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High-Barrier Poly(hydroxy amide ethers): Effect of Polymer Structure on Oxygen Transmission Rates. 2[1]

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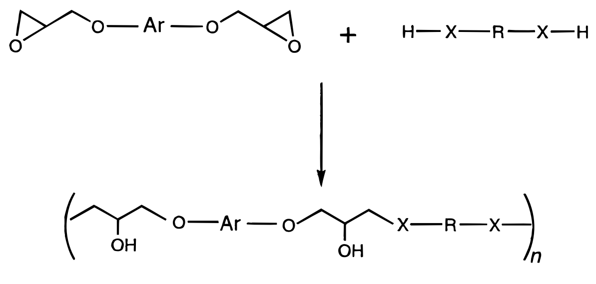
ABSTRACT: The synthesis of a series of new high-barrier poly(hydroxy amide ethers) is described. The polymers are formed by the reactions of Bisphenol A diglycidyl ether, $\overline{\mathrm{OCH_2C}}\mathrm{HCH_2OC_6H_4C(CH_3)_2C_6H_4}$-$\mathrm{OCH_2}\overline{\mathrm{CHCH_2O}}$, with a series of *N,N′*-alkylenebis(4-hydroxybenzamides) of general formula HOC_6H_4-$CONHRNHCOC_6H_4OH$ [R = $-(CH_2)_{2-6}-$, $-CH_2CH(OH)CH_2-$, $-CH_2C_6H_4CH_2-$, or $-C_6H_4-$] at 140−160 °C in propylene glycol monophenyl ether solvent using ethyltriphenylphosphonium acetate as initiator. Poly(hydroxy amide ethers) of general structure $[-CH_2CH(OH)CH_2OC_6H_4C(CH_3)_2C_6H_4OCH_2CH(OH)$-$CH_2OC_6H_4CONHRNHCOC_6H_4O-]_n$ are readily prepared in high molecular weight. These amorphous thermoplastics have glass transition temperatures (T_g) of 110−152 °C and oxygen transmission rates (O_2TR) which range from 1.0 to 2.8 cc·mil/(100 in.^{2}·atm·day) (barrier units or BU) at 23 °C and 58−86% relative humidity. The effect that polymer structure has on O_2TR and T_g is discussed. Of special interest is the poly(hydroxy amide ether) in which R = m-C_6H_4-. This polymer combines a good oxygen barrier (1.5 BU) with the T_g of an engineering thermoplastic (152 °C).

Introduction

As polymers continue to replace glass and metal in various packaging applications, special efforts must be made to design materials which retard the permeation of gases such as oxygen, carbon dioxide, or water vapor through the polymer matrix.[2,3] This is important for preventing contact of atmospheric oxygen with oxygen-sensitive foods and beverages or to prevent loss of certain gases out of a container, as is the case with retention of carbon dioxide in poly(ethylene terephthalate) (PET) beverage bottles. A number of organic polymers are known which provide a barrier to such atmospheric gases. These include the well-known poly(vinylidene chloride)-based copolymers,[4] ethylene−vinyl alcohol copolymers (EVOH),[5,6] polyamides,[7,8] polyesters,[9−12] and acrylonitrile copolymers.[13,14]

An additional, emerging class of high-barrier polymers are "phenoxy-type" thermoplastics (**1**),[15−25] prepared by the reactions of aromatic diglycidyl ethers with bisphenols, primary amines, bis-secondary amines, dicarboxylic acids, dithiols, bis(*N,N′*-dialkyldisulfonamides), and other dinucleophilic species (Scheme 1). It is believed that the high barrier properties of phenoxy-type thermoplastics are due, in part, to the ability of the polymer chains to pack efficiently, which impedes the migration of oxygen and other gases through the polymer matrix.[2] This strong interchain cohesion is presumably a consequence of (a) of strong hydrogen bonding interactions, due to the presence of polar backbone units and (b) a compact backbone structure without bulky side groups. To date, over 100 different phenoxy-type thermoplastics of general structure **1** have been prepared,[15−41] with oxygen transmission rates (O_2-TR) of 0.1−20 cc·mil/(100 in.^{2}·atm·day) (barrier units or BU) and glass transition temperatures ranging from subambient temperatures to well over 200 °C.

Scheme 1



1

[X = -O-, -N(R)-, -C(O)O-, -SO_2N(R)-, etc.]

In a previous paper,[24] we reported the synthesis, characterization, and oxygen barrier properties of poly(hydroxy amide ethers) (**2**), a subclass of phenoxy-type barrier thermoplastics. In that paper, we described the advantages of combining amide and hydroxyl moieties in the same polymer backbone, as a means by which to improve oxygen barrier properties of the polymers. This powerful combination of polar functionalities is believed to yield strong intermolecular adhesion through hydrogen bonding interactions,[42] which leads to the excellent barrier properties observed. In addition to the presence of polar amide and hydroxy units in the polymer backbone, barrier properties improve even further when the polymer repeat unit contains either (a) a high concentration of polar functionalities (i.e., two amide units instead of one, few nonpolar methylene backbone segments, etc.) or (b) the presence of *m*-phenylene vs *p*-phenylene segments. The best barrier properties result when the polymer repeat unit incorporates both of these structural features.

