polymer repeat unit contains one primary and two secondary hydroxyl units, as well as a tertiary amine unit. In spite of the number of polar functionalities, polymer **1** is insoluble in water but dissolves readily in polar aprotic solvents such as THF and DMF. Polymer **1** was purified by reprecipitation techniques and was isolated in high molecular weight, with η_{inh} = 0.68 dL/g.[8] The inherent viscosity data, coupled with the fact that polymer **1** exists as a robust, creasable film after compression molding, are evidence for its high molecular weight. A glass transition temperature for **1** was detected at 54 °C by DSC analysis,[9] but no evidence was found for a crystalline melting temperature (T_m) between 0 and 250 °C. The structure of polymer **1** was confirmed by a combination of ^{1}H and ^{13}C NMR spectroscopy[10] and microanalysis[11] (see the Experimental Section).

Scheme 1



Scheme 2



Although reactions between amines and epoxides are well-known, this is the first known synthesis of poly(hydroxy amino ether) **1**. The synthesis of polymer **1** differs from conventional reactions of epoxides with amines, used mainly for the cross-linking or "curing" of epoxy resins. In Scheme 1, the precise control of 1:1 reaction stoichiometry between epoxide and N−H functionalities, along with the use of two exclusively difunctional monomers, leads to the synthesis of soluble, high-molecular-weight polymer **1**.[12] The presence of multifunctional monomers and/or deviation from 1:1 reaction stoichiometry would lead to a cross-linked or low-molecular-weight polymer.

Poly(hydroxy amide ether) **2** was prepared by the reaction of *N,N'*-bis(3-hydroxyphenyl)glutaramide (**3**) with 1 equiv of epichlorohydrin in the presence of sodium hydroxide in hot ethanol (Scheme 2). During the reaction, half of the available phenolic groups of **3** react with epichlorohydrin to yield chlorohydrin species, which are then converted to glycidyl ether units. The residual phenolic groups react with the glycidyl ether units to yield the 2-hydroxy-1,3-propylidene linkages shown as part of structure **2**. As high molecular weight is reached, the polymer precipitates from solution and is then purified by reprecipitation procedures. Polymer **2** was isolated as a soluble, high-molecular-weight thermoplastic (η_{inh} = 0.54 dL/g), with a glass transition temperature (T_g) of 115 °C. The structure of polymer **2** was confirmed as described previously.

The synthesis of high-molecular-weight phenoxy thermoplastics by the reactions of bisphenols and epichlo-

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rohydrin has been known for over 30 years.[13] However, polymer **2** is the first example of an amide-containing phenoxy thermoplastic [poly(hydroxy amide ether)] to be prepared by reaction of an *amide-containing* bisphenol with epichlorohydrin.[14] The synthesis of poly(hydroxy amide ethers) such as **2** (and others[15]) is remarkable, when one considers the fact that amides are well-known curing agents for epoxy resins.[16] No disruption of the 1:1 stoichiometry between the amide-containing bisphenol (which is potentially tetrafunctional) and epichlorohydrin apparently occurs, since **2** is formed in high molecular weight and is not cross-linked. This indicates that little, if any, side reaction between epoxide and amide functionalities occurs under the reaction conditions which lead to the formation of **2**.

Barrier Properties. Polymer **1** has an O_2TR of 0.04 cc·mil/100 in.^{2}·atm·day (barrier units or BU) at 57–62% relative humidity of oxygen, while polymer **2** has an O_2TR of 0.11 BU at high relative humidity (74–80%) of oxygen.[17] The O_2TR for **1** and **2** are the lowest known for any amorphous thermoplastic, which includes phenoxy-type polymers, polyamides, polyesters, and other materials. The low O_2TR of polymer **1** is especially impressive, since it approaches those of crystalline materials such as PVDC and EVOH but remains completely amorphous. Important factors which are likely to contribute to the low O_2TR observed for **1** and **2** are (a) an abundance of hydrogen-bonding groups leading to strong interchain cohesion and (b) an efficiently packed, compact backbone structure which is free of bulky side units.

Polymer **1** contains polar hydroxyl and tertiary amine units, which can participate in hydrogen-bonding interactions. Polymer **2** contains one secondary hydroxyl and two amide groups as part of the polymer repeat unit. Semiempirical calculations by Salame[18] indicate that the amide and hydroxyl groups are two of the most powerful contributors to a high barrier in polymers. The low O_2TR for **1** and **2** were obtained at high relative humidity of oxygen (57–80%), which indicates that moisture does not adversely affect their barrier properties. It appears that polymers **1** and **2** have the right combination of polar and nonpolar units to yield strong interchain cohesion yet retain a high barrier in the presence of moisture.

The *m*-phenylene units in **1** and **2** are also critical to the low O_2TR obtained. The *m*-phenylene backbone segment is especially effective at yielding a polymer backbone with low O_2TR. Macromolecules which contain the *m*-phenylene backbone segment have O_2TR that are 30–40% lower than their *p*-phenylene counterparts. This is true for a series of poly(hydroxy amide ethers),[4] as well as polyesters derived from isophthalic and terephthalic acids.[19] The "kinked" structure of polymers containing the 1,3-phenylene unit probably allows the backbone to adopt more preferential chain conformations for enhanced packing efficiency than is possible with backbones dominated by more rigid *p*-phenylene segments. Future reports will address the effects that polymer structure, humidity, and temperature have on the high-barrier properties of other phenoxy-type thermoplastics.

Experimental Section. Synthesis of Poly(hydroxyamino ether) 1. Monoethanolamine (Fluka, 4.644 g, 76.03 mmol), resorcinol diglycidyl ether (HYTEC Polymers, 17.644 g, 76.05 mmol),[20] and dipropylene glycol methyl ether (DOWANOL DPM glycol ether; 4 mL) were added to a 100-mL resin kettle. The flask was fitted with a thermometer, an overhead mechanical stirrer shaft, and a nitrogen inlet adapter. The reaction mixture was heated to approximately 100 °C, at which point an exotherm to 165 °C was observed accompanied by a buildup in solution viscosity. The reaction was diluted with dipropylene glycol methyl ether (16 mL) over the course of 1.5 h, while the temperature was maintained at 150 °C. (Hydroxyethyl)piperazine (1 mL) was then added to react with any residual epoxide end groups and the reaction solution was cooled to 80 °C. After dilution with 30 mL of DMF, the polymer was isolated by precipitation into excess water. After filtration and washing with water, the polymer was dried in vacuo for 20 h at 120 °C. Yield: 15.4 g (69%). Inherent viscosity (η_{inh}): 0.68 dL/g (DMF, 25.0 °C, 0.5 g/dL). ^{1}H NMR (DMSO-d_6): δ 7.13 (m, 1H), 6.47 (m, 3H), 4.83 (s, 2H), 4.41 (s, 1H), 3.85 (m, 6H), 3.44 (m, 2H), 2.60 (m, 6H). ^{13}C NMR (DMSO-d_6): δ 159.91, 129.82, 106.63, 101.37, 70.62, 70.52, 67.43, 67.31, 59.08, 58.92, 58.64, 57.87 (all singlets).[21] Elem anal. Calcd: C, 59.35; H, 7.47; N, 4.94. Found: C, 59.84; H, 7.90; N, 4.98.

Synthesis of *N,N'*-Bis(3-hydroxyphenyl)glutaramide (3).[22] A solution of glutaryl dichloride (Aldrich; 42.3 g, 0.25 mol) in THF (300 mL) was added dropwise to a solution of 3-aminophenol (Aldrich; 110.4 g, 1.01 mol), also in THF (1000 mL). On completion of the addition, the mixture was stirred at room temperature for 18 h and a small amount of precipitate formed. The solution was heated to reflux (66 °C) for 4 h, which yielded more precipitate. The precipitate (aminophenol hydrochloride) was collected by filtration, and the solvent was removed from the filtrate under reduced pressure. The resultant dark, oily residue was poured into 1 L of water to yield an amber-colored solid. The solid was collected via filtration and was recrystallized twice from 5:1 water/ethanol (1000–1200 mL) with use of decolorizing charcoal. The material was dried *in vacuo* at 120 °C for 24 h to yield an amber-colored solid. Yield: 56 g (70%). Mp: 184–186 °C. MS: 314 (found) 314 (calc). ^{1}H NMR (DMSO-d_6): δ 9.73 (s, 2H), 9.29 (s, 2H), 7.18 (s, 2H), 7.06–6.92 (m, 4H), 6.41(m, 2H), 2.33 (t, 4H), 1.87 (p, 2H). ^{13}C NMR (DMSO-d_6): δ 170.61, 157.46, 140.27, 129.15, 110.03, 109.81, 106.23, 35.56, 20.92 (all singlets). Elem anal. Calcd: C, 64.96; H, 5.77; N, 8.91. Found: C, 64.95; H, 5.67; N, 8.85.

