High-Barrier Poly(hydroxy amide ethers): Effect of Polymer Structure on Oxygen Transmission Rates. 3[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 aromatic diglycidyl ethers, $\overline{OCH_2CHCH_2}OArOCH_2\overline{CHCH_2O}$, with N,N'-bis(3-hydroxyphenyl)adipamide, $HOC_6H_4NHCO(CH_2)_4CONHC_6H_4OH$, at 140−160 °C in propylene glycol monophenyl ether solvent using ethyltriphenylphosphonium acetate as initiator. Poly(hydroxy amide ethers) of general structure $[-CH_2CH(OH)CH_2OArOCH_2CH(OH)CH_2OC_6H_4NHCO(CH_2)_4-CONHC_6H_4O-]_n$ are readily prepared in high molecular weight. The mainly amorphous thermoplastics have glass transition temperatures (T_g) of 78−146 °C and oxygen transmission rates (O_2TR) that range from 0.2 to 1.8 cc·mil/(100 in.^{2}·atm·day) (barrier units or BU) at 23 °C and 45−90% relative humidity. It was determined that barrier properties improve (i.e., O_2TR decreases) as the aromatic core unit, Ar, becomes less bulky or more polar. For example, the poly(hydroxy amide ether) in which Ar is the aromatic unit based on 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane has an O_2TR of 1.8 BU, while the poly(hydroxy amide ethers) in which Ar is based on the more compact 2,6-dihydroxynaphthylene or more polar 1,1-bis(4-hydroxyphenyl)acetamide units have lower O_2TR of 0.2 BU. In one instance, an amorphous poly(hydroxy amide ether) was induced to crystallize, yielding a semicrystalline polymer with significantly lower O_2TR. The derivative in which Ar is the 4,4′-biphenylene unit (O_2TR = 0.3 BU, T_g = 110 °C) was annealed at 160 °C to yield a crystalline material with significant improvement in oxygen barrier (O_2TR = 0.06 BU, T_g = 117 °C, T_m = 195 °C). Other effects that polymer structure has on O_2TR and T_g are discussed.

Introduction

A number of organic polymers are known which provide barrier toward gases such as oxygen, carbon dioxide, and water vapor. These include the well-known poly(vinylidene chloride)-based copolymers (PVDC),[2] ethylene-vinyl alcohol copolymers (EVOH),[3,4] poly-amides,[5,6] polyesters,[7−10] and acrylonitrile copolymers.[11,12] In each system, polymer structure and morphology play a key role in retarding the permeation of gases through the polymer matrix.[13,14] For example, 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. In other polymers, such as certain polyamides, subtle structural variations in the polymer backbone have been found to affect the oxygen barrier properties of the polymers.[5]

An additional, emerging class of high-barrier polymers are "phenoxy-type" thermoplastics (**1**),[15−29] 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. 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.[13,14] 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,[15−45]


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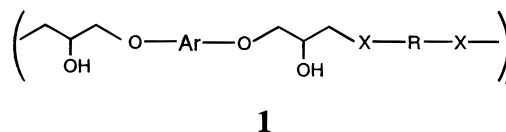
with oxygen transmission rates (O_2TR) of 0.04−20 cc·mil/(100 in.^{2}·atm·day) (barrier units or BU) and glass transition temperatures (T_g) that range from subambient temperatures to well over 200 °C.

In several of our previous papers,[24,26,27] we reported the synthesis, characterization, and oxygen barrier properties of poly(hydroxy amide ethers) (**2**), one subclass of phenoxy-type thermoplastics. The polymers were prepared by the reactions of Bisphenol A diglycidyl ether with amide-containing bisphenols in alcohol solvent at elevated temperatures. Two dozen poly(hydroxy amide ethers) of general structure **2** were prepared,

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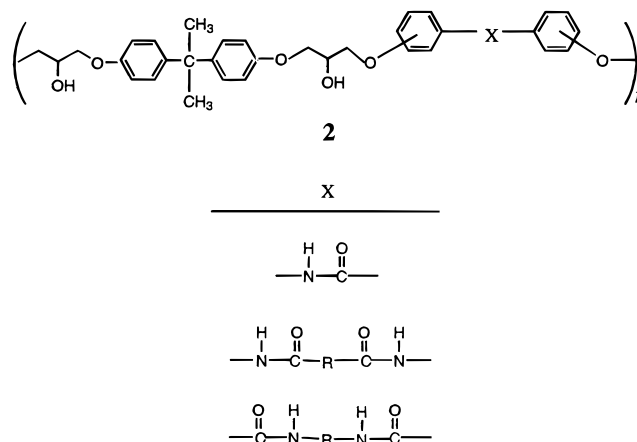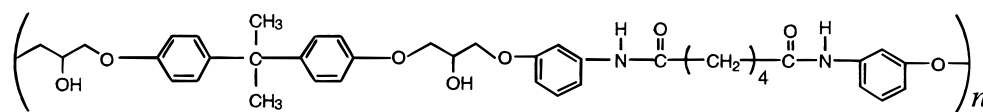
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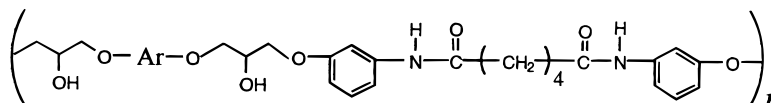
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yielding a wealth of information as to how changes in the amide portion of the polymer backbone affect oxygen transmission rates.[26,27] That work demonstrated the advantages of combining amide and hydroxyl moieties in the same polymer backbone, as a means to improve the oxygen barrier properties of the polymers.

Of special interest was polymer **3**, prepared by the reaction of Bisphenol A diglycidyl ether and *N,N*-bis-(3-hydroxyphenyl)adipamide.[26] The O_2TR of polymer **3** (0.8 BU) is one of the lowest reported for poly(hydroxy amide ethers) of general structure **2** (i.e., those that contain the isopropylidenediphenylene nucleus). This is attributed to the following key structural features of the amide unit that lead to low O_2TR: (a) *m*-phenylene units, (b) two amide units per repeat unit, and (c) a relatively short methylene segment between the amide groups.[26] In this paper, the synthesis of new poly-(hydroxy amide ethers) **4** has been carried out, in which the adipamide unit is held constant while the isopropylidenediphenylene unit is replaced with a wide variety of other aromatic (Ar) linkages. By following this strategy, both (a) the effects that various Ar groups have on O_2TR and T_g can be determined and (b) the synthesis of poly(hydroxy amide ethers) with exceptionally low O_2TR might be realized.

Specifically, we wanted to answer the following questions: (1) How are O_2TR and T_g affected by changing the aromatic unit (Ar) in poly(hydroxy amide ethers) **4**? (2) Can extraordinarily low O_2TR be obtained by the introduction of compact Ar units or those that contain additional hydrogen bonding moieties? (3) Do particular Ar groups induce crystallinity into the normally amorphous poly(hydroxy amide ether) backbone? (4) Can exceptionally high glass transition temperatures be realized without sacrificing barrier properties? These questions were answered by the synthesis of various aromatic diglycidyl ethers, followed by the subsequent incorporation of these units into the poly(hydroxy amide ether) backbone via reaction with *N,N*-bis(3-hydroxyphenyl)adipamide.

Results and Discussion

Monomer Synthesis. The synthesis of *N,N*-bis(3-hydroxyphenyl)adipamide (**5**) has been reported previously[26] and involves the reaction between adipoyl chloride and excess 3-aminophenol in THF solvent (Scheme 1). The excess aminophenol acts as the hydrogen chloride acceptor during this reaction and precipitates from solution along with bisphenol **5**. Bisphenol **5** was isolated and purified by extraction and recrystallization techniques. The yield of **5** after purification was typically 80–90%.

The aromatic diglycidyl ethers **6**–**22** (Table 1) were prepared by a standard procedure in which the ap-
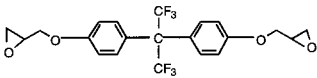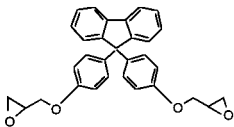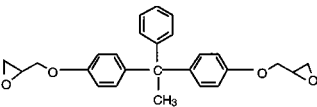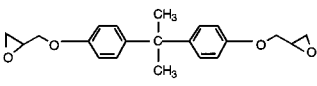
Scheme 1
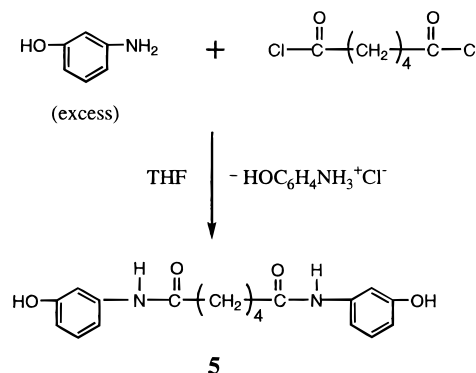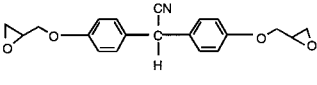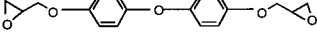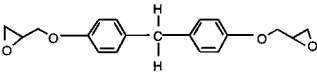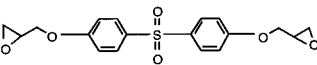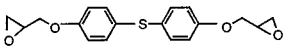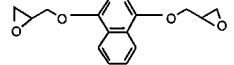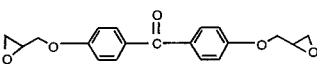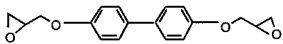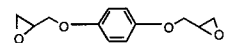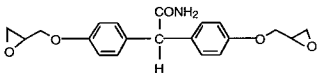
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propriate bisphenol is treated with an excess of epichlorohydrin in the presence of benzyltrimethylammonium chloride catalyst. Initially, the phenolic functionalities react with the epichlorohydrin to yield chlorohydrin and epoxide intermediate species over 24–48 h at 90 °C (Scheme 2). Conversion to the oxirane (epoxide) functionalities is completed by treatment with excess sodium hydroxide at 30 °C over 3–24 h. The unoptimized yields of the diglycidyl ethers ranged from 8 to 79% (Table 1). Species **6**–**22** were characterized by ^{1}H and ^{13}C NMR spectroscopy (Tables 2 and 3, respectively, Supporting Information). Epoxy equivalent weights (EEW) for the diglycidyl ethers were determined (Table 1) by standard methods prior to their use in polymerization reactions (see Experimental Section).

Most of the diglycidyl ethers shown in Table 1 are known in the literature.[32,41,46–58] However, various synthetic methodologies were used during their preparation and complete characterization was not carried out in most cases. In this work, diglycidyl ethers **6**–**22** were prepared using the same synthetic procedure and were fully characterized by a combination of NMR methods and epoxide equivalent weight determination. Additionally, many of the diglycidyl ethers described in the prior literature were prepared for use in *thermoset* applications, in which rigorous difunctionality (and, therefore, purity) was not a concern. However, to prepare *thermoplastic* polymers such as poly(hydroxy amide ethers) **23**–**39**, with the highest molecular weights possible, species **6**–**22*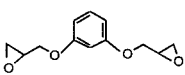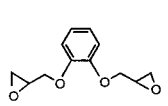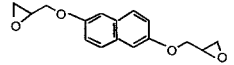* were required to be completely difunctional (i.e., no mono- or polyfunctional epoxides). Species **6**–**22** were purified by multiple recrystallizations or, in some cases, column chromatography on silica gel before use in polymerization reactions with bisphenol **5**. As a consequence, yield was sacrificed in order to isolate the purest sample of each diglycidyl ether used.