As part of our continuing efforts to understand the effect that polymer structure has on oxygen transmission rates and glass transition temperatures of poly(hydroxy amide ethers), a series of new derivatives (general structure **3**) have been prepared. The main general difference between the new derivatives (**3**) and

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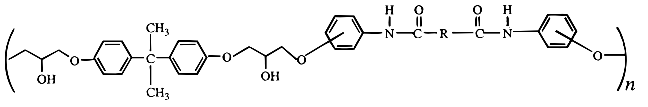
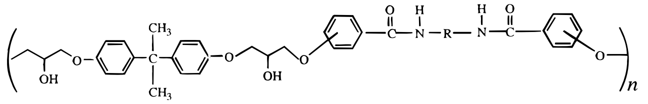
those originally reported (**2**) is that the amide linkages in the polymer backbone are reversed. In addition, poly(hydroxy amide ethers) **3** contain backbone linkages not included in our earlier study of polymers **2**. The synthesis of poly(hydroxy amide ethers) **3** was accomplished by first carrying out the synthesis of new amide-containing bisphenol monomers which contained a variety of structural subunits. The bisphenols were then incorporated into the polymer backbone, yielding poly(hydroxy amide ethers) **3** with various "R" groups. This diversity in polymer structure allows a number of structure vs property comparisons to be made between the different examples of **3**. In addition, comparisons can be made between polymers **3** and **2**, in which there is a different arrangement of the amide groups in the polymer backbone.



2 (Previous work)



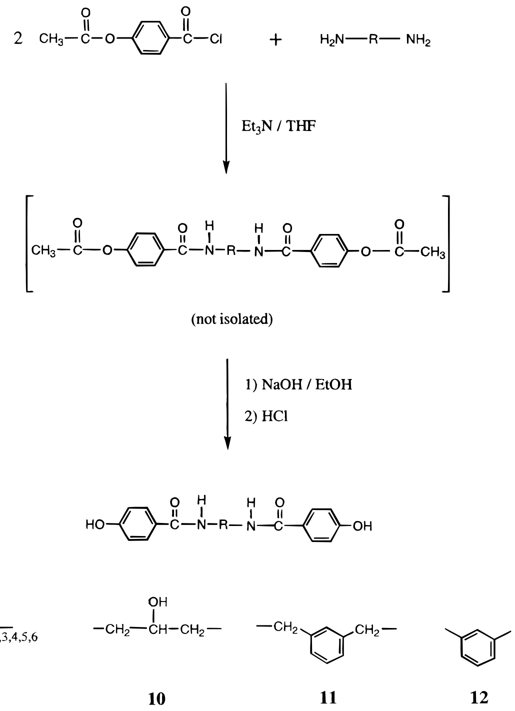
3 (This work)

The primary objective of this study was to understand more about the effect that polymer structure has on oxygen transmission rates (O_2TR) and glass transition temperatures (T_g) of poly(hydroxy amide ethers). Specifically, we wanted to answer the following questions: (1) How is O_2TR affected as the number of methylene units between amide linkages increases? (2) Can exceptionally high glass transition temperatures be realized without sacrificing barrier properties? (3) Can barrier properties be fine-tuned by the addition (or removal) of hydrogen bonding sites in the polymer backbone. (4) How are O_2TR and T_g affected by reversing the amide linkages in the poly(hydroxy amide ether) backbone (i.e., comparision of polymers **2** and **3**)? 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 series of amide-containing bisphenols based on *N*,*N*′-alkylenebis(4-hydroxybenzamides).

Results and Discussion

Synthesis of Amide-Containing Bisphenols. The synthesis of *N*,*N*′-alkylenebis(4-hydroxybenzamides) **5**−**13** (Table 1) was carried out by the reactions of 4-acetoxybenzoyl chloride with various diamines, followed by removal of the acetoxy protecting group with base (Scheme 2). The intermediate acetoxy-protected bisphenols (not isolated) were prepared in THF using triethylamine as the hydrochloride acceptor. Removal of the acetoxy group was accomplished by treatment of the crude acetate esters with hot aqueous ethanolic NaOH, without any detectable hydrolysis of the amide linkages. The bisphenols were isolated as high-melting white solids in 31−74% yield after two recrystallizations from ethanol. The amide-containing bisphenols were characterized by a combination of ^1H NMR spectroscopy, ^{13}C NMR spectroscopy (Tables 2 and 3 respectively, Supporting Information), and mass spectrometry (Table 1), which confirmed the identity of the materials.

Scheme 2

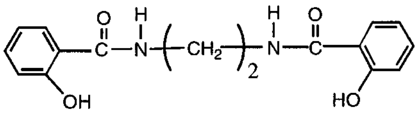
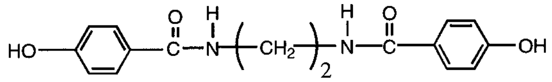
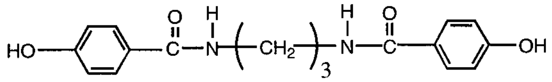
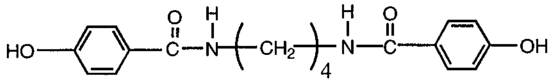
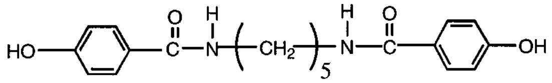
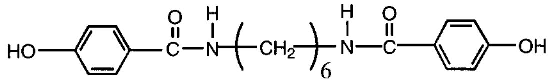
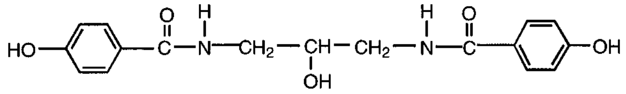
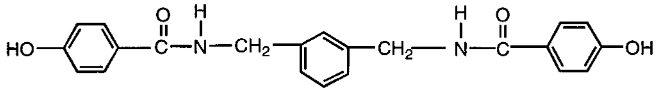
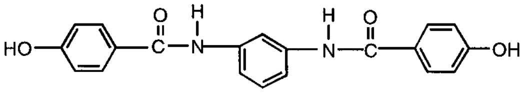
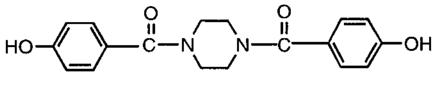


Although many *N*,*N*′-alkylenebis(2-hydroxybenzamides) [or bis(salicylamides)] such as **4** are known,[43−50] only a few of the analogous 4-hydroxybenzamides (**5**−**13**, Table 1) have been reported.[32,33,51−53] The process shown in Scheme 2 provides a straightforward general synthesis for amide-containing bisphenols **5**−**12**. Piperazine-based **13** (not shown in Scheme 2) was prepared by the same method. During the synthesis of species **10** via reaction of 1,3-diamino-2-propanol with excess of acetoxybenzoyl chloride, some of the hydroxyl groups of the diaminopropanol unit were esterified. However, all of the ester groups were removed by treatment of the ester species with ethanolic NaOH. The ethylenediamine-based bis(salicylamide) **4** was prepared by an alternative procedure, which made use of the reaction of ethylenediamine with phenyl salicylate in hot toluene (see Experimental Section).

Poly(hydroxy amide ether) Synthesis and Characterization. Poly(hydroxy amide ethers) **14**−**23** (Table 4) were prepared by the reactions of the amide-containing bisphenols with Bisphenol A diglycidyl ether (BA−DGE) (Scheme 3), using a previously described synthetic methodology.[24] The reactions are carried out in propylene glycol monophenyl ether at elevated temperatures (140−165 °C) with the use of a ethyltriphenylphosphonium acetate−acetic acid complex (70% in methanol) as catalyst. During the polymerization, 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 83−91%. The poly(hydroxy amide ethers) were characterized by a combination of ^1H NMR and ^{13}C NMR spectroscopy (Tables 5 and 6, respectively, Supporting Information), differential scanning calorimetry (DSC), and inherent viscosity (η_{inh}) determination (Table 4). Oxygen transmission rates (O_2TR) were determined (Table 4) and are described in detail later in the text.

During the synthesis of poly(hydroxy amide ethers), the potential exists for amide units in the bisphenol

Table 1. Characterization Data for Amide-Containing Bisphenols

No.	Amide-Containing Bisphenol	M.P. (°C)	Yield (%)	Mass Spec. (*m/e*) found	Mass Spec. (*m/e*) calc
4		181-183 (lit.[44,45]: 187-189) (lit.[46]: 184-186) (lit.[47]: 181) (lit.[43]: 183-184)	45	300	300
5		254-256	51	300	300
6		216-217	70	314	314
7		244-246	74	328	328
8		211-213	64	342	342
9		225-227 (lit.[51]: 225-227) (lit.[52]: 220-222)	60	356	356
10		199-203	31	312[a]	330
11		229-231	74	376	376
12		303-305	73	348	348
13		259-265	91	326	326

[a] Observed peak corresponds to M − 18 (loss of water).

monomers (or newly-formed polymer backbone) to react with the oxirane rings of the diglycidyl ether species. However, there appears to be little or no reaction between amide and oxirane units during polymer synthesis. Poly(hydroxy amide ethers) **14**−**23** are formed in high molecular weight and no cross-linked materials were detected. It was also determined that soluble, melt-stable, high-molecular-weight poly(hydroxy amide ethers) are only formed when the following reaction conditions are employed: (a) careful control of reaction temperature and solution viscosity during synthesis, (b) the use of 2% excess diglycidyl ether monomer, and (c) consumption of residual epoxide species with an end-capping unit such as *tert*-butylphenol at the end of the polymerization reaction. These observations are consistent with our previous work,[24] in which poly(hydroxy amide ethers) **2** were prepared by reactions of amide-containing bisphenols and diglycidyl ethers.

One curious exception to the syntheses described above was the preparation of bis(salicylamide) polymer **14** (Table 4), based on the bis-*ortho*-substituted monomer **4**. The polymer could not be prepared in high-molecular-weight under the reaction conditions used to prepare polymers **15**−**23**. Only low-molecular-weight **14** ($\eta_{\mathrm{inh}} \le 0.3$ dL/g) was obtained when ethyltriphenylphos-

