

Preparation and Characterization of High Molecular Weight Poly(hydroxy ethers) with Unusually High Glass Transition Temperatures

H. CRAIG SILVIS^{1*}, JERRY E. WHITE¹, and STEVEN P. CRAIN²

¹The Dow Chemical Company, Central Research, Midland, Michigan 48674, and ²The Dow Chemical Company, Designed Thermoplastics Research, Midland, Michigan 48667

SYNOPSIS

A series of novel poly(hydroxy ethers) have been prepared via polymerization of the diglycidyl ethers of bisphenol-A (**4**), 4,4'-tribromotetramethylbiphenol (**6a**), and 4,4'-tetrabromotetramethylbiphenol (**6b**) with a variety of rigid diols in an effort to systematically modify structural features of the phenoxy repeat unit in order to control the torsional mobility of polymer backbones and produce materials with softening temperatures higher than are typical for the class. The resulting poly(hydroxy ethers) displayed glass transition temperatures ranging from 109 to 242°C. Three of the polymers were characterized with respect to tensile and impact properties and were compared to the polymer synthesized from bisphenol-A (**1**) and bisphenol-A diglycidyl ether (**4**).

INTRODUCTION

Reactions of bisphenols with arylene diglycidyl ethers to afford high molecular weight phenoxy thermoplastics or poly(hydroxy ethers) (e.g., **5**, Table I) are well established.¹ As a class, these generally amorphous materials are characterized by moderate glass transition temperatures ($T_g = 60\text{--}130^\circ\text{C}$), although examples with T_g as high as 170°C have been reported.^{1d} The present study was undertaken to systematically modify various features of the phenoxy repeat unit in order to control the torsional mobility of the polymers and to increase their softening temperatures. Therefore, we now describe a series of new poly(hydroxy ethers) with T_g 's ranging from 109°C to over 240°C ; mechanical properties of representative examples of these thermoplastics also are presented.²

EXPERIMENTAL

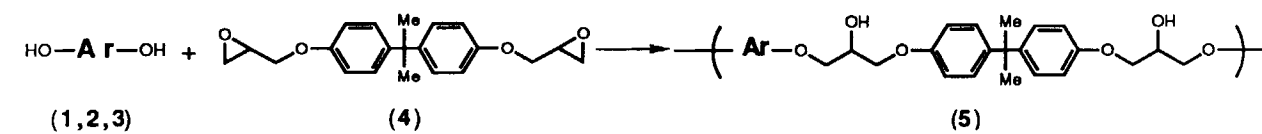
General

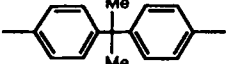
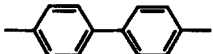
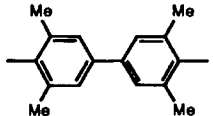
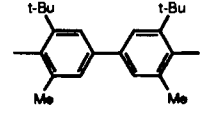
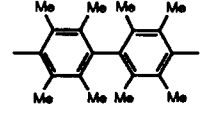
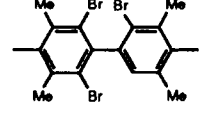
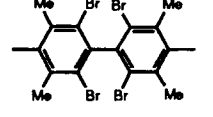
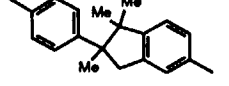
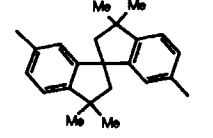
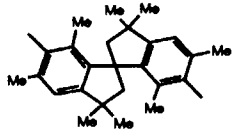
Bisphenol-A (**1**) and 4,4'-biphenol (**2a**) were purchased from Aldrich Chemical Co. and were recryst-

allized from toluene and 2-propanol/heptane, respectively. Substituted biphenol diols **2b**, **2c**, **2e**, and **2f** were prepared via oxidative coupling of the appropriate 2,6-dialkylphenol by methods described in the literature.^{3,4} These materials were then purified by recrystallization from toluene (**2b**, **2c**), acetone (**2f**), and ethyl acetate (**2e**). Indanedi-phenol (**3a**) was synthesized⁵ from 4-isopropenylphenol.⁶ Spirobiindanediphenol (**3b**) and tetramethylspirobiindanediphenol (**3c**) were prepared from bisphenol-A or tetramethylbisphenol-A as described.⁷ The diglycidyl ether of bisphenol-A (**4**) was obtained as DER 332 (Dow Chemical) and was purified by titration in methanol. Dipropylene glycol methyl ether (Dowanol, DPM) was treated with anhydrous K_2CO_3 and then vacuum distilled prior to use. $\text{EtPh}_3\text{P}^+\text{OAc}^-$ (Al catalyst) was obtained from Alfa Chemical Co. as a 70% solution in methanol. All other solvents employed were standard reagent grade.

DSC and TGA data were obtained on a DuPont 1090 thermal analyzer that was calibrated using indium metal. The scan rate for DSC measurements was $10^\circ\text{C}/\text{min}$ under nitrogen; T_g 's reported represent inflection point values. Weight-average molecular weight data were obtained using a Waters gel permeation chromatograph using THF as solvent. All data are relative to polystyrene standards.

* To whom correspondence should be addressed.

Table I Synthesis and Characterization of Poly(hydroxy ether) Copolymers

Diol No.	—Ar—	Polymer No.	MW × 10 ⁻⁴	T _g (°C)
1		5a	9.6	100
2a		5b	10.3	109
2b		5c	11.4	118
2c		5d	6.1	126
2d		5e	9.0	152
2e		5f	7.0	157
2f		5g	14.9	171
3a		5h	13.9	121
3b		5i	12.2	131
3c		5j	4.7	147

NMR spectra were obtained in d_6 -DMSO or $CDCl_3$ using a Varian VXR 300 spectrometer operated at 300 MHz. Chemical shifts are relative to TMS at $\delta = 0$ ppm. Mass spectral data were determined using a Hewlett-Packard 5995C GC/MS system. Epoxide equivalent weights were determined using a Mettler DL21 titrator according to the method of Jay.⁸ Melting point data are uncorrected. Tensile and impact properties were determined on 0.125 in.-thick compression-molded samples according to ASTM procedures.

4,4'-Octamethylbiphenol (2d)

To a solution of 235 mL of 55% HI in 300 mL of glacial HOAc, 52.0 g (215 mmol) of 4,4'-tetramethylbiphenