Poly(hydroxy amide ethers): New High-Barrier Thermoplastics

David J. Brennan,* Jerry E. White,* Anthony P. Haag, Shari L. Kram, Michael N. Mang, Steven Pikulin,† and Charles N. Brown

Materials Research and Development Laboratory, Central Research and Development, The Dow Chemical Company, Midland, Michigan 48674

Received November 20, 1995; Revised Manuscript Received February 12, 1996[⊗]

ABSTRACT: The synthesis of a new class of high-barrier polymers, poly(hydroxy amide ethers), is described. The polymers are formed by the reactions of bisphenol-A diglycidyl ether, $\overline{OCH_2CHCH_2}$-$OC_6H_4C(CH_3)_2C_6H_4OCH_2\overline{CHCH_2}O$, and amide-containing bisphenols of the general formula HOC_6H_4-$NHC(O)RC(O)NHC_6H_4OH$ [R = $-(CH_2)_n-$, $-CH_2C_6H_4CH_2-$, or $-C_6H_4-$] or $HOC_6H_4NHC(O)C_6H_4OH$ at 140−160 °C in propylene glycol monophenyl ether solvent using ethyltriphenylphosphonium acetate as initiator. High-molecular-weight poly(hydroxy amide ethers) of the general structure $[-CH_2CH(OH)$-$CH_2OC_6H_4C(CH_3)_2C_6H_4OCH_2CH(OH)CH_2OC_6H_4NHC(O)RC(O)NHC_6H_4O-]_n$ or $[-CH_2CH(OH)CH_2OC_6$-$H_4C(CH_3)_2C_6H_4OCH_2CH(OH)CH_2OC_6H_4NHC(O)C_6H_4O-]_n$ are readily prepared. The amorphous thermoplastics have glass transition temperatures (T_g) of 90−133 °C and oxygen transmission rates (O_2TR) which range from 0.7 to 4.6 cc·mil/100 in.^{2}·atm·day (barrier units or BU) at 23 °C and 47−85% relative humidity. The effect that polymer structure has on oxygen barrier properties and T_g is described. The characterization, structure determination, and properties of the poly(hydroxy amide ethers), as well as the amide-containing bisphenol precursors, are also presented.

Introduction

Polymers that exhibit high barrier to oxygen and other gases (carbon dioxide and water vapor) have become increasingly important in packaging and other applications.[1,2] Many foods and beverages that were once packaged in metal or glass now make use of plastic containers, mainly due to the convenience, weight savings, and processing ease associated with these materials. A prime example of this conversion has been the replacement of glass by poly(ethylene terephthalate) (PET) in beverage bottles,[3] owing to the ability of PET to retain carbon dioxide within the container during the shelf life of the product.[4] In most barrier packaging applications, exclusion of oxygen is especially important for the preservation and quality of many foods and beverages. High oxygen barrier in organic polymers is believed to be due, in part, to the ability of polymer chains to pack efficiently, which impedes the migration of oxygen through the polymer matrix.[1] Factors which contribute to high oxygen barrier in organic polymers include (a) strong interchain cohesion through hydrogen bonding interactions, (b) a compact backbone structure without bulky side groups, and (c) the presence of crystalline domains, which retard permeation by forcing penetrant molecules to follow a more tortuous path through amorphous regions of the polymer matrix.

Poly(vinylidene chloride)-based resins (PVDC)[2,5] and ethylene−vinyl alcohol (EVOH) copolymers[2,6] have oxygen permeabilities that are among the lowest known for organic polymers. The barrier performance of PVDC resins is due to crystallinity, as well as strong chain packing interactions in the amorphous regions of the polymer matrix. EVOH polymers owe their barrier function to both hydrogen bonding interactions and crystallinity. Other high to moderate oxygen barrier polymers include polyamides,[7,8] polyesters,[9−12] acrylonitrile copolymers,[13,14] and various poly(hydroxy ethers) or "phenoxy-type" thermoplastics.[15−20] However, there are deficiencies associated with some of these conventional barrier polymers. For example, the permeability of oxygen in EVOH increases rapidly in the presence of moisture.[21] PVDC-based polymers have low glass transition temperatures which limits their use to flexible film applications. It would be an advantage to synthesize new materials that combine high oxygen barrier with high T_g, good processability, and resistance to the effects of moisture.

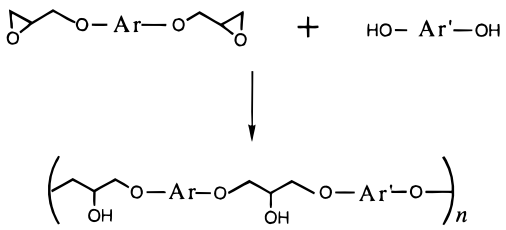
In the design of new materials that might retard the permeation of oxygen through a polymer matrix, the combination of amide and hydroxyl moieties in the same polymer backbone is especially attractive. Semi-empirical calculations by Salame[22] have shown that hydroxyl and amide units are two of the most powerful contributors to high barrier in polymers. This is believed to be due to superior hydrogen bonding interactions that increase interchain cohesion and retard oxygen permeation. One approach to combining amide and hydroxyl moieties in the same macromolecule is to carry out conventional polyamide syntheses in which the diamine or dicarboxylic acid monomers contain pendent hydroxyl groups. However, the potential for cross-linking is high in such a system, due to the lack of strict difunctionality in the monomers. A second approach, which we have followed, is to generate hydroxyl groups *during* the polymerization of preformed amide-containing monomers.

Poly(hydroxy ethers) (**1**) are a class of macromolecules formed by reactions of bisphenols with aromatic diglycidyl ethers (Scheme 1).[16−19,23,24] During poly(hydroxy ether) synthesis, pendent hydroxyl groups are generated as the phenolic units of the bisphenol open the oxirane rings of the diglycidyl ether. By using *amide-containing* bisphenols, the preformed amide moiety can be effectively incorporated into the polymer backbone as the pendent hydroxyl groups are being generated (Scheme 1, where Ar′ contains an amide unit). The hybrid poly(hydroxy ether)/polyamides [or *poly(hydroxy amide ethers*) (**2**)] prepared by this process differ from conventional poly(hydroxy ethers) (**1**) in that they contain amide units as part of the polymer backbone. Although several

† Present address: Ohmeda PPD, Inc., Liberty Corner, NJ.
⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1996.

S0024-9297(95)01720-7 CCC: $12.00

Scheme 1



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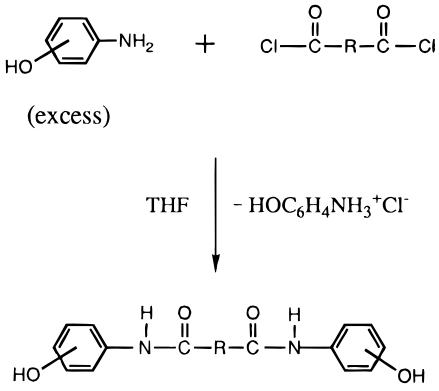
Scheme 2



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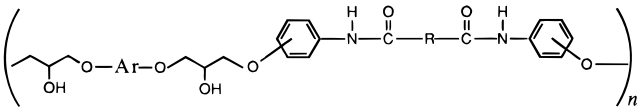
patents and one preliminary report on this work have appeared,[25−29] the details of poly(hydroxy amide ether) synthesis, characterization, and barrier properties are reported for the first time in this paper.