Scheme 3

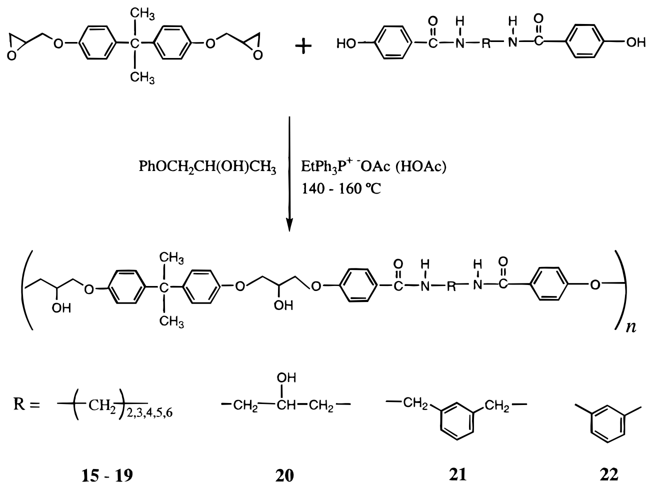
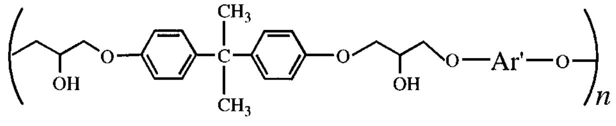
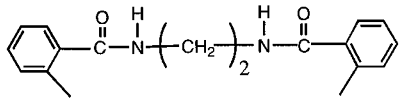
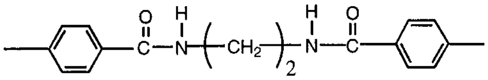
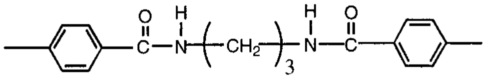
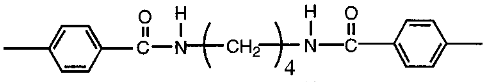
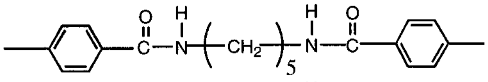
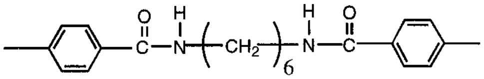
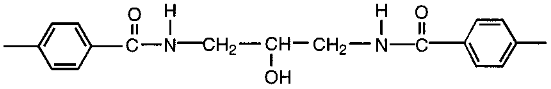
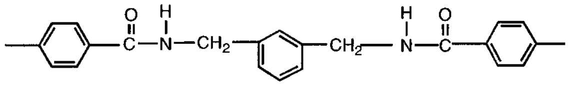
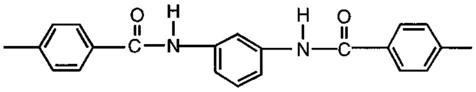
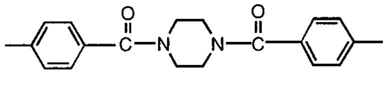


Table 4. Characterization Data for Poly(hydroxy amide ethers)



No.	Ar'	% yield	O_2TR $(BU)^{a,b,c}$	RH $(\%)^{d}$	T_g (°C)	η_{inh} $(dL/g)^{e}$
14		83	1.4 $(---)^{g}$	60-65 $(---)^{g}$	112 $(107)^{f}$	0.78 $(0.28)^{f}$
15		85	1.4	63-65	133	0.49
16		83	1.0	69-82	112	0.41
17		87	1.3	63-65	126	0.49
18		87	1.7	59-63	110	0.44
19		91	1.9	58-60	111	0.49
20		83	1.0	58-60	129	0.56
21		84	1.4	59-61	129	0.44
22		89	1.5	78-86	152	0.44
23		84	2.8	58-61	130	0.66

[a] ASTM method D3985-81. [b] Oxygen transmission rate (O_2TR) in cc·mil/(100 in.^{2}·atm·day) or barrier units (BU). [c] 1 BU = 5.996 × 10^{-3} Barrers (see ref 55). [d] Relative humidity (RH) of oxygen. [e] Concentration of 0.5 g/100 mL in DMF at 25.0 °C. [f] Low molecular weight polymer obtained from conventional synthesis. [g] Not measured due to the low molecular weight of the polymer, which yielded brittle compression molded films.

phonium acetate was used as the catalyst. However, a different catalyst, bis(triphenylphosphoranylidene)ammonium chloride,[54] effectively catalyzes formation of high-molecular-weight **14** (η_{inh} = 0.78 dL/g). Earlier, it was reported that bis(triphenylphosphoranylidene)ammonium chloride is an especially effective catalyst for the preparation of high-molecular-weight poly(hydroxy ethers).[54] However, the reasons for the efficacy of this catalyst during the preparation of polymer **14** are not clear at this time.

All of the poly(hydroxy amide ethers) prepared are of high molecular weight, yielding creasable films after fabrication by compression molding. Molecular weight data were obtained by inherent viscosity (η_{inh}) determination. Inherent viscosities of 0.41–0.78 dL/g were obtained in DMF at 25.0 °C. Polymers with inherent viscosities greater than approximately 0.40 dL/g yielded compression molded films which maintained their integrity during oxygen barrier testing. The ^{1}H NMR spectral data for the poly(hydroxy amide ethers) are given in Table 5 (Supporting Information) and are entirely consistent with the structures shown. Amide protons were detected at δ 8.2–10.2 while the resonances for the aromatic protons were found at δ 6.8–8.3. The hydroxyl, methine, and methylene protons of the 2-hydroxy-1,3-propylidene linkages were found at approximately δ 5.4, 4.1, and 4.0 respectively. Methylene protons between amide groups were generally detected at δ 1.3–3.5 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. Similarly, the ^{13}C NMR spectra (Table 6, Supporting Information) for poly(hydroxy amide ethers) **14**–**23** gave further evidence for the structures shown. The aromatic and carbonyl carbons were detected at 113–169 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 26–44 ppm, with those carbons closest to the amide linkages shifted downfield.

Effect of Polymer Structure on Oxygen Transmission Rates and Glass Transition Temperatures