Poly(hydroxy amide ether) Synthesis and Characterization. Poly(hydroxy amide ethers) **23**–**39** (Table

Table 1. Characterization Data for Aromatic Diglycidyl Ethers

No.	Diglycidyl Ether	Approximate M.P. (°C)[a]	Yield (%)	EEW[b] found	calc
6	(structure)	84	8	222.6	224.2
7	(structure)	160	79	239.0	231.3
8	(structure)	oil	63	205.7	201.3
9	(structure)	53	---	171.1	170.2
10	(structure)	90 - 125	24	180.0	168.7
11	(structure)	91	73	158.7	157.2
12	(structure)	64	60	158	156.2
13	(structure)	170	47	195	181.2
14	(structure)	62	48	166	165.2
15	(structure)	114	58	140.2	136.2
16	(structure)	144	57	164.5	163.2
17	(structure)	140 - 165	28	151.6	149.2
18	(structure)	104	64	111.9	111.1
19	(structure)	49	44	112.1	111.1
20	(structure)	53	11	113.9	111.1
21	(structure)	145	17	141.3	136.2
22	(structure)	118	24	184.0	177.7

[a] As determined by DSC analysis (melting endotherm maximum). [b] Epoxide equivalent weight (EEW). Units of grams per equivalent weight of epoxide.

4) were prepared by the reactions of *N,N*-bis(3-hydroxy-phenyl)adipamide (**5**) with diglycidyl ethers **6−22** using a previously described synthetic methodology[26] (Scheme 3). 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 phe-

Scheme 2

6 - 22

Scheme 3

23 - 39
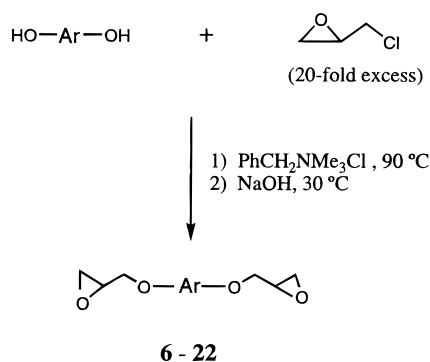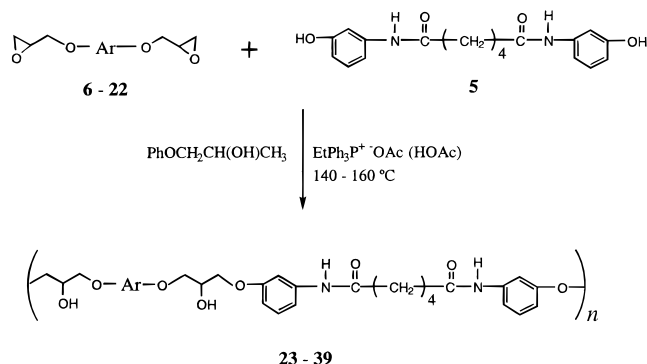
nolic groups react with the epoxide functionalities, generating the pendent secondary hydroxyl groups along the polymer backbone. Simultaneously, the amide units of **5** and the aromatic core units (Ar) of diglycidyl ethers **6−22** are incorporated into the polymer backbone. The polymers were isolated as granular or fibrous materials in yields of 61−95%. The poly(hydroxy amide ethers) were characterized by a combination of ^{1}H 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$_2$TR) 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 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 under the conditions used for these polymerization reactions. Poly(hydroxy amide ethers) **23−39** are formed in high molecular weight, and no cross-linked materials were detected. These observations are consistent with our previous work.[26,27] Even during the synthesis of polymer **39**, which has the more accessible pendent primary amide functionality, no cross-linked materials were obtained.