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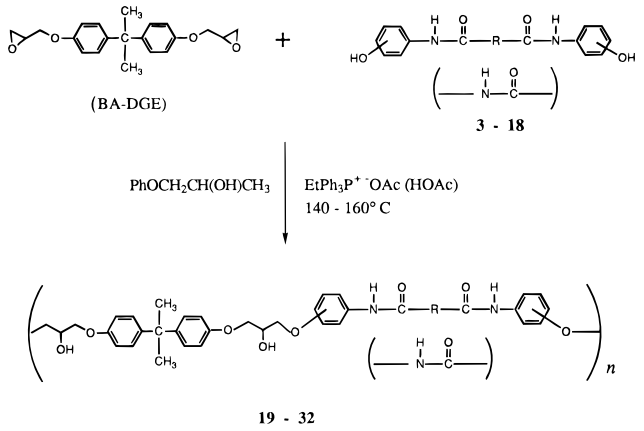
The main objectives of this work were to determine (a) the scope and limitations of poly(hydroxy amide ether) synthesis and (b) the effect that polymer structure has on oxygen transmission rates (O_2TR) and glass transition temperatures (T_g) of the polymers. Specifically, we wanted to answer the following questions: (1) Do the amide functionalities in the bisphenol monomers interfere with the chain-building reactions between the glycidyl ether and phenolic moieties? (2) What effect does increasing the density of hydrogen bonding groups have on O_2TR? (3) How are O_2TR and T_g affected by structural changes in the amide portion of the polymer backbone (such as *m*- vs *p*-phenylene units, or the nature of the R group in structure **2**)? To answer these questions, the synthesis of poly(hydroxy amide ethers) was carried out by the reactions of bisphenol-A diglycidyl ether (BA-DGE) with a variety of amide-containing bisphenols.

Results and Discussion

Synthesis of Amide-Containing Bisphenols. Amide-containing bisphenols **3**−**15** (Table 1) and **16**−**18** (next column) were prepared and studied as part of this work. Diamide bisphenols **3**−**15** were synthesized by the reactions of various diacid chlorides with an excess of 3- or 4-aminophenol in tetrahydrofuran (Scheme 2). The hydrogen chloride liberated during this process is scavenged by the excess aminophenol, yielding the

Scheme 3



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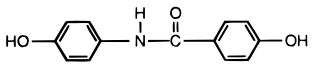
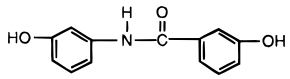
aminophenol hydrochloride salt as a byproduct. Products of the reaction between the phenolic groups and acid chlorides (esters) were not detected. Although some of the amide-containing bisphenols shown in Table 1 have been prepared previously (using various synthetic methodologies),[20,25,27,30−38] the process shown in Scheme 2 provides a straightforward general synthesis of **3**−**15**. Bisphenols which contain a single amide unit (**16**−**18**) are known in the literature.[39−42] The syntheses of 4,4′-dihydroxybenzanilide (**16**) and 3,3′-dihydroxybenzanilide (**17**) were carried out using modifications of existing procedures as described in the Experimental Section. Compound **18**, *N*-(4-hydroxyphenyl)salicylamide, was obtained commercially. Amide-containing bisphenols **3**−**17** were characterized by a combination of ^1H NMR and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis to unequivocally confirm the identity of the materials (Tables 1−3 and the Experimental Section).



16



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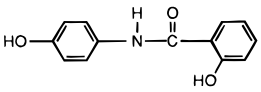

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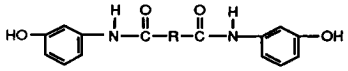
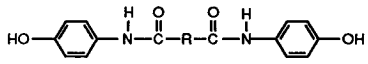
Poly(hydroxy amide ether) Synthesis and Characterization. Poly(hydroxy amide ethers) **19**−**32** (Table 4) were prepared by the reactions of the amide-containing bisphenols with bisphenol-A diglycidyl ether (BA-DGE) (Scheme 3).[43,44] The reactions are carried out in propylene glycol monophenyl ether at elevated temperatures (140−165 °C) with the use of an ethyltriphenylphosphonium acetate−acetic acid complex (70% in methanol) as catalyst. During the polymerization reaction, the phenolic groups react with the epoxide functionalities, generating the pendent secondary hydroxyl groups, as well as incorporating the amide units into the polymer backbone. The polymers were isolated as granular or fibrous materials in yields of 70−90%. The poly(hydroxy amide ethers) were characterized by a combination of ^1H NMR and ^{13}C NMR spectroscopy, elemental analysis, differential scanning calorimetry (DSC), gel permeation chromatography (GPC), and inherent viscosity (η_{inh}) determination (Tables 4−6). Oxygen transmission rates (O_2TR) were determined (Table 4) and are described later in the text.

Table 1. Characterization Data for Amide-Containing Bisphenols

No.	R	M.P. (°C)	Yield (%)	Mass Spec. (*m/e*) found	Mass Spec. (*m/e*) calc		Elem. Anal. found	Elem. Anal. calc
								
3	nil	280-282	85	272	272	C H N	61.42 4.23 10.33	61.76 4.44 10.29
4		203-207 (lit.[31]: 206-208)	14	286	286	C H N	62.53 4.91 9.68	62.93 4.93 9.78
5		247(dec) (lit.[33]: 248)	72	300	300	C H N	63.26 5.31 9.27	63.99 5.37 9.33
6[20]		184-186 (lit.[30]: 171-172)	71	314	314	C H N	64.95 5.67 8.85	64.96 5.77 8.91
7		247-250 (lit.[34]: 238-240)	85	328	328	C H N	65.40 6.25 8.51	65.84 6.14 8.53
8		219-222	48	342	342	C H N	65.75 6.60 8.09	66.65 6.48 8.18
9		287-290	95	356	356	C H N	67.39 7.12 7.77	67.40 6.79 7.86
10		164-166 (lit.[35]: 150-161)	71	412	412	C H N	69.60 7.97 6.75	69.88 7.82 6.79
11		196-198	53	376	376	C H N	70.13 5.42 7.35	70.20 5.36 7.44
12		262-263 (lit.[34]: 260-261) (lit.[36]: 265)	71	348	348	C H N	68.44 4.49 8.01	68.96 4.63 8.04
								
13		239-241 (lit.[37]: 232-235)	51	314	314	C H N	64.73 5.97 8.90	64.96 5.77 8.91
14		278-280 (lit.[31]: 265-268) (lit.[34]: 258-260)	85	328	328	C H N	65.74 6.08 8.48	65.84 6.14 8.53
15		233-235	70	342	342	C H N	66.21 6.48 8.05	66.65 6.48 8.18

During poly(hydroxy amide ether) synthesis, the potential exists for amide units in the bisphenol monomers to react with the oxirane rings of the diglycidyl ether species. However, the formation of high-molecular-weight poly(hydroxy amide ethers) indicates that the amide units do not interfere to any appreciable extent with the chain building reactions between the epoxide and phenolic functionalities. Cross-linking or the formation of low-molecular-weight species would occur if the stoichiometric balance was significantly disrupted by participation of amide units in the polymerization process. However, several factors were found to be critical for the preparation of soluble, melt-stable, high-molecular-weight poly(hydroxy amide ethers). They include (a) careful control of reaction temperature and solution viscosity during synthesis, (b) the use of 2% excess diglycidyl ether monomer, and (c) the consumption of residual epoxide species at the end of the polymerization by treatment with an end-capping unit such as *tert*-butylphenol.