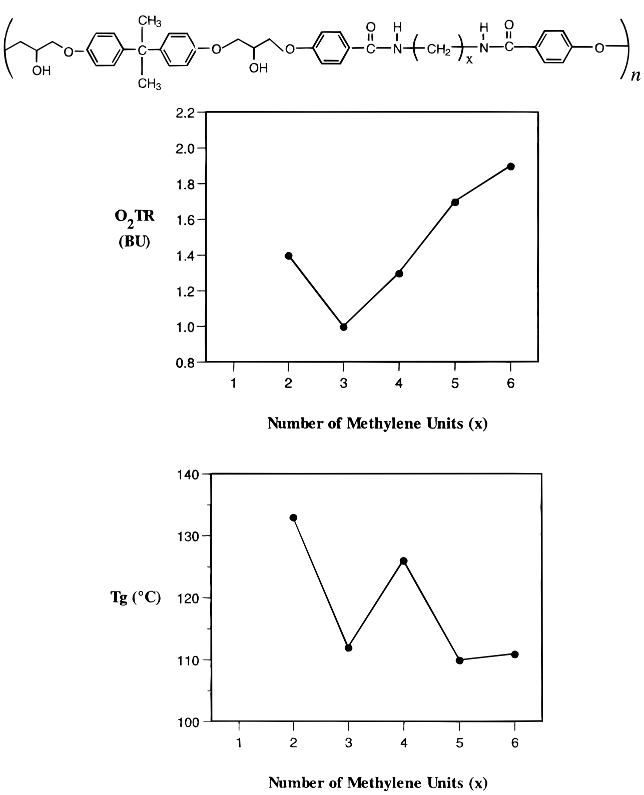
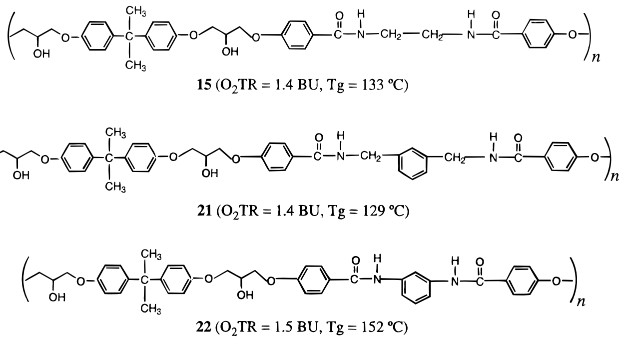


Figure 1. Effect of the number of backbone methylene units on O_2TR and T_g in polymers **15**−**19**.

of Poly(hydroxy amide ethers). Poly(hydroxy amide ethers) **14**−**23** exhibit good barrier to oxygen,[2] with oxygen transmission rates (O_2TR) that range from 1.0 to 2.8 cc·mil/(100 in.^{2}·atm·day) (barrier units or BU)[55] at 23 °C and 58−86% relative humidity. These values are intermediate between those of crystalline high-barrier materials such as poly(vinylidene chloride) copolymers and EVOH ($O_2TR < 0.2$ BU) and moderate oxygen barrier materials such as PET ($O_2TR = 5−10$ BU).[3] The oxygen barrier properties of poly(hydroxy amide ethers) **14**−**23** are more similar to those of amorphous polyamides, which have O_2TR of 0.5−4 BU at high humidity.[7] Although the poly(hydroxy amide ethers) reported in this paper have O_2TR of >1 BU, other amorphous poly(hydroxy amide ethers) have been prepared with O_2TR of 0.1−1 BU at high relative humidities.[19,23,24]

The glass transition temperatures (T_g) of poly(hydroxy amide ethers) **14**−**23** range from 110 to 152 °C, as determined by DSC analysis (Table 4). All of **14**−**23** are amorphous thermoplastics, with no evidence for crystalline melting transitions from 50 to 250 °C. Thus, effects of structural features on O_2TR behavior can be readily assessed without the complicating influences of morphological differences in the polymer matrix.[56]

(a) Length of Methylene Chain between Amide Units. Increasing the length of the methylene chain between amide groups in poly(hydroxy amide ethers) causes oxygen transmission rates to increase (Figure 1). In the series of **15**−**19**, ($x = 2−6$) oxygen transmission rates increase from 1.0 to 1.9 BU as the number of methylene units increases from three to six, a pattern which has been observed for other poly(hydroxy amide ethers).[24] This increase in O_2TR is believed to result from a reduction in the number of hydrogen bonding units (amide and hydroxyl) per unit chain length, as the number of methylene units increase. One exception to this trend is polymer **15** ($x = 2$, Figure 1), which has an O_2TR of 1.4 BU. This is higher than the O_2TR of 1.0 BU determined for **16** ($x = 3$). One explanation, which we have proposed for other anomalies of this type,[24] is that the polar amide backbone units require some minimal separation in order to act as two effective and independent hydrogen bonding sites. In polymer **15**, the amide units may act as one localized hydrogen bonding site due to the relatively short dimethylene segment between them. Also, the close proximity of the amide units to one another may lead to *intra*molecular hydrogen bonding interactions, at the expense of *inter*molecular hydrogen bonding interactions. Both of these effects minimize the full benefit of having the two strong hydrogen bonding functionalities in the polymer repeat unit.



15 (O_2TR = 1.4 BU, Tg = 133 °C)

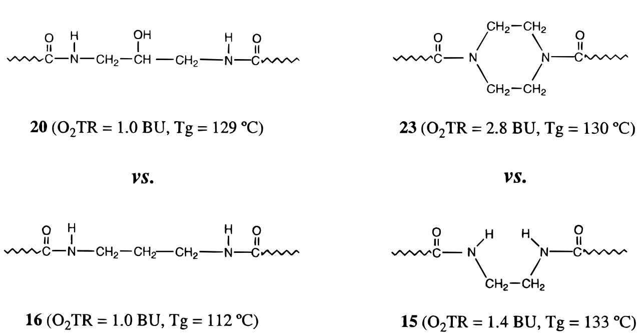
21 (O_2TR = 1.4 BU, Tg = 129 °C)

22 (O_2TR = 1.5 BU, Tg = 152 °C)

Figure 2. Effect of various backbone units on O_2TR and T_g in polymers **15**, **21**, and **22**.