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 0.37−0.65 dL were obtained in DMF at 25.0 °C. 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 approximately δ 9.9, while the resonances for the aromatic protons were found at δ 6.6−8.2. The hydroxyl, methine, and meth-
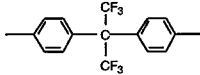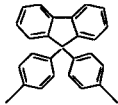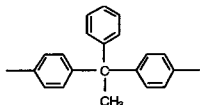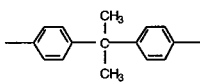
ylene protons of the 2-hydroxy-1,3-propylidene linkages were found at approximately δ 5.4, 4.1, and 4.0, respectively. Methylene protons between amide groups were detected at δ 1.6 and 2.3. Other protons associated with the particular Ar units were also detected. The integration areas for the protons matched the calculated values. Similarly, the ^{13}C NMR spectra for poly(hydroxy amide ethers) **23−39** gave further evidence for the structures shown. The aromatic and carbonyl carbons were detected at 101−193 ppm, while the aliphatic carbons of the 1,3-propylidene linkage were found at 63−71 ppm. Aliphatic carbon atoms between the amide functionalities were detected at approximately 25 and 36 ppm. Other carbon resonances were consistent with the particular Ar units incorporated into the poly(hydroxy amide ether) backbone.
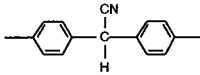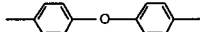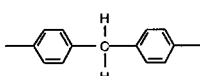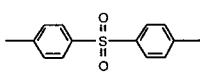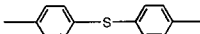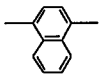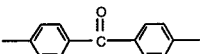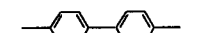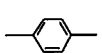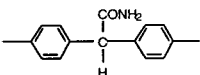
Influence of the Ar Unit on T_g. Poly(hydroxy amide ethers) **23−39** are amorphous thermoplastics with glass transition temperatures (T_g) of 78−146 °C, as determined by DSC analysis (Table 4). No evidence for crystallinity was detected during DSC analysis from 50 to 250 °C (except for 4,4′-biphenylene polymer **34**, which can be induced crystallize, as described later in the text). The T_g of poly(hydroxy amide ethers) increases as the Ar portion of the polymer repeat becomes more rigid, restricting torsional mobility of the polymer chain. For example, species **24** has the highest T_g at 146 °C and contains a rigid bisphenylenefluorene unit. Likewise, derivatives **23** ($T_g = 120$ °C) and **25** ($T_g = 118$ °C) have relatively high T_g's when compared to the other poly(hydroxy amide ethers), presumably due to the bulky trifluoromethyl and phenyl groups present, respectively. Poly(hydroxy amide ether) **39**, with a pendent amide group, also has a relatively high T_g of 122 °C. This presumably is a consequence of hydrogen bonding interactions between the amide and other polar backbone units, which restricts torsional mobility in the polymer backbone. Intermediate glass transition temperatures for this series of poly(hydroxy amide ethers) are found (105−115 °C) when Ar is a rigid unit without bulky side groups, such as the diphenyl ketone (**33**), biphenylene (**34**), and naphthylene (**32**, **38**) units. The lowest T_g (78−103 °C) results when Ar is based on a single phenylene unit (**35−37**) or contains two phenylene rings linked by flexible isopropylidene, methylene, oxygen, or sulfur-containing units (**26−31**).

Effect of the Ar Unit on Oxygen Transmission Rates of Poly(hydroxy amide ethers). Poly(hydroxy amide ethers) **23−39** exhibit a good to excellent barrier to oxygen,[14] with oxygen transmission rates (O$_2$TR) that range from 0.2 to 1.8 cc·mil/(100 in.^{2}·atm·day) (barrier units or BU) at 23 °C and 45−90% relative humidity.[59] These values approach those of crystalline high-barrier resins such as poly(vinylidene chloride) copolymers and EVOH (O$_2$TR < 0.2 BU), while being substantially lower than those of moderate oxygen barrier materials such as poly(ethylene terephthalate) (PET) (O$_2$TR = 5−10 BU). The oxygen barrier proper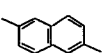ties of poly(hydroxy amide ethers) **23−39** are most similar to those of amorphous polyamides, which have O$_2$TR of 0.5−4 BU at high humidity.[5] However, the poly(hydroxy amide ethers) with O$_2$TR values of 0.2−0.3 BU (**33** − **39**) possess some of the lowest oxygen transmission rates known for completely amorphous polymers.

These low oxygen permeabilities are a reflection of the strong intermolecular hydrogen bonding interactions implicit in the structures of **23−39**. Such interactions

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

$$\left(\text{O}-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{O}-\text{Ar}-\text{O}-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\overset{\text{H}}{\text{N}}-\overset{\text{O}}{\text{C}}-(\text{CH}_2)_4-\overset{\text{O}}{\text{C}}-\overset{\text{H}}{\text{N}}-\text{C}_6\text{H}_4-\text{O}\right)_n$$

No.	Ar	yield (%)	O_2TR (BU)[a,b,c]	RH (%)[d]	T_g (°C)	η_{inh} (dL/g)[e]
23	—C6H4—C(CF3)2—C6H4—	79	1.8	75 - 85	120	0.52
24	9,9-fluorenyl bis(phenyl)	75	1.2	59 - 61	146	0.47
25	—C6H4—C(C6H5)(CH3)—C6H4—	87	1.0	45 - 55	118	0.37
26	—C6H4—C(CH3)2—C6H4—	70	0.8	75 - 80	103	0.62
27	—C6H4—C(CN)(H)—C6H4—	90	0.6	70 - 90	98	0.49
28	—C6H4—O—C6H4—	95	0.6	70 - 80	103	0.50
29	—C6H4—C(H)2—C6H4—	71	0.5	75 - 85	92	0.43
30	—C6H4—SO2—C6H4—	61	0.5	70 - 80	93	0.46
31	—C6H4—S—C6H4—	92	0.4	80 - 90	94	0.51
32	naphthalene	94	0.4	80 - 90	108	0.54
33	—C6H4—CO—C6H4—	89	0.3	70 - 90	113	0.54
34	—C6H4—C6H4—	92	0.3	80 - 90	110	0.45
35	—C6H4—	85	0.3	70 - 80	97	0.63
36	—C6H4— (meta)	86	0.2	80 - 90	97	0.55
37	indane	82	0.2	75 - 85	78	0.40
38	naphthalene	82	0.2	80 - 90	109	0.65
39	—C6H4—C(CONH2)(H)—C6H4—	80	0.2	60 - 80	122	0.35

[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 59). [d] Relative humidity (RH) of oxygen. [e] Concentration of 0.5 g/100 mL in DMF at 25.0 °C.

between polymer chains contribute to high cohesive energy density and low free volume, both of which would be expected to discourage oxygen diffusion through the matrixes of these thermoplastics.[60,61] This is reflected by the fact that the barrier properties for poly(hydroxy amide ethers) **23**−**39** improve (i.e., O_2TR decreases) as the aromatic core unit (Ar) either (a) becomes less bulky and more compact or (b) contains strong hydrogen

bonding groups.[14] In the sections that follow, the 17 poly(hydroxy amide ethers) shown in Table 4 (**23**−**39**) are compared to one another to show the effects that key structural features have on O_2TR in the polymers.

(a) Effect of Size and Geometry of the Ar Unit on Oxygen Transmission Rates. Oxygen transmission rates (O_2TR) decrease as the Ar unit in the poly-(hydroxy amide ether) backbone becomes less bulky and more planar or compact. Figure 1 shows a plot of O_2TR vs size/shape of the Ar group in the poly(hydroxy amide ether) repeat unit. Overall, O_2TR decreases from 1.8 BU for the hexafluoroisopropylidenebisphenol-based **23** to 0.2 BU for polymer **38**, which contains the 2,6-naphthylene unit. O_2TR decreases incrementally as the Ar unit converts from tetrahedral geometry (**23**−**26**, **29**) to the more spacially efficient trigonal planer orientation (**33**) to a geometry where the aromatic rings are joined linearly (**34**) or are fused together (**32**, **38**). A more in-depth analysis is described in the sections that follow.

Replacement of trifluoromethyl and aromatic groups in the Ar units of **23**−**25** by less bulky methyl groups and hydrogen atoms of **26** and **29**, respectively, causes oxygen transmission rates (O_2TR) to decrease. For example, poly(hydroxy amide ether) **23** (O_2TR = 1.8 BU)[62] has two trifluoromethyl groups attached to the central tetrahedral carbon atom of the Ar unit. Replacement of the trifluoromethyl groups with the smaller methyl substituents (**26**) lowers the O_2TR from 1.8 to 0.8 BU. Further reduction in steric bulk by replacing both methyl groups with hydrogen atoms (**29**) lowers O_2TR even further, to 0.5 BU. This trend is also evident when poly(hydroxy amide ether) **26** is compared to polymers **24** and **25**. The replacement of one of the methyl groups of **26** by a larger phenyl unit in **25** causes O_2TR to increase from 0.8 to 1.0 BU. When both methyl groups have been replaced with aromatic units (**24**), O_2TR increases even further, to 1.2 BU. In each of these comparisons, as the steric bulk of the Ar moiety increases, oxygen transmission rates also increase, presumably as a consequence of poorer chain packing.

The poly(hydroxy amide ethers) in which the Ar groups are naphthylene (**32**, **38**), biphenylene (**34**), diphenyl ketone (**33**), and phenylene (**35**) units exhibit especially low O_2TR (0.2−0.4 BU). This appears to be due to the ability of the polymer chains to pack better as Ar becomes more planar and moves away from the tetrahedral geometry described earlier with species **23**−**26** and **29**. For example, derivative **33**, which contains the trigonal planer diphenyl ketone unit, has a lower oxygen transmission rate (0.3 BU) than diphenyl-methane species **29** (0.5 BU), in which the core of the Ar unit has tetrahedral geometry. Similarly, low oxygen transmission rates (0.2−0.3 BU) are realized when the rigid 4,4′-biphenylene (**34**), 1,4-phenylene (**35**), and 2,6-naphthylene (**38**) Ar segments are introduced. In each of these cases, the planarity associated with the Ar unit presumably leads to more efficient chain packing. The lowest O_2TR (0.2 BU) is obtained when the 2,6-naphthylene unit is incorporated into the poly-(hydroxy amide ether) backbone (**38**). Presumably, the 2,6-substitution on the naphthylene ring allows the polymer to take full advantage of this compact, planer unit to yield the most efficient chain packing possible in this series.

Incorporation of isomeric aromatic units into the poly-(hydroxy amide ether) backbone also affects barrier properties to some degree. This is shown by the comparison of the poly(hydroxy amide ethers) with the 1,4- and 2,6-naphthylene units (**32** and **38** respectively) to one another, as well as the polymers in which the Ar segments are the *para-*, *meta-*, and *ortho*-phenylene units (**35**−**37** respectively, Table 4). Poly(hydroxy amide ether) **32**, which contains the 1,4-naphthylene segment, has an O_2TR of 0.4 BU. Barrier properties improve (O_2TR decreases from 0.4 to 0.2 BU) when the 1,4-naphthylene unit in **32** is replaced by the isomeric 2,6-naphthylene group in **38**. Chain packing is presumably more efficient in **38**, since the naphthalene ring is completely incorporated into the polymer backbone. In polymer **32**, only a part of the planar naphthylene group is incorporated into the polymer backbone, while the other part of the group is "perpendicular" to the polymer chain.

Phenylene-based polymers **35**−**37** all have comparable O_2TR of 0.2−0.3 BU, values which are among the best for all of the poly(hydroxy amide ethers) described in this paper. The excellent barrier properties associated with phenylene species **35**−**37** are probably due to the compact nature of this unit, which provides more hydrogen bonding sites per unit chain length, when compared to other Ar units. The slight difference in O_2TR between 1,4-phenylene species **35** (0.3 BU) and 1,3-phenylene polymer **36** (0.2 BU) is consistent with observations made previously with other poly(hydroxy amide ethers). Typically, better barrier properties are obtained when the 1,3-phenylene unit is used in place of the 1,4-phenylene unit in otherwise identical poly-(hydroxy amide ethers).[24,26] The effect of the *ortho*-phenylene unit on the barrier properties of poly(hydroxy amide ethers) is ambiguous. In this work, incorporation of the *o*-phenylene unit in the polymer backbone (polymer **36**) yields a poly(hydroxy amide ether) with an exceptional barrier to oxygen (O_2TR = 0.2 BU). However, incorporation of the *o*-phenylene unit into the backbone of other poly(hydroxy amide ethers) has, in some cases, diminished barrier properties significantly.[26]

(b) Effect of Heteroatoms (O, S) and Polar Functionalities (−CN, −CONH$_2$) on O_2TR. Poly(hydroxy amide ethers) **27**, **28**, **30**, **31**, and **39** contain either heteroatom linkages (−O−, −S−, −SO$_2$−) or polar functionalities (−CN, −CONH$_2$) in the Ar units (Table 7). Surprisingly, the presence of the ether (**28**), sulfone (**30**), or sulfide (**31**) linkages offers little or no improvement in O_2TR when compared to a methylene unit (**29**). Apparently, these polar backbone segments do not appreciably improve hydrogen bonding interactions between polymer chains, when compared to the non-polar methylene group in **29**. Likewise, the pendent nitrile group in **27** imparts no special improvement in barrier properties when compared to the other Ar groups shown in Table 7.