Cross-linking can occur during poly(hydroxy amide ether) synthesis if the reaction temperature exceeds about 180−190 °C or if high solution viscosity is obtained, which prevents efficient mixing. To avoid cross-linking, the reaction temperature is maintained at 155−165 °C and additional solvent is added as bulk viscosity increases. The propylene glycol phenyl ether solvent ensures reaction homogeneity and provides a

Table 2. ^{1}H NMR Data for Amide-Containing Bisphenols

no.	^{1}H NMR (δ)[a]
3	10.61 (s, 2H), 9.49 (s, 2H), 7.40 (m, 2H), 7.24 (m, 2H), 7.14 (m, 2H), 6.57 (m, 2H)
4	9.99 (s, 2H), 9.37 (s, 2H), 7.19 (m, 2H), 7.08 (m, 2H), 6.97 (m, 2H), 6.47 (m, 2H), 3.43 (s, 2H)
5	9.82 (s, 2H), 9.30 (s, 2H), 7.18 (m, 2H), 7.05 (t, 2H), 6.96 (m, 2H), 6.44 (m, 2H), 2.62 (s, 4H)
6	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)
7	9.71 (s, 2H), 9.29 (s, 2H), 7.17 (s, 2H), 7.03 (t, 2H), 6.94 (m, 2H), 6.40 (m, 2H), 2.29 (s, 4H), 1.60 (s, 4H)
8	9.71 (s, 2H), 9.31 (s, 2H), 7.19 (m, 2H), 7.04 (m, 2H), 6.95 (m, 2H), 6.44 (m, 2H), 2.28 (t, 4H), 1.61 (m, 4H), 1.33 (m, 2H)
9	9.70 (s, 2H), 9.30 (s, 2H), 7.19 (s, 2H), 7.04 (m, 2H), 6.95 (m, 2H), 6.42 (m, 2H), 2.27 (t, 4H), 1.59 (m, 4H), 1.32 (m, 4H)
10	9.69 (s, 2H), 9.30 (s, 2H), 7.18 (s, 2H), 7.04 (m, 2H), 7.01 (m, 2H), 6.43 (m, 2H), 2.26 (t, 4H), 1.56 (m, 4H), 1.27 (m, 12H)
11	10.01 (s, 2H), 9.34 (s, 2H), 7.27−6.93 (m, 10H), 6.43 (m, 2H), 3.57 (s, 4H)
12	10.28 (s, 2H), 9.43 (s, 2H), 8.48 (s, 1H), 8.12 (d, 2H), 7.67 (m, 1H), 7.38 (s, 2H), 7.13 (m, 4H), 6.54 (m, 2H)
13	9.62 (s, 2H), 9.11 (s, 2H), 7.37 (d, 4H), 6.68 (d, 4H), 2.31 (t, 4H), 1.88 (p, 2H)
14	9.58 (s, 2H), 9.10 (s, 2H), 7.35 (d, 4H), 6.68 (d, 4H), 2.26 (s, 4H), 1.60 (s, 4H)
15	9.55 (s, 2H), 9.08 (s, 2H), 7.34 (m, 4H), 6.66 (m, 4H), 2.24 (t, 4H), 1.60 (p, 4H), 1.32 (p, 2H)

[a] DMSO-d_6 solution.

Table 3. ^{13}C NMR Data for Amide-Containing Bisphenols

no.	^{13}C NMR (ppm)[a]
3	158.49, 157.50, 138.53, 129.29, 111.70, 111.21, 107.25
4	165.27, 157.58, 139.92, 129.35, 110.50, 109.82, 106.24, 45.94
5	170.34, 157.61, 140.38, 129.34, 110.16, 109.87, 106.28, 31.41
6	170.61, 157.46, 140.27, 129.15, 110.03, 109.81, 106.23, 35.56, 20.92
7	170.92, 157.50, 140.29, 129.19, 110.05, 109.81, 106.23, 36.30, 24.89
8	171.07, 157.51, 140.34, 129.21, 110.05, 109.83, 106.24, 36.32, 28.32, 24.96
9	171.09, 157.51, 140.34, 129.20, 110.04, 109.82, 106.24, 36.42, 28.48, 25.05
10	171.13, 157.50, 140.34, 129.19, 110.02, 109.81, 106.23, 36.44, 28.90, 28.77, 28.66, 25.14
11	168.82, 157.51, 140.17, 136.00, 129.67, 129.26, 128.18, 127.23, 110.30, 109.82, 106.25, 43.25
12	164.97, 157.51, 140.05, 135.24, 130.53, 129.24, 128.50, 126.93, 111.09, 110.93, 107.47
13	170.05, 153.07, 130.99, 120.86, 114.94, 35.46, 21.21
14	170.29, 153.04, 130.96, 120.82, 114.92, 36.10, 25.00
15	170.36, 153.00, 130.96, 120.80, 114.87, 36.06, 28.29, 24.97

[a] DMSO-d_6 solution.

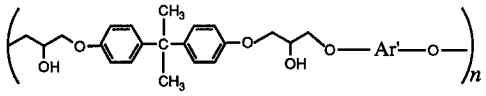
vehicle for dissipation of localized heating. Unlike the typical case in step-growth polymerizations, a 2 mole percent excess of diglycidyl ether is used to obtain the highest molecular weight possible. An unidentified side reaction occurs (possibly branching or reaction of epoxide with solvent or catalyst) which consumes the small amount of excess epoxide. However, the use of excess epoxide is not unique to the synthesis of poly(hydroxy amide ethers). Similar side reactions are also believed to occur during the preparation of high polymeric poly(hydroxy ethers), in which the amide linkages are totally absent.[18,19] The use of an end-capping agent such as *tert*-butylphenol is critical for the preparation of poly(hydroxy amide ethers) that are stable in the melt. Epoxy end groups which remain at the end of the polymerization can cause chain coupling (molecular weight advancement) or cross-linking to occur when the isolated polymers are heated above their glass transition temperatures.[45] Reactions of residual epoxide species with the end-capping unit prevents advancement and cross-linking, to yield polymers that are melt stable for up to 1 h at 230 °C.[46]

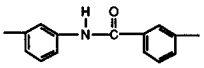
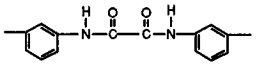
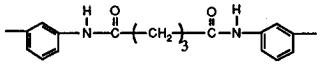
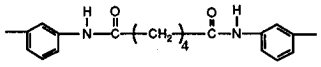
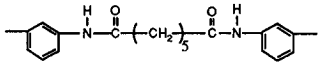
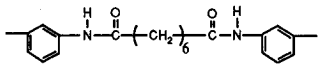
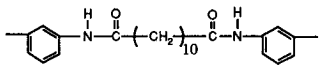
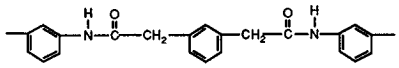
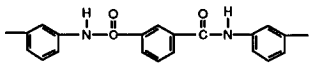
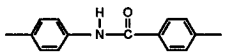
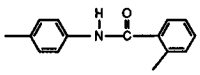
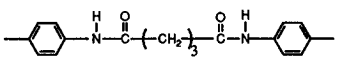
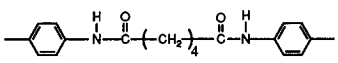
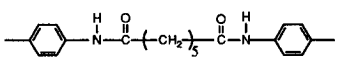
Poly(hydroxy amide ethers) **19**−**32** are amorphous thermoplastics with glass transition temperatures (T_g) of 90−133 °C, as determined by DSC analysis (Table 4). No evidence for crystallinity was detected during DSC analysis from 50 to 250 °C. The T_g of poly(hydroxy amide ethers) increases as the amide-containing portion of the polymer repeat unit (Ar′) becomes more rigid, restricting torsional mobility of the polymer chain. For example, species **27** has the highest T_g at 133 °C and contains a rigid *m*-phenylene unit between amide linkages. By comparison, derivative **25** has the lowest T_g at 90 °C, due to the flexibility and greater chain mobility imparted by the decamethylene unit. In general, poly(hydroxy amide ethers) with flexible linkages between amide groups (**21**−**25**, **30**−**32**) have lower T_g than their counterparts with more rigid linkages in the amide portion of the polymer repeat unit (**19**, **20**, **26**−**29**).

The polymers are of high molecular weight, yielding creasable films after fabrication by compression molding. Molecular weight data were obtained both by inherent viscosity (η_{inh}) determination and gel permeation chromatography (GPC) analysis. Inherent viscosities of 0.36−0.92 dL/g were obtained in DMF at 25.0 °C. Polymers with inherent viscosities greater than approximately 0.4 dL/g yielded compression molded films which did not crack during oxygen barrier testing. Poly(hydroxy amide ethers) with inherent viscosities below 0.3 dL/g (such as the polymer derived from bisphenol **5** and BA-DGE)[43] yielded compression molded films which were too brittle for O_2TR determination. Molecular weight analysis by gel permeation chromatography (GPC) in DMF with 0.05% LiCl showed that most of the polymers analyzed had weight average molecular weights (M_w) of greater than 125 000 with polydispersities (M_w/M_n) of 2−5 when compared to polystyrene standards. However, it should be noted that molecular weight analysis for poly(hydroxy amide ethers) is extremely sensitive to the solvent used and whether or not salts are added to the DMF eluent.

The ^{1}H NMR spectral data for the poly(hydroxy amide ethers) are given in Table 5 and are entirely consistent with the structures shown. Amide protons were detected at δ 9.7−10.6 while the resonances for the aromatic protons were found at δ 6.5−8.5. The hydroxyl, methine, and methylene protons of the 2-hydroxy-1,3-propylidene linkages were found at approximately δ 5.3, 4.1, and 4.0, respectively. Methylene protons between amide groups were detected at δ 1.5−3.6 with the expected coupling patterns detected. Singlets assigned to the methyl groups of the isopropylidene linkage were found at δ 1.5−1.6. The integration areas for the protons matched the calculated values. Simi-

Table 4. Characterization Data for Poly(hydroxy amide ethers)



						Molecular Weight Data			Elemental Analysis		
No.	Ar'	% yield	O_2TR (BU)[a,b]	RH (%)[c]	Tg (°C)	M_w (10^3)	M_n (10^3)	η_{inh} (dL/g)[d]		found	calc
19		70	1.2	70-80	117	---[e]	---[e]	0.92	C H N	70.82 6.22 2.36	71.69 6.19 2.46
20		79	1.6	78-83	119	124	66	0.40	C H N	68.37 5.73 4.40	68.61 5.92 4.57
21		90	0.7	75-85	111	213	91	0.47	C H N	68.81 6.41 4.11	69.71 6.47 4.28
22		70	0.8	75-80	103	126	38	0.62	C H N	69.44 6.58 4.01	70.04 6.63 4.19
23		73	1.2	47-52	107	232	108	0.54	C H N	69.34 6.61 3.92	70.36 6.79 4.10
24		83	1.2	55-60	92	130	65	0.36	C H N	70.81 6.88 3.80	70.67 6.94 4.02
25		86	4.6	50-55	90	194	80	0.47	C H N	71.07 7.39 3.53	71.78 7.50 3.72
26		73	0.7	64-77	119	204	50	0.58	C H N	71.34 6.22 3.74	72.05 6.19 3.91
27		87	1.0	65-70	133	100	35	0.37	C H N	71.03 5.74 3.81	71.50 5.85 4.07
28		78	1.9	60-62	127	209	96	0.63	C H N	70.25 6.32 2.34	71.69 6.19 2.46
29		82	3.5	70-82	121	281	63	0.44	C H N	71.14 6.01 2.36	71.69 6.19 2.46
30		83	1.1	73-80	105	403	85	0.72	C H N	68.74 6.41 4.06	69.71 6.47 4.28
31		76	1.3	75-85	112	315	97	0.72	C H N	69.48 6.62 3.95	70.04 6.63 4.19
32		79	2.0	60-62	116	344	123	0.70	C H N	69.22 6.77 3.90	70.36 6.79 4.10

[a] ASTM method D3985-81. [b] Oxygen transmission rate (O_2TR) in cc·mil/100 in.^{2}·atm·day or barrier units (BU). [c] Relative humidity (RH) of oxygen. [d] Concentration of 0.5 g/100 mL in DMF at 25.0 °C. [e] Not determined.

larly, the ^{13}C NMR spectra for poly(hydroxy amide ethers) **19**−**32** gave further evidence for the structures shown. The aromatic and carbonyl carbons were detected at 105−172 ppm, while the aliphatic carbons of the 1,3-propylidene linkage were found at 67−71 ppm. Aliphatic carbon atoms of the isopropylidene unit and those between the amide functionalities were detected at 20−42 ppm, with those carbons closest to the amide linkages shifted downfield. Microanalytical data (Table 4) were consistent for poly(hydroxy amide ethers) which contained 0.5−1.0% water.

The Effect of Polymer Structure on Oxygen Transmission Rates. The poly(hydroxy amide ethers) described in this paper exhibit high to moderate barrier to oxygen,[2] with oxygen transmission rates (O_2TR) that range from 0.7 to 4.6 cc·mil/100 in.^{2}·atm·day (Barrier Units or BU) at 23 °C and 47−85% relative humidity.[47] The structure of the amide backbone segment in poly(hydroxy amide ethers) (Ar′ in Table 4) has a pronounced effect on the oxygen transmission rates (O_2TR) of the polymers. Overall, the structure vs property relationship indicates that lower O_2TR (higher barrier to oxygen) is obtained when the polymer backbone becomes more efficiently packed through (a) the introduction of compact backbone segments and (b) increased hydrogen bonding interactions. Structural features which contribute to an efficiently packed polymer matrix include (1) the presence of *m*-phenylene instead of