The glass transition temperatures in amorphous polymers **15**−**19** follow an unusual even/odd “sawtooth” pattern (Figure 1). Glass transition temperatures decrease from 133 to 126 to 111 °C in the polymers with two, four, and six methylene groups respectively (**15**, **17**, **19**). The polymers with the odd number of methylene units (**16**, **18**) also appear to follow this trend. In either series, the lower T_g values are presumably due to the increase in torsional mobility of the polymer backbone as the length of the methylene chain increases. This sawtooth pattern has also been observed for the change in crystalline melting points (T_m) of aliphatic polyamides as methylene segment length changes.[57] This similarity is curious since the T_g and T_m are measures of completely different phenomena. Interestingly, the melting points of the amide-containing bisphenol monomers **5**−**9** also follow this trend.

(b) Effect of Incorporating Additional Aromatic Units into the Polymer Backbone. The replacement of some or all of the methylene groups by *m*-phenylene units in the poly(hydroxy amide ether) backbone improves T_g without detrimentally affecting the barrier properties of the polymers. This is shown by the comparison of polymers **15**, **21**, and **22** in Figure 2. Polymers **21** and **22**, which contain the *m*-xylylene and *m*-phenylene groups between amide units, respectively, have O_2TR of 1.4−1.5 BU which is equivalent to that of ethylidene-based **15** (1.4 BU). The comparison of **15** to **21** (Figure 2) is of interest, since the $-CH_2CH_2-$ and m-$CH_2C_6H_4CH_2-$ backbone segments have about the same effect on O_2TR and T_g of poly(hydroxy amide ethers). Both polymers have of O_2TR of 1.4 BU, with glass transition temperatures near 130 °C. Apparently, the additional *m*-phenylene group in **21** disrupts neither chain packing nor backbone flexibility relative to **15**.



20 (O_2TR = 1.0 BU, Tg = 129 °C) **23** (O_2TR = 2.8 BU, Tg = 130 °C)

vs. *vs.*

16 (O_2TR = 1.0 BU, Tg = 112 °C) **15** (O_2TR = 1.4 BU, Tg = 133 °C)

Figure 3. Effect of additional hydrogen bonding groups on O_2TR and T_g in polymers **20** vs **16** and **23** vs **15**.

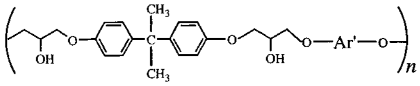
Polymer **22**, which contains the *m*-phenylene unit between the amide groups, is of special interest. In the first case, it has the highest T_g yet reported for a poly(hydroxy amide ether) of general structures **2** or **3** (i.e. derived from an amide-containing bisphenol and Bisphenol A diglycidyl ether). Second, it couples good oxygen barrier with an exceptionally high glass transition temperature of 152 °C. This is an unusual combination for high-heat amorphous thermoplastics, which typically are rather permeable to oxygen and other gases.[18,25]

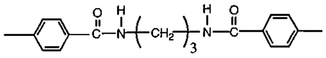
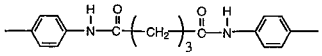
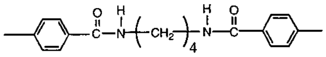
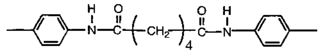
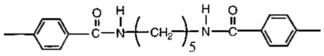
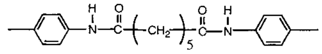
(c) Effect of Introduction and Removal of Hydrogen Bonding Sites. In simple terms, the incorporation of additional hydrogen bonding sites into polymer backbone might be expected to improve oxygen barrier properties by increasing interchain cohesion. However, as is the case for polymers with an abundance of polar functionalities (such as EVOH), an excess of polar functionalities can impart a sensitivity to the effects of moisture, which may diminish barrier properties. To determine the effect that the addition or removal of hydrogen-bonding sites would have on the oxygen transmission rates (and glass transition temperatures) of poly(hydroxy amide ethers), polymers **20** and **23** were prepared and compared to their structurally similar counterparts **16** and **15**, respectively (Table 4 and Figure 3).

The first example shows the comparison of polymer **20** to **16**. Both contain a three carbon linking unit between the amide segments, with an additional pendent hydroxyl group attached to the central carbon atom in **20**. Although **20** contains an additional hydrogen bonding site, no change in O_2TR is detected, since both polymers have O_2TR of 1.0 BU.[58] One possible explanation is that the benefit of the additional polar hydroxyl group is counteracted by the close proximity to the amides linkages. The group of two amides and one hydroxyl in **20** may lead to one localized hydrogen bonding site, instead of the two separate hydrogen bonding sites which exist when the hydroxyl group is not present (i.e. in **16**). This difference may diminish the overall interchain cohesion in the polymer backbone. However, polymer **20** has a T_g which is 17 °C higher than **16**, which does not contain the additional hydroxyl group. The additional hydroxyl group in **20** probably causes a decrease in the torsional mobility of the polymer chain relative to **16**, resulting in the higher T_g observed.

In the second example, piperazine-based **23** is compared to polymer **15**, derived from ethylenediamine. The additional ethylene bridge of the piperazine unit effectively converts the secondary amide nitrogen atoms into tertiary amides, essentially removing two powerful hydrogen bonding groups from the polymer backbone structure. This presumably causes a decrease in interchain cohesion, reflected by the higher O_2TR obtained for **23** vs **15** (2.8 vs 1.4 BU). These results are entirely consistent with previous work on the barrier properties of other poly(hydroxy amide ethers) which contain pendent primary, secondary, and tertiary amide units.[30] O_2TR increases as N-alkylation of the amide occurs, effectively reducing the number of N−H groups available for hydrogen bonding. Glass transition temperatures of **15** and **23** are comparable at 130 to 133 °C, apparently due to a trade-off in which torsional mobility of the polymer backbone is affected equally by the hydrogen-bonding interactions in **15** or by the increased backbone rigidity of the piperazinyl linking unit in **23**.