Synthesis of Poly(hydroxy amide ether) 2. To a 100-mL polymerization kettle (equipped as described above) was added *N,N'*-bis(3-hydroxyphenyl)glutaramide (**3**; 15.62 g, 50.0 mmol), ethanol (30 mL), epichlorohydrin (Aldrich; 4.63 g, 50.0 mmol), and sodium hydroxide (2.00 g, 50.0 mmol) dissolved in water (30 mL). The contents of the flask were stirred at 25 °C under nitrogen for 17 h, after which time more sodium hydroxide (0.3 g, 7.5 mmol) in water (5 mL) was added to the reaction mixture. The contents of the flask were then heated at 80–90 °C for 8 h, after which a polymeric material precipitated from solution. The polymeric mass was superficially washed with water, dissolved in DMF (75 mL), and then precipitated into a cold solution of 3:1 methanol/water (400 mL) in a high-speed blender. After washing with methanol (100 mL) and water (100 mL), the off-white polymer was redissolved in 100 mL of THF/water (95/5) to which acetic acid (10 mL) was added. The polymer was precipitated and washed a second time and then was dried in vacuo at 80 °C for 24 h. Yield: 12.1 g (65%). Inherent viscosity (η_{inh}): 0.54 dL/g (DMF, 25.0 °C, 0.5 g/dL). Glass transition temperature (T_g): 115 °C. ^{1}H NMR (DMSO-d_6): δ 9.86 (s, 2H), 7.37 (s, 2H), 7.17 (m, 4H), 6.63 (m, 2H), 5.37 (d, 1H), 4.14 (m, 1H), 3.99 (m, 4H), 2.35 (t, 4H), 1.89 (p, 2H). ^{13}C NMR (DMSO-d_6): δ 170.84, 158.74, 140.44, 129.40, 111.47, 108.95, 105.49, 69.11, 67.39, 35.59, 20.80 (all singlets). Elem anal. Calcd: C, 64.85; H, 5.99; N, 7.56. Found: C, 65.29; H, 6.02; N, 7.49.

References and Notes

(1) Salame, M. *J. Plast. Film Sheet.* **1986**, *2*, 321.

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(6) Silvis, H. C.; White, J. E. (The Dow Chemical Co.). U.S. Patent 5 275 853, 1994.

(7) "Phenoxy-type" thermoplastic describes a broad family of macromolecules which contain aryloxy groups linked to 2-hydroxy-1,3-propylidene units [$-ArOCH_2CH(OH)CH_2-$]. The polymers are formed by the reactions of dinucleophiles (bisphenols, primary amines, bis-secondary amines, dicarboxylic acids, etc.) with a diglycidyl ether (diepoxide) or epichlorohydrin. Poly(hydroxy ethers), poly(hydroxy amide ethers), poly(hydroxy amino ethers), and poly(hydroxy ester ethers) are some examples of phenoxy-type thermoplastics.[3–6,14]

(8) Inherent viscosities ($\eta_{\rm inh}$) of the polymers were obtained in DMF at 25.0 °C (0.5 g/100 mL) with use of a Schott–Ubbelohde dilution viscometer.

(9) Glass transition temperatures (T_g) were determined with a DuPont Instruments 2910 differential scanning calorimeter (DSC) with a DuPont Instruments Thermal Analyst 2100 system. A heating rate of 10 °C/min between 50 and 250 °C was used. The glass transition temperature was recorded as the inflection point of the second scan.

(10) ^{1}H (300 MHz) and ^{13}C (75.4 MHz, ^{1}H decoupled) NMR spectra were recorded with use of a Varian VXR 300 NMR spectrometer. Chemical shifts are relative to tetramethylsilane at $\delta = 0$ (^{1}H) and internal tetramethylsilane at 0 ppm (^{13}C).

(11) Elemental analyses were obtained with a Perkin-Elmer PE2400 CHN elemental analyzer.

(12) Although the polymer is believed to be linear, the potential exists for the formation of macrocyclic species based on the step-growth nature of the polymerization. The concentrated reaction conditions employed (50–80% solids; see the Experimental Section) tend to favor the formation of linear species. Cyclic polymers might form under more dilute conditions.

(13) Hale, W. F. Phenoxy Resins. *Encyclopedia of Polymer Science and Technology*; Wiley: New York, 1969; Vol. 10, pp 111–122.

(14) Brennan, D. J., White, J. E. (The Dow Chemical Co.). U.S. Patent 5 134 218, 1992.

(15) Poly(hydroxy amide ethers) are also prepared by the reactions of amide-containing bisphenols with diglycidyl ethers.[4]

(16) McAdams, L. V.; Gannon, J. A. Epoxy Resins. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1986; Vol. 6, pp 322–382.

(17) Oxygen transmission rates (O_2TR) were determined according to ASTM method D3985–81 with use of an OxTran 1050 system operated at 55–90% relative humidity of oxygen between 23 and 25 °C.

(18) Salame, M. *Polym. Eng. Sci.* **1986**, *26* (22), 1543.

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(20) Epoxide equivalent weight (EEW) of 116 g/equiv wt (or mol) of epoxide, determined according the following procedure: Jay, R. R. *Anal. Chem.* **1964**, *36* (3), 667.

(21) Additional carbon resonances were detected at 57–71 ppm due to the effect of isomers in the $-CH_2CH(OH)CH_2N(CH_2CH_2OH)CH_2CH(OH)CH_2-$ linkages.

(22) For previous descriptions of amide-containing bisphenol **3**, see: *Chem. Abstr.* **1986**, *104,* 139409 and ref 14.

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