Table 5. Poly(hydroxy amide ether) ^{1}H NMR Data

polymer	^{1}H NMR (δ)[a]
19	10.14 (s, 1H), 7.50 (s, 3H), 7.39 (m, 2H), 7.19 (m, 2H), 7.07 (d, 4H), 6.84 (d, 4H), 6.69 (m, 1H), 5.37 (m, 2H), 4.14 (m, 4H), 4.01 (m, 6H), 1.54 (s, 6H)
20	10.77 (s, 2H), 7.57 (s, 2H), 7.46 (m, 2H), 7.26 (t, 2H), 7.08 (m, 4H), 6.82 (m, 4H), 6.75 (m, 2H), 5.37 (d, 2H), 4.14 (m, 2H), 4.00 (m, 8H), 1.56 (s, 6H)
21	9.86 (s, 2H), 7.38 (s, 2H), 7.10 (m, 8H), 6.84 (d, 4H), 6.62 (d, 2H), 5.35 (d, 2H), 4.12 (m, 2H), 4.00 (m, 8H), 2.36 (t, 4H), 1.89 (p, 2H), 1.56 (s, 6H)
22	9.83 (s, 2H), 7.35 (s, 2H), 7.06 (m, 8H), 6.85 (d, 4H), 6.61 (d, 2H), 5.33 (d, 2H), 4.11 (m, 2H), 3.99 (m, 8H), 2.31 (m, 4H), 1.61 (m, 4H), 1.55 (s, 6H)
23	9.82 (s, 2H), 7.37 (m, 2H), 7.11 (m, 8H), 6.86 (m, 4H), 6.62 (m, 2H), 5.35 (d, 2H), 4.13 (m, 2H), 4.00 (m, 8H), 2.30 (m, 4H), 1.57 (m, 10H), 1.33 (m, 2H)
24	9.81 (s, 2H), 7.37 (s, 2H), 7.11 (m, 8H), 6.86 (m, 4H), 6.61 (m, 2H), 5.35 (d, 2H), 4.13 (m, 2H), 4.00 (m, 8H), 2.29 (m, 4H), 1.57 (m, 10H), 1.32 (m, 4H)
25	9.79 (s, 2H), 7.35 (m, 2H), 7.08 (m, 8H), 6.84 (m, 4H), 6.59 (m, 2H), 5.34 (s, 2H), 4.11 (m, 2H), 3.98 (m, 8H), 2.26 (s, 4H), 1.55 (s, 10H), 1.24 (s, 12H)
26	10.11 (s, 2H), 7.35 (s, 2H), 7.18 (m, 12H), 6.83 (d, 4H), 6.62 (d, 2H), 5.33 (s, 2H), 4.11 (m, 2H), 3.98 (m, 8H), 3.60 (s, 4H), 1.55 (s, 6H)
27	10.37 (s, 2H), 8.52 (s, 1H), 8.12 (d, 2H), 7.68 (t, 1H), 7.55 (s, 2H), 7.39 (m, 2H), 7.26 (m, 2H), 7.08 (d, 4H), 6.82 (d, 4H), 6.74 (m, 2H), 5.38 (d, 2H), 4.12 (m, 2H), 4.02 (m, 8H), 1.56 (s, 6H)
28	9.95 (s, 1H), 7.93 (d, 2H), 7.65 (d, 2H), 7.09 (m, 6H), 6.93 (d, 2H), 6.86 (d, 4H), 5.40 (d, 1H), 5.34 (d, 1H), 4.15 (m, 2H), 4.03 (m, 8H), 1.57 (s, 6H)
29	10.17 (s, 1H), 7.82 (m, 1H), 7.68 (d, 2H), 7.50 (m, 1H), 7.47 (d, 1H), 7.05 (m, 6H), 6.80 (m, 5H), 5.65 (d, 1H), 5.33 (d, 1H), 4.24 (m, 3H), 3.99 (m, 7H), 1.53 (s, 6H)
30	9.72 (s, 2H), 7.49 (d, 4H), 7.09 (d, 4H), 6.85 (m, 8H), 5.31 (s, 2H), 4.10 (m, 2H), 3.99 (m, 8H), 2.32 (t, 4H), 1.88 (p, 2H), 1.57 (s, 6H)
31	9.71 (s, 2H), 7.49 (d, 4H), 7.09 (d, 4H), 6.85 (m, 8H), 5.32 (d, 2H), 4.10 (m, 2H), 3.98 (m, 8H), 2.29 (m, 4H), 1.62 (m, 4H), 1.56 (s, 6H)
32	9.68 (s, 2H), 7.47 (d, 4H), 7.09 (d, 4H), 6.85 (m, 8H), 5.31 (s, 2H), 4.09 (m, 2H), 3.97 (m, 8H), 2.25 (t, 4H), 1.59 (m, 4H), 1.57 (s, 6H), 1.35 (m, 2H)

[a] DMSO-d_6 solution.

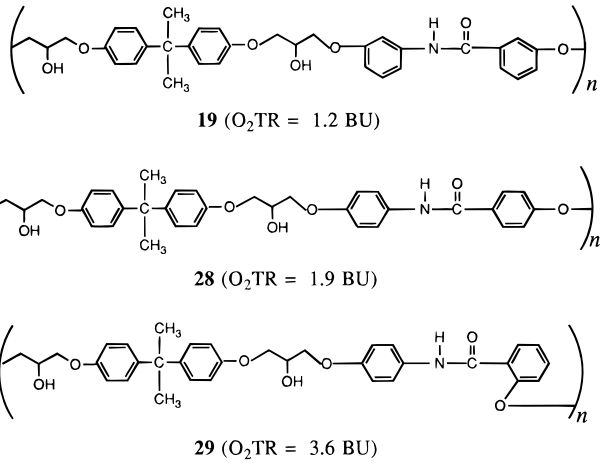
Table 6. Poly(hydroxy amide ether) ^{13}C NMR Data

polymer	^{13}C NMR (ppm)[a]
19	165.14, 158.68, 158.46, 156.24, 142.70, 140.25, 136.25, 129.54, 129.33, 127.39, 120.00, 117.78, 113.87, 113.54, 112.70, 109.80, 106.66, 69.46, 69.19, 69.10, 69.03, 67.45, 67.34, 41.12, 30.70
20	158.70, 158.47, 156.22, 142.69, 138.70, 129.54, 127.38, 113.85, 112.72, 110.77, 106.72, 69.27, 69.07, 67.38, 41.12, 30.69
21	170.82, 158.74, 156.25, 142.69, 140.44, 129.38, 127.39, 113.86, 111.44, 108.97, 105.48, 69.10, 67.44, 41.12, 35.58, 30.70, 20.81
22	171.07, 158.73, 156.24, 142.66, 140.21, 129.37, 127.37, 113.84, 111.41, 108.93, 105.43, 69.10, 67.42, 41.11, 36.29, 30.69, 24.79
23	171.19, 158.73, 156.24, 142.67, 140.45, 129.36, 127.37, 113.84, 111.40, 108.91, 105.43, 69.09, 67.42, 41.11, 36.30, 30.69, 28.26, 24.83
24	171.22, 158.73, 156.24, 142.67, 140.47, 129.36, 127.37, 113.84, 111.41, 108.90, 105.43, 69.09, 67.42, 41.11, 36.41, 30.69, 28.45, 24.95
25	171.29, 158.73, 156.24, 142.68, 140.47, 129.35, 127.37, 113.85, 111.41, 108.91, 105.43, 69.08, 67.43, 41.11, 36.45, 30.69, 28.88, 28.76, 28.65, 25.05
26	169.04, 158.77, 156.25, 142.68, 140.34, 135.88, 129.77, 129.46, 128.22, 127.38, 127.33, 113.86, 111.49, 109.30, 105.48, 69.16, 69.09, 67.44, 43.29, 41.12, 30.71
27	165.01, 158.73, 156.25, 142.69, 140.19, 135.13, 130.59, 129.43, 128.56, 127.39, 126.92, 113.86, 112.66, 109.92, 106.62, 69.22, 69.09, 67.45, 41.12, 30.69
28	164.41, 161.05, 156.24, 154.66, 142.70, 132.51, 129.41, 127.39, 127.11, 121.86, 114.36, 114.06, 113.88, 69.45, 69.13, 69.00, 67.51, 67.40, 41.13, 30.71
29	163.09, 156.24, 156.08, 155.99, 154.68, 142.70, 132.53, 132.26, 130.57, 127.34, 123.62, 121.20, 121.03, 114.48, 113.84, 113.37, 70.28, 69.45, 69.12, 69.02, 67.50, 67.29, 41.08, 30.68
30	170.22, 156.25, 154.26, 142.67, 132.62, 127.37, 120.50, 114.43, 113.85, 69.42, 69.11, 67.48, 41.12, 35.45, 30.70, 21.04
31	170.49, 156.24, 154.25, 142.66, 132.60, 127.36, 120.50, 114.44, 113.85, 69.41, 69.11, 67.48, 41.11, 36.12, 30.69, 24.93
32	170.61, 156.25, 154.24, 142.67, 132.64, 127.37, 120.50, 114.45, 113.86, 69.42, 69.11, 67.50, 41.12, 36.13, 30.70, 28.32, 24.95

[a] DMSO-d_6 solution.

p-phenylene units, (2) a reduction in the number of nonpolar methylene units in the polymer backbone, and (3) increasing the density of polar amide linkages in the polymer repeat unit. The effect that these structural features have on O_2TR is discussed below.