Table 7. Effect of Amide Reversal on O_2TR and T_g in Polymers 16−18



No.	Ar'	Tg (°C)	O_2TR (BU)[a]
16		112	1.0 (69-82 % RH)[b]
16' **(Ref 24)**		105	1.1 (73-80 % RH)[b]
17		126	1.3 (63-65 % RH)[b]
17' **(Ref 24)**		112	1.3 (75-85 % RH)[b]
18		110	1.7 (59-63 % RH)[b]
18' **(Ref 24)**		116	2.0 (60-62 % RH)[b]

[a] Oxygen transmission rate (O_2TR) in cc·mil/(100 in.^{2}·atm·day) or barrier units (BU). [b] Relative humidity (RH) of oxygen.

(d) Effect of Amide Reversal O_2TR and T_g. Not surprisingly, reversal of the amide linkages in otherwise identical poly(hydroxy amide ethers) does not appear to affect O_2TR in the polymers (Table 7). Poly(hydroxy amide ethers) species **16**, **17**, and **18** were compared to their counterparts **16′**, **17′**, and **18′** (see ref 24), in which the amide linkages in the polymer backbone are reversed. In each set of comparisons (**16**/**16′**, **17**/**17′**, and **18**/**18′**), O_2TR is approximately the same. This is consistent with a previous study in which barrier properties of a series of polyamides were compared, in which the amide linkages were also reversed.[7] The effect that amide reversal has on T_g is ambiguous, since increases in glass transition temperatures were detected in two of the three examples. Polymers **16** and **17** have T_g that are 7 and 14 °C higher than their counterparts **16′** and **17′** respectively, while species **18** has a lower T_g than does **18′** (110 vs 116 °C).

Conclusions

Several new high-barrier poly(hydroxy amide ethers) have been prepared by the reactions of Bisphenol A diglycidyl ether with a series of amide-containing bisphenols based on *N,N′*-alkylene-bis(4-hydroxybenzamides). These amorphous thermoplastics have oxygen transmission rates (O$_2$TR) which range from 1.0 to 2.8 cc·mil/(100 in.^{2}·atm·day) (barrier units or BU) at 23 °C and 58−86% relative humidity and have glass transition temperatures (T_g) of 110−152 °C. A detailed structure vs property analysis was carried out which determined the following: (1) Decreasing the number of methylene units between amide backbone segments tends to yield lower oxygen permeabilities. (2) Poly(hydroxy amide ethers) can be prepared which combine the glass transition temperature of an engineering thermoplastic (152 °C) with good barrier to oxygen (1.5 BU) by replacing methylene backbone segments with *m*-phenylene units. (3) O$_2$TR and T_g are affected by the addition or removal of various hydrogen bonding groups. (4) Amide reversal has little or no effect on oxygen barrier properties of poly(hydroxy amide ethers).

Experimental Section

Materials. Ethylenediamine, 1,3-diaminopropane, 1,3-diamino-2-hydroxypropane, 1,4-diaminobutane, 1,5-diaminopentane, hexamethylenediamine, *m*-xylylenediamine, phenyl salicylate, 4-acetoxybenzoic acid, thionyl chloride, triethylamine, bis(triphenylphosphoranylidene)ammonium chloride and bis(2-methoxy)ethyl ether were obtained from Aldrich and were used as received. The compound 1,3-phenylenediamine was obtained from Fluka and was used as received. Bisphenol A diglycidyl ether was purified by crystallization of liquid D.E.R. 332 epoxy resin (Dow Chemical) by seeding the liquid with crystalline Bisphenol A diglycidyl ether and allowing the mixture to stand for several weeks. The solidified D.E.R. 332 epoxy resin was then washed with methanol in a high speed blender to remove methanol-soluble impurities. The resulting white solid was filtered and dried *in vacuo* to remove residual methanol. Epoxy equivalent weights (EEW) were determined using a previously described procedure.[59] An ethyltriphenylphosphonium acetate−acetic acid complex (Alfa Products) was used as a 70% solution in methanol. HPLC-grade tetrahydrofuran (THF), dimethylformamide (DMF), toluene, and methanol were obtained from Fisher Scientific Co. Sodium hydroxide and hydrochloric acid were also obtained from Fisher Scientific Co. Ethanol was obtained from Aldrich and was 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. 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$_2$TR) were determined according to ASTM method D3985-81 with use of an OxTran 1050 system operated at 55 to 90% relative humidity of oxygen between 23 and 25 °C. Preparation of thin polymer films for O$_2$TR determination has been described previously.[29]

Synthesis of *N,N′*-1,2-Ethylenebis(salicylamide) (4). A modification of a previously described procedure was used.[43,60] Ethylenediamine (61.5 g, 1.02 mol) was added to a solution of phenyl salicylate (439 g, 2.05 mol) in toluene (600 mL). The reaction mixture was heated to reflux for 8 h and then allowed to cool. The precipitated solids were collected by suction filtration, were washed with toluene (400 mL), and then were allowed to air dry. The crude product was recrystallized twice from ethanol to yield a white solid, which was dried in vacuo at 100 °C for 16 h. Yield: 138.7 g (45%). Mp: 181−183 °C. (See Table 1 for other published melting points for **4**).

Synthesis of 4-Acetoxybenzoyl Chloride. The compound, 4-acetoxybenzoic acid (250 g, 1.39 mol), was added in 10−25 g portions over a 4 h period to thionyl chloride (300 g, 2.52 mol) at 60 °C. On completion of addition, the reaction mixture was heated to reflux for 3 h. Excess thionyl chloride was remove under reduced pressure. The residue was distilled at 120 °C (0.9 mmHg) to yield 4-acetoxybenzoyl chloride, which crystallized on standing. Yield: 258 g (93%).