However, the pendent amide group in **39** is an especially powerful group for improving the barrier properties of poly(hydroxy amide ethers). Polymer **39** has an O_2TR of 0.2 BU, which is one of the lowest O_2TR values obtained for any amorphous poly(hydroxy amide ether).[63] As we and others have described previously,[13,26,27] the amide unit is perhaps the best contributor to high barrier properties in a polymer. In **39**, the pendent amide group can readily participate in hydrogen bonding interactions with pendent hydroxyl groups or other amide units in the poly(hydroxy amide ether) backbone. This presumably provides optimal chain
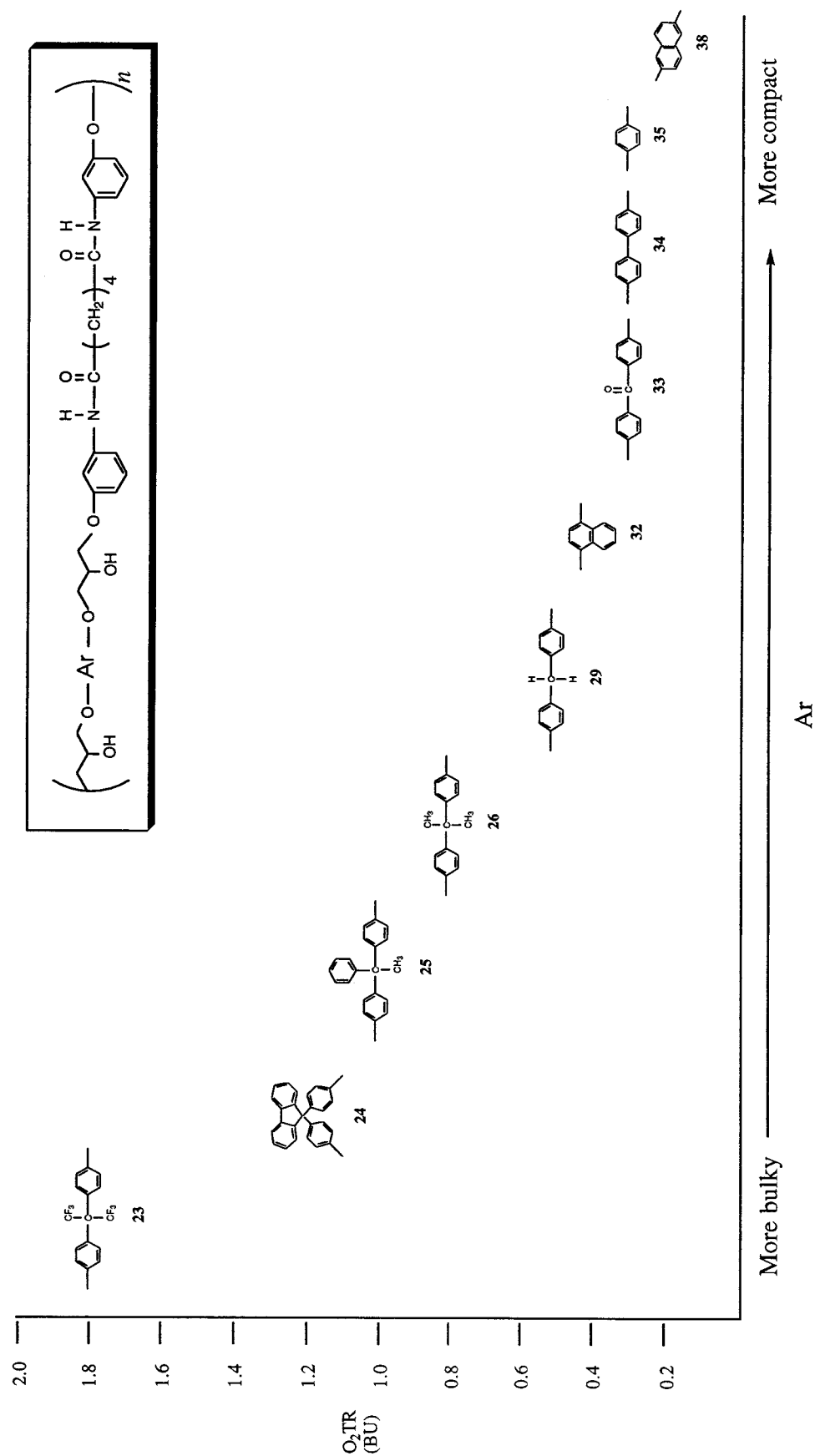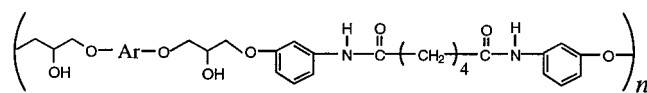
Figure 1. Effect of the size/shape of the Ar unit on O$_2$TR.