(a) Comparison of *Meta*- vs *Para*-Phenylene Units. Oxygen transmission rates (O_2TR) are 30−40% lower in poly(hydroxy amide ethers) that contain *m*-phenylene units when compared to their *p*-phenylene counterparts. For example, *m*-substituted poly(hydroxy amide ether) **19** (Figure 1) has an oxygen transmission rate (O_2TR) of 1.2 cc·mil/100 in.^{2}·atm·day (barrier units or BU) at 70−80% relative humidity (RH), while its *para*-substituted counterpart, **28**, has a higher O_2TR of 1.9 cc·mil/100 in.^{2}·atm·day, also at high relative humidity (60−62%). Other examples include *m*-phenylene polymers **21**, **22**, and **23**, all of which exhibit lower oxygen permeabilities than their *p*-phenylene counterparts **30**, **31**, and **32** respectively (see Table 4 and Figure 2).[48] The irregular structure of polymers containing the *m*-phenylene unit may allow the backbone to adopt more preferential chain conformations for enhanced packing efficiency. The presence of an *o*-phenylene group in the polymer repeat unit appears to yield the poorest chain packing. For example, salicylamide derivative **29** (Figure 1), which contains an *ortho*-substituted phenylene ring, has the highest oxygen transmission rate for the three polymers shown in Figure 1. The O_2TR of **29** (3.6 BU) is significantly higher than that of its closely related *p*-phenylene counterpart **28** (O_2TR of 1.9 BU).



19 (O_2TR = 1.2 BU)

28 (O_2TR = 1.9 BU)

29 (O_2TR = 3.6 BU)

Figure 1. The effect of *p*-, *m*-, and *o*-phenylene units on oxygen barrier properties.

The *o*-phenylene linkage in **29** probably does not allow the polymer backbone to pack as efficiently as does the *p*-phenylene units of **28**, resulting in the relatively high O_2TR obtained.

(b) Increasing Hydrogen Bonding Interactions. Lower oxygen permeabilities are obtained when hydrogen bonding interactions in the polymer backbone are increased by either reducing the number of nonpolar methylene units or increasing the population density of polar amide groups. Examination of polymers **21**−**25** and **30**−**32** (Figure 2 and Table 4) reveals that as the number of nonpolar methylene units between amide linkages increases, higher oxygen permeabilities are obtained. For example, polymer **21** contains three methylene units between amide linkages and has an O_2-TR of 0.7 BU. O_2TR successively increases to 0.8, 1.2, and 4.6 BU as four (**22**), five (**23**) [or six (**24**)], and ten (**25**) methylene units respectively are present between the amide groups. Likewise, polymers **30**−**32** show the same trend. Similar trends have been reported for various amorphous polyamides[7] and certain polyesters.[49] It appears that as the number of methylene groups in the polymer repeat unit decreases, the density of hydrogen bonding interactions in the polymer matrix (via backbone amide or pendent hydroxyl groups) increases. This presumably leads to stronger interchain cohesion and the lower oxygen permeabilities obtained.

Oxygen permeabilities also tend to be lowest when the Ar′ backbone segment contains a high concentration of amide linkages. However, one must strike a balance between the number of amide backbone units and the type of nonpolar linkages between them. For example, examination of polymers **19**−**27** (Table 4) indicates that the lowest permeabilities are obtained (1.0 BU or less) when the Ar′ backbone segment contains two amide units separated by relatively short methylene-type spacer units (as in polymers **21** and **22**) or phenylene units (**26**, **27**). Oxygen transmission rates then increase (1.0−2.0 BU) as the amide groups in the polymer repeat unit are spaced further apart by the addition of more methylene units (polymers **23** and **24**) or by incorporating only one amide group per repeat unit, such as in **19**. The highest oxygen permeability obtained (4.6 BU) results when the amide groups are separated by the exceptionally long decamethylene segment (**25**). This trend is amplified in polymers **28** and **30**−**32**, which additionally contain *p*-phenylene backbone linkages.

Examination of oxalamide species **20** suggests that the two amide groups in the polymer repeat unit must

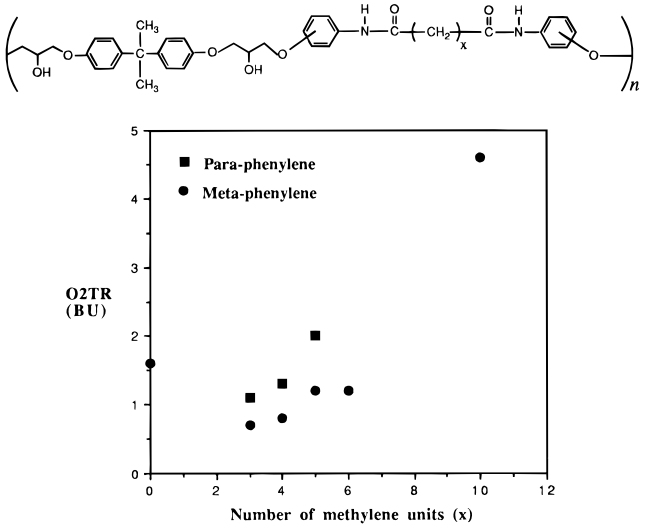


Figure 2. Plot of oxygen transmission rates (O_2TR) vs number of methylene units (*x*).

be separated by some type of spacer unit in order to obtain the full benefit of their hydrogen bonding capability.[50] For example, Figure 2 shows that polymer **20** ($x = 0$) does not follow the trend indicated for the other *m*-phenylene poly(hydroxy amide ethers). Polymer **20**, without methylene units between the amide groups, has a higher O_2TR (1.6 BU) than species **21**−**24** (O_2TR = 0.7−1.2 BU), in which the amide linkages are separated by 3−6 methylene units. It appears that the two amide units in oxalamide polymer **20** generate a localized site for hydrogen bonding interactions, which yields an O_2-TR that is more comparable to single amide species **19**, than it is to diamide polymers **21**−**24**.

Combining High T_g with Low O_2TR. Polymers **26** and **27** provide the best overall combination of low O_2-TR (0.7 and 1.0 BU, respectively) and high T_g (119 and 133 °C, respectively) for the poly(hydroxy amide ethers) described in this paper. They are the only two species which contain aromatic groups between the amide linkages in the polymer backbone (i.e., a *m*-xylylene group in **26** and a *m*-phenylene group in **27**). When compared to their counterparts which contain only methylene units between amide segments, polymers **26** and **27** provide comparable barrier to oxygen, but with significant increases in T_g (10−30 °C). The lower O_2-TR obtained for *m*-xylylene species **26** (O_2TR = 0.7 BU) vs *m*-phenylene-containing **27** (O_2TR = 1.0 BU) might be due to the ability of the polymer backbone to undergo a more facile reorientation as the polymer cools from the melt, due to the lower T_g and increased flexibility provided by its two additional methylene units.

Effect of Humidity on Oxygen Barrier Properties. The barrier properties of poly(hydroxy amide ethers) improve in the presence of moisture, unlike other hydroxyl-containing barrier polymers such as EVOH. For example, polymer **22** has an O_2TR of 1.4 BU at about 5% relative humidity, which gradually decreases to 0.8 BU at 75−80% relative humidity (Figure 3). By contrast, ethylene−vinyl alcohol copolymers (EVOH) lose barrier properties dramatically in the presence of moisture.[2,21] Some conventional polyamides, such as poly(hexamethylene iso-*co*-terephthalamide, exhibit a similar "moisture assisted" improvement in barrier properties.[7,51] Maintenance of barrier performance in the presence of moisture is advantageous, since most packaging used in barrier applications is in contact with

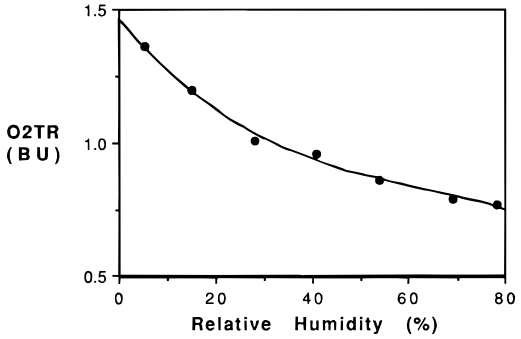


Figure 3. Oxygen transmission rate (O_2TR) vs percent relative humidity for polymer **22**.

atmospheric moisture or with water-containing foodstuffs.