General Procedure for the Synthesis of Amide-Containing Bisphenols 5−13. A solution of the diamine (0.075 mol) and triethylamine (42 mL, 0.3 mol) in THF (75 mL) was added dropwise to a stirred solution of 4-acetoxybenzoyl chloride (29.8 g, 0.150 mol) in THF (300 mL) over a 1 h period. As the amine reacted with the acid chloride, a white precipitate formed immediately. On completion of addition, the reaction mixture was stirred for 2−3 h and the white precipitate was collected via filtration. The white filter cake was stirred in water (250 mL) for several minutes, was collected via filtration, and was washed with water (100 mL). The white solid was then heated in a solution of sodium hydroxide (35 mL of 5 N, 0.175 mol) in 50% aqueous ethanol (400 mL) for 2 h at reflux. The solution was then cooled to room temperature and acidified with concentrated HCl until acidic to wet litmus (ca. 15 mL of concentrated HCl, 0.18 mol). The white precipitate was collected via suction filtration, was stirred in 500 mL of water for several minutes, was again collected via filtration, and was washed with water (1 L). Species **5**−**11** were typically recrystallized twice from 500 mL of 50% aqueous ethanol. Compound **12** was recrystallized from 1−2 L of 3:1 ethanol/water. Compound **13** had limited solubility in hot ethanol and hot ethanol/water mixtures. It was used as-synthesized, without recrystallization prior to use. Complete characterization data are given in Tables 1−3.

General Procedure for the Synthesis of Poly(hydroxy amide ethers) 15−23. Polymers **15**−**23** were prepared using the following procedure. Bisphenol A diglycidyl ether [6.98 g of EEW = 171.1 g/equiv wt of epoxide, 40.80 mequiv (or mmol) of epoxide], the amide-containing bisphenol (20.00 mmol, 40.00 mmol of phenolic groups), and propylene glycol monophenylether (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 monophenylether (10−20 mL) 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 monophenylether (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, 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 ranged from 83 to 91%. Complete characterization data are given in Tables 4−6.

Synthesis of Poly(hydroxy amide ether) 14. Bisphenol A diglycidyl ether [9.19 g of EEW = 170.2 g/equiv wt of epoxide, 54.00 mequiv (or mmol) of epoxide], the salicylamide bisphenol **4** (7.95 g, 26.50 mmol, 53.00 mmol of phenolic groups), bis(2-methoxy)ethyl ether (18 mL), and bis(triphenylphosphoranylidene)ammonium chloride (0.31 g) were added to a 100 mL polymerization reactor as described above. The reaction mixture was heated at 150 °C for 2 h, which caused a two phase system to form. Propylene glycol monophenylether (5 mL) was then added and heating was continued at 150 °C for an additional 3 h, and then the reaction mixture was diluted by the addition of DMF (20 mL). The solution was poured into methanol (400 mL) in a high-speed blender, which caused a gummy polymeric material to precipitate. The liquid was decanted, and the polymer was blended with a 2:1 methanol/water mixure. The liquid was decanted once again, and the polymer was allowed to stand in methanol for 72 h. Methanol was decanted, and the polymer was dissolved in DMF (50 mL), and then precipitated into water (500 mL) using the blender. The polymer was collected via filtration, air dried, and then dried *in vacuo* at 90 °C for 24 h. Yield: 14.3 g (83%). Inherent viscosity (η_{inh}): 0.78 dL/g (DMF, 25.0 °C, 0.5 g/dL). Glass transition temperature (T_g): 112 °C. Complete characterization data are given in Tables 4−6.

Acknowledgment. We thank Dan Murray for providing the modified procedure for the synthesis of bisphenol **4**. Chet Pawloski is thanked for providing the sample of bisphenol **13** used to prepare polymer **23**.

Supporting Information Available: Tables of NMR data for amide-containing bisphenols **4**−**13** (Tables 2 and 3) and poly(hydroxy amide ethers) **14**−**23** (Tables 5 and 6) (4 pages). Ordering and access information is given on any current masthead page.

References and Notes

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(55) Another well-recognized unit of gas permeability is the Barrer (10^{-10} cc (STP)·cm/(cm^2·s·cmHg)). Since one barrier unit (BU) equals 5.996 × 10^{-13} cc (STP)·cm/(cm^2·s·cmHg), *1 BU* = *5.996* × *10^{-3} Barrers*. Therefore, the oxygen transmission rates (O_2-TR) of poly(hydroxy amide ethers) **14**−**23** range from 6.0 × 10^{-3} to 17 × 10^{-3} Barrers.

(56) Additionally, there is no correlation between O_2TR and T_g in polymers **14**−**23** (nor other phenoxy-type thermoplastics that we have studied). For example, poly(hydroxy amide

ethers) **14**, **15**, and **21** all have O_2TR of 1.4 BU, but have T_g values of 112, 133, and 129 °C respectively. A plot of O_2TR vs T_g for **14**−**23** shows scattered data points that follow no discernible trend. Similar observations have been reported with other polymeric systems. See ref 7, Chapter 7.

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(58) It could be argued that the O_2TR of **16** (1.0 BU, 69−82 % RH) and **20** (1.0 BU, 58−60 % RH) would be different if measured at exactly the same relative humidity. However, we have found that there is little change in O_2TR (∼0.1−0.2 BU) for poly(hydroxy amide ethers) when determined at about 50−80 % relative humidity (RH).[24]

(59) Jay, R. R. *Anal. Chem.* **1964**, *36*, 667.

(60) Bertram, J. L.; Woo, E. P. (The Dow Chemical Company). U.S. Patent 4 367 328, 1983.

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