Table 7. Effect of Heteroatoms and Polar Functionalities on O$_2$TR
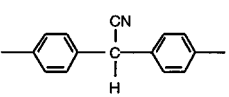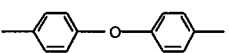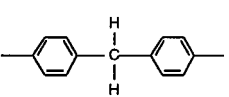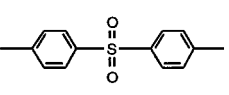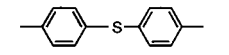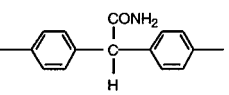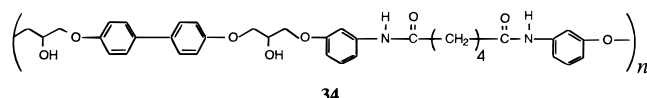
Polymer	-Ar-	O$_2$TR (BU)
27		0.6
28		0.6
29		0.5
30		0.5
31		0.4
39		0.2

Table 8. Effect of Morphology on O$_2$TR and T_g in Polymer 34

34

morphology	O$_2$TR (BU)[b]	RH (%)	T_g (°C)	T_m (°C)
amorphous	0.3	80−90	110	−
semicrystalline[a]	0.06	80−90	117	195

[a] Crystallizes when annealed at 160 °C. [b] Oxygen transmission rate (O$_2$TR) in cc·mil/(100 in.^{2}·atm·day) or barrier units (BU).

packing, due to strong intermolecular cohesion, yielding the superb barrier properties obtained. This influence is clearly seen when **39** is compared to polymers **27** and **29**, which respectively contain a nitrile group and hydrogen atom in place of the amide group of **39**. Significant improvements in both O$_2$TR and T_g are obtained as the strongly hydrogen bonding amide unit is compared to the less polar nitrile group and nonpolar hydrogen atom.

(c) Effect of Crystallinity on Barrier Properties. Poly(hydroxy amide ether) **34**, which contains the 4,4′-biphenylene unit, is of special interest since it is one of the only poly(hydroxy amide ethers) that can be induced to crystallize. The as-synthesized *amorphous* 4,4′-biphenylene polymer **34** has a T_g of 110 °C and excellent barrier to oxygen, with an O$_2$TR of 0.3 BU (Table 8). When compression-molded films of **34** are annealed at approximately 160 °C, the normally transparent films become opaque, indicating that crystallization has occurred. DSC analysis shows the presence of a melting endotherm (T_m) at 190 °C, with an improvement in T_g from 110 to 117 °C. *Crystalline* **34** also shows an

impressive improvement in barrier properties, in which O$_2$TR decreases from 0.3 BU in the amorphous polymer to 0.06 BU when the crystalline morphology dominates (Table 8). Since oxygen is unlikely to dissolve in or diffuse through the crystalline regions of a polymer,[13] the decrease in oxygen permeability in annealed **34** upon crystallization is consistent with expectation. Although no attempt was made to determine the level of crystallinity in **34**, other amide containing polymers such as poly(caprolactam) (nylon 6) show similar decreases in oxygen permeation when the amorphous material is annealed to a level of 60% crystallinity.[13] Consequently, one might reasonably suppose that the level of crystallinity in annealed **34** is similar.

Combining Good Barrier Properties with High T_g. Poly(hydroxy amide ether) **24**, which contains the bisphenylenefluorene unit, combines good barrier to oxygen (1.2 BU) with excellent T_g (146 °C). Although polymer **24** does not possess the extraordinarily low O$_2$TR of other poly(hydroxy amide ethers) (<0.5 BU), it nevertheless exhibits barrier properties that are comparable or better than well-known commercial barrier packaging materials such as PET or certain polyamides. The combination of good barrier and high T_g (near 150 °C) classifies **24** as a barrier polymer with the heat resistance of an engineering thermoplastic. Good barrier and high heat resistance are an unusual combination for amorphous thermoplastics. Other poly(hydroxy amide ethers)[26,27] [as well as some poly(hydroxy ethers) and poly(hydroxy amino ethers),[19,21,22,29]] have also been prepared which combine these two features in the same polymer structure.

Conclusions

A series of new poly(hydroxy amide ethers) have been prepared, which exhibit good to excellent barriers to oxygen. In some cases, oxygen transmission rates (O$_2$TR) as low as 0.2 cc·mil/(100 in.^{2}·atm·day) (barrier units or BU) were obtained, exceptional for completely amorphous thermoplastics. In one case, an amorphous poly(hydroxy amide ether) was induced to crystallize, yielding impressive improvements in barrier properties (O$_2$TR decrease from 0.3 to 0.06 BU). Overall, improvements in barrier properties (i.e., lower O$_2$TR) were realized as the aromatic core unit (Ar) in the poly(hydroxy amide ether) backbone, became either (a) more planer or compact or (b) contained a strongly polar pendent functional group such as a primary amide. Presumably, these structural features yield improvements in interchain cohesion via (a) lack of bulky side units or (b) increased hydrogen bonding interactions, at the expense of oxygen permeation. A poly(hydroxy amide ether) was also prepared in which a good barrier to oxygen (O$_2$TR = 1.2 BU) was combined with the heat resistance of an engineering thermoplastic (T_g = 146 °C).