Conclusions

A new family of linear, high-molecular-weight thermoplastic polymers has been prepared by the reactions of difunctional epoxy resins (diglycidyl ethers) with various amide-containing bisphenols. Reaction temperature, efficient mixing, stoichiometry modification, and end-capping are factors which play an important role in the ability to prepare the polymers in high molecular weight. It was also determined that little, if any, reaction between the oxirane units of the diglycidyl ether monomer and the amide units of the bisphenols occurs during polymerization. Evidence for this is the isolation of soluble, high-molecular-weight polymers that could be fabricated into robust, thermoplastic films.

Poly(hydroxy amide ethers) exhibit good to excellent barrier to oxygen. It was found that several structural features of the poly(hydroxy amide ether) backbone influence the ability of the polymers to retard permeation of oxygen through the polymer matrix. These include (a) the presence of *m*-phenylene instead of *p*-phenylene segments in the backbone and (b) increasing the hydrogen bonding interactions in the polymer matrix. The latter feature was realized by reducing the number of nonpolar methylene backbone segments in the polymer, as well as by increasing the population density of polar amide groups in the polymer repeat unit. Finally, barrier performance was found to improve as the relative humidity of the test gas increased. This should be an advantage in practical barrier applications where a container is likely to encounter a range of humidities during normal use.

Experimental Section

Materials. Oxalyl chloride, malonyl dichloride, succinyl chloride, glutaryl dichloride, adipoyl chloride, pimeloyl chloride, suberoyl dichloride, dodecanoyl dichloride, isophthaloyl chloride, 3-aminophenol, 4-aminophenol, and 3-hydroxybenzoic acid were obtained from Aldrich and were used as received. The diacid chloride of 1,3-phenylenediacetic acid (Aldrich) was prepared by the standard reaction with excess thionyl chloride. Compound **18**, *N*-(4-hydroxyphenyl)salicylamide, was obtained from Aldrich and used without further purification. Bisphenol-A diglycidyl ether was purified by crystallization of liquid D.E.R.® 332 epoxy resin (Dow Chemical), followed by washing the solid with methanol (in a blender). The resulting white solid was dried *in vacuo* to remove residual methanol. Epoxy equivalent weights (EEW) were determined using a previously described procedure.[52] Ethyltriphenylphosphonium acetate−acetic acid complex (Alfa Products) was used as a 70% solution in methanol. HPLC-grade tetrahydrofuran (THF), dimethylformamide (DMF), and methanol were obtained from Fisher Scientific Co. Ethanol and anhydrous DMF were obtained from Aldrich and were used without further purification. Propylene glycol monophenyl ether (DOWANOL® PPh glycol ether) was obtained from Dow Chemical and was distilled over anhydrous potassium carbonate (with a small amount of $SnCl_2$) before use.

Analytical Techniques. ^{1}H NMR spectra were recorded with use of a Varian VXR 300 NMR spectrometer operated at 300 MHz. Chemical shifts are relative to tetramethylsilane at $\delta = 0$. ^{13}C NMR (^{1}H decoupled) spectra were recorded with use of a Varian VXR 300 NMR spectrometer operated at 75.4 MHz. Spectra were referenced to internal tetramethylsilane at 0 ppm. Mass spectral analyses were carried out with a Hewlett-Packard 5989A mass spectrometer. Neat samples were introduced by the direct insertion probe (DIP) method using a temperature program of 25−300 °C over 12 min. Elemental analyses were obtained with a Perkin-Elmer PE2400 CHN elemental analyzer.

Gel permeation chromatography (GPC) was carried out with the use of a Hewlett-Packard 1090 Series II HPLC system fitted with an autosampler and diode array detector interfaced to a Pascal Series ChemStation. Sample concentrations were approximately 1% by weight, and a typical injection volume was 25 μL. DMF containing 0.05% (w/v) LiCl was used as eluent for all GPC analyses. Analyses were carried out at 40 °C with a flow rate of 0.5 mL/min. Detection was limited to 264 ± 2 nm, and calibration was carried out with use of a series of narrow polystyrene standards (Polymer Laboratories EasiCal™ M_w = 3 000 000−580). A Polymer Laboratories 10 μm mixed D column was used. Use of the GPC software supplied with the ChemStation allowed construction of a third-order calibration based on the polystyrene standards. The parameters from this calibration were used along with the observed elution profile of the sample at 264 nm to arrive at values for M_w and M_n. Inherent viscosities (η_{inh}) of the polymers were obtained with use of a Schott-Ubbelohde dilution viscometer maintained at 25.0 °C. Viscosity measurements were carried out in DMF solvent at a concentration of 0.5 g/100 mL. 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. 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. Preparation of thin polymer films for O_2TR determination has been described previously.[25]

General Procedure for the Synthesis of Amide-Containing Bisphenols 3−15. The diacid chloride (0.25 mol) was dissolved in THF (300 mL) and added dropwise over 1 h to a solution of 3- or 4-aminophenol (110.4 g, 1.01 mol) in THF (1000 mL). On completion of addition, the mixture was stirred at room temperature for 18 h. In most cases, the bisphenol precipitated from solution. The precipitated solids were collected by filtration, washed with water, and washed with THF. In cases where the bisphenol did not precipitate from solution, the THF solution was evaporated to dryness and then poured into water to isolate the crude amide-containing bisphenol. Generally, the crude solid was recrystallized twice from an ethanol/water solvent system[53] with use of decolorizing charcoal. In cases where the bisphenols were difficult to recrystallize due to insolubility (such as **9** and **14**), the compounds were heated in ethanol/water and acetone/water mixtures to extract impurities before use in polymerization reactions. The bisphenols were dried *in vacuo* at 120 °C for 24 h. Yields ranged between 14% and 95%. Characterization data are given in Tables 1−3. Details regarding the synthesis of **6** are given in a previous publication.[20] The synthesis of amide-containing bisphenol **7** is given below.

Synthesis of *N,N′*-Bis(3-hydroxyphenyl)adipamide (7). Adipoyl chloride (46.5 g, 0.25 mol) was dissolved in THF (300 mL) and added dropwise to a solution of 3-aminophenol (110 g, 1.01 mol) in THF (1000 mL). Within several minutes, a precipitate of **7** and 3-aminophenol hydrochloride appeared. On completion of addition, the mixture was stirred at room

temperature for 18 h. The precipitated solids were collected by filtration and were washed with water followed by washing with THF. The crude solid was recrystallized twice from 1:1 ethanol/water with use of decolorizing charcoal. Pure **7** was dried *in vacuo* at 120 °C for 24 h to yield a white solid with a melting point of 247−250 °C. Yield: 70 g (85%).

Synthesis of *N*-(4-Hydroxyphenyl)-4-hydroxybenzamide (4,4′-Dihydroxybenzanilide) (16). A published procedure was used[39] with the following modifications. The crude amide (56.1 g) was recrystallized by dissolving the material in boiling absolute ethanol (1.2 L) and reducing the volume to 700 mL. The solution was diluted with water (150 mL) and was cooled to 25 °C, which caused a white solid to precipitate. Yield: 28.4 g after air-drying, mp 268−269 °C (lit.[40] 256−258 °C). An additional 17.0 g was obtained from a second crop. Total yield = 45.4 g (42%). Mass spectrum (*m*/*e*): Found: 229; calcd: 229. ^{1}H NMR (acetone-d_6): δ 9.40 (s, 1H), 9.1 (br s, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.4, 2H). ^{13}C NMR (acetone-d_6): 165.94, 161.66, 154.90, 132.39, 130.34, 127.19, 123.13, 115.96, 115.90 ppm (all singlets). Elemental Anal. Found: C, 67.83; H, 4.62; N, 5.99. Calcd: C, 68.11; H, 4.84; N, 6.11.

Synthesis of *N*-(3-Hydroxyphenyl)-3-hydroxybenzamide (3,3′-Dihydroxybenzanilide) (17). To a solution of thionyl chloride (652 g, 5.48 mol) and anhydrous dimethylformamide (0.50 mL) was added 3-hydroxybenzoic acid (60.0 g, 0.434 mol) in several portions over a 40 min period. The magnetically stirred slurry was heated at 45 °C during the addition, and the temperature was gradually increased to 80 °C over the next hour. After a total of 2.5 h, the reaction mixture was concentrated under reduced pressure at 50 °C. Further concentration under high vacuum for 2 h yielded 96.7 g of a pale yellow liquid. A solution of the yellow liquid (78 g) in acetonitrile (50 mL) was added dropwise to a solution of 3-aminophenol (115 g, 1.05 mol) in acetonitrile (550 mL) over 1.5 h. The temperature was maintained at 20−30 °C with use of a cooling bath. After stirring at 20−30 °C for a total of 2 h, the reaction mixture was filtered and the filtrate was concentrated. The resulting black gum was partitioned between methyl isobutyl ketone (400 mL) and 6% aqueous HCl (150 mL). The organic layer was washed with another portion of 6% aqueous HCl (50 mL) and concentrated under reduced pressure to yield a black gum (96.5 g). The gum was recrystallized twice from water after decanting the hot solution from an insoluble black oil. The product was then recrystallized from butyl acetate. Yield: 28.0 g (28%), mp 191−193 °C (lit.[42] 197 °C). Mass spectrum (*m*/*e*): Found: 229; calcd: 229. ^{1}H NMR (acetone-d_6): δ 9.41 (s, 1H), 8.74 (s, 1H), 8.45 (s, 1H), 7.57 (t, J = 2.1 Hz, 1H), 7.46−7.42 (m, 2H), 7.30 (t, J = 8.0 Hz, 1H), 7.26 (dm, J = 8.0 Hz, 1H), 7.15 (t, J = 8.0 Hz, 1H), 7.03 (ddd, J = 8.0, 2.4, and 1.1 Hz, 1H), 6.62 (ddd, J = 8.0, 1.4, and 1.1 Hz, 1H). ^{13}C NMR (acetone-d_6): 166.61, 158.55, 158.34, 141.23, 137.78, 130.32, 130.18, 119.31, 119.19, 115.32, 112.27, 111.77, 108.33 ppm (all singlets). Elemental Anal. Found: C, 67.26; H, 4.62; N, 5.88. Calcd: C, 68.11; H, 4.84; N, 6.11.

General Procedure for the Synthesis of Poly(hydroxy amide ethers) 19−32. Polymers **19−32** were prepared using the following procedure. Bisphenol-A diglycidyl ether [6.98 g of EEW = 171.1 g/ equiv wt epoxide, 40.80 mequiv (or mmol) of epoxide], the amide-containing bisphenol (20.00 mmol, 40.00 mmol phenolic groups), and propylene glycol monophenyl ether (15 mL) were added to a 100 mL polymerization reactor, which was then fitted with a thermometer, overhead mechanical stirrer assembly, and nitrogen inlet and outlet adapters. The mixture was heated to 140 °C, and 15 drops of ethyltriphenylphosphonium acetate−acetic acid complex (70% in methanol) were added. The temperature of the reaction mixture rose to 145 °C and was maintained at 155−165 °C. During this time, the amide-containing bisphenol reacted and the solution became increasingly viscous over a 10−15 min period. More propylene glycol monophenyl ether (10−20 mL)[54] was added as the solution reached maximum viscosity and was maintained at 155 °C for several minutes. A solution of *tert*-butylphenol (0.6 g, 4.0 mmol) in propylene glycol monophenyl ether (5 mL) was then added along with more phosphonium catalyst (5 drops). The solution was stirred at 160−165 °C for 30−60 min and then was diluted to a volume of 100 mL with DMF. The solution was precipitated into a 3:1 mixture of methanol and water (400 mL) in a high-speed blender. Solvent was decanted, and the polymer was washed in the blender by the addition of methanol (300 mL), followed by water (100 mL) after several minutes. The white granular or fibrous polymer was collected via filtration, air-dried, and then redissolved in 95:5 THF/water (100 mL). The polymer was precipitated a second time as described previously and then dried *in vacuo* at 80 °C for 24 h. Yields were typically 70−90%. Complete characterization data are given in Tables 4−6.

Acknowledgment. We thank Tom Chamberlin for carrying out GPC analyses.

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(43) Low-molecular weight polymers were obtained when the malonamide (**4**) and succinamide (**5**) bisphenols were allowed to react with bisphenol A diglycidyl ether by the route shown in Scheme 3. The reaction between malonamide **4** and bisphenol-A diglycidyl ether gave a highly discolored solution and showed no increase in solution viscosity, suggesting that little or no polymerization occurred. The methylene protons of **4** are potentially acidic enough to participate in side reactions which might disrupt the stoichiometry and prevent formation of high-molecular-weight species. The polymerization of succinamide **5** with bisphenol-A diglycidyl ether routinely yielded poly(hydroxy amide ethers) with inherent viscosities of 0.2−0.3 dL/g, too low to fabricate films for O_2-TR determination.
(44) During the reactions of isomeric bisphenols **16**−**18** with bisphenol-A diglycidyl ether, it appeared that (qualitatively) the 3,3′-isomer (**17**) reacted fastest, followed by the 4,4′-isomer (**16**), then the 2,4′-isomer (**18**) (slowest). The differences in reactivity between the 3,3′- and 4,4′-isomers may be due, in part, to the poorer solubility of the 4,4′-isomer (**16**) in the reaction medium when compared to the 3,3′-isomer (**17**). With respect to 2,4′-isomer **18**, it has been our experience that *ortho*-substituted phenols are more sluggish in their reactions with glycidyl ethers than their *meta*- and *para*-substituted counterparts, presumably for steric reasons. This might provide an explanation for the slower buildup of molecular weight observed during the reaction of **18** with bisphenol-A diglycidyl ether to yield polymer **29**.
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(46) Polymer **22** (which was end-capped with *tert*-butylphenol) was heated at 230 °C for 1 h without change in melt flow rate or molecular weight (as determined by inherent viscosity analysis). By contrast, samples of **22** prepared without the use of end-capping agent either cross-linked or advanced in molecular weight under the same conditions. The melt stability and mechanical property evaluation of **22** and other poly(hydroxy amide ethers) will be described in a future publication.
(47) We report and compare all oxygen transmission rate (O_2TR) data at about 50−80% relative humidity (RH). In this humidity range, we have found that there is little change in O_2TR for poly(hydroxy amide ethers) and other "phenoxy-type" thermoplastics. For example, the difference in O_2TR for polymer **22** at 50−60% vs 70−80% RH is small, about 0.1 BU (Figure 3). This allows comparisons to be made between different poly(hydroxy amide ethers) in order to determine the effect that polymer structure has on O_2TR.
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(53) The bisphenol was recrystallized by (a) heating in water to boiling, followed by the addition of ethanol until dissolved, or (b) heating in ethanol to boiling, followed by the addition of water until dissolved.
(54) It was sometimes necessary to modify the procedure slightly depending on the amide-containing bisphenol used. For example, the synthesis of polymer **28** required a more dilute solution (15 mmol of each monomer, 20−30 mL of propylene glycol monophenyl ether) to prevent cross-linking.

MA9517207