Experimental Section

Materials. Adipoyl chloride, 3-aminophenol, 4,4′-(hexafluoroisopropylidene)diphenol, bis(4-hydroxyphenyl)methane, 4,4′-sulfonyldiphenol, 4,4′-thiodiphenol, 1,4-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, 4,4′-dihydroxybenzophenone, 4,4′-biphenol, hydroquinone, resorcinol, catechol, and epichlorohydrin were obtained from Aldrich and were used as received. The compounds 9,9-bis(4-hydroxyphenyl)fluorene and 1,1-bis-(4-hydroxyphenyl)-1-phenylethane were respectively obtained from Ken Seika Corp. and Mutsubishi. The compound 4,4′-oxydiphenol was obtained from Kodak and was used as

received. The compounds 1,1-bis(4-hydroxyphenyl)acetamide and 1,1-bis(4-hydroxyphenyl)acetonitrile were prepared as described previously.[32,34] 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. Ethyltriphenylphosphonium acetate–acetic acid complex (Alfa Products) was used as a 70% solution in methanol. HPLC-grade tetrahydrofuran (THF), dimethylformamide (DMF), toluene, methanol, and methylene chloride were obtained from Fisher Scientific Co. Sodium hydroxide (50%) was obtained from Fisher Scientific Co. Ethanol was obtained from Aldrich and was used without further purification. Propylene glycol monophenyl ether (DOW-ANOL 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. ^1H NMR spectra were recorded with use of a Varian VXR 300 NMR spectrometer operated at 300 MHz. Chemical shifts are relative to tetramethylsilane at δ 0. ^{13}C NMR (^1H decoupled) spectra were recorded with the use of a Varian VXR 300 NMR spectrometer operated at 75.4 MHz. Spectra were referenced to internal tetramethylsilane at 0 ppm. Diglycidyl ether syntheses were monitored by reversed-phase liquid chromatography with the use of a Hewlett-Packard 1090 liquid chromatograph that contained a C18-based Hewlett-Packard 79916OD-554 column. An injection volume of 1 μL, flow rate of 0.5 mL/min, and solvent gradient of 50% acetonitrile/50% water to 90% acetonitrile/10% water over a 3-min period were typical. 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 the use of an OxTran 1050 system operated at 55–90% relative humidity of oxygen between 23 and 25 °C. Epoxy equivalent weights (EEW) were determined using a previously described procedure.[64] Preparation of thin polymer films for O_2TR determination has been described previously.[33]

Synthesis of *N,N*-Bis(3-hydroxyphenyl)adipamide (5). This compound was prepared as described previously.[26]

Synthesis of Diglycidyl ethers 6–22. The bisphenol (0.30 mol), benzyltrimethylammonium chloride (0.15 g, 0.81 mmol), and epichlorohydrin (600 mL, 710 g, 7.67 mol) were heated at 90 °C under nitrogen for periods between 18 and 36 h. The reactions were monitored by reversed-phase HPLC with the use of various acetonitrile/water solvent mixtures to detect the formation of chlorohydrin and glycidyl ether species. Once all of the bisphenol had reacted, the reaction mixture was cooled to 30 °C and 50% aqueous NaOH (72 g, 0.9 mol NaOH) was added dropwise to the vigorously stirred solution over 1 h. On completion of addition, the mixture was stirred until >90% formation of the diglycidyl ether was detected by HPLC analysis (3–24 h). It was sometimes necessary to add additional base (0.1 mol) to complete the conversion of the chlorohydrin species to glycidyl ether units. The reaction mixture was then poured into methylene chloride (1L) and washed with water (3 × 500 mL). The organic layer was separated, dried over magnesium sulfate, and filtered to yield a clear filtrate. Solvent was removed under reduced pressure to yield crude **6–22** as either oils or solids. Diglycidyl ethers **10–16**, **18**, and **21** were purified by two recrystallizations from ethanol. Diglycidyl ethers **6**, **8**, **19**, and **20** were purified via column chromatography on silica gel using 100% methylene chloride as the eluent. Diglycidyl ether **7** was purified by recrystallization from 50/50 methanol/chloroform. Diglycidyl ether **22** was purified by two recrystallizations from toluene. During the purification of 4,4′-diglycidyloxybiphenyl (**17**), 2 L

of methylene chloride is used during the extraction/washing procedure due to the low solubility of this material in this solvent. Purification of **17** was completed by two recrystallizations from acetone. Yields of **6–22** ranged between 8 and 79%. Epoxy group concentrations were determined by titration with a standardized solution of 0.1 N $HClO_4$ in acetic acid, as described previously.[64] See Tables 1–3 for complete characterization data.

General Procedure for the Synthesis of Poly(hydroxy amide ethers) 23–39. Polymers **23–39** were prepared by using the following procedure. The diglycidyl ether (20.40 mmol, 40.80 mequiv (or mmol) epoxide], *N,N*′-bis(3-hydroxyphenyl)adipamide (6.57 g, 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) was added. The temperature of the reaction mixture rose to 145 °C and was maintained at 155–165 °C. During this time, *N,N*′-bis(3-hydroxyphenyl)adipamide reacted with the diglycidyl ether and the solution became increasingly viscous over a 10–15 min period. More propylene glycol monophenyl ether (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 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 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 70–95%. Complete characterization data are given in Tables 4–6.

Supporting Information Available: Tables of NMR data for aromatic diglycidyl ethers **6–22** (Tables 2 and 3) and poly(hydroxy amide ethers) **23–39** (Tables 5 and 6) (4 pages). Ordering and access information is given on any current masthead page.

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(1) For the first two papers in this series, see refs 26 and 27. For other papers and patents on high barrier poly(hydroxy amide ethers), see refs 20, 24, 33, 34, 36, 37, and 41.

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(59) Another well-recognized unit of gas permeability is the Barrer [10^{-10} cc(STP)·cm/(cm^2·s·cmHg)]. Since one Barrer 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) **23**–**39** range from 1.2×10^{-3} to 11×10^{-3} Barrers.

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(62) The relatively high O$_2$TR of 1.8 BU for trifluoromethyl species **23** may also be due, in part, to the well-known solubility of oxygen in fluorine-containing polymers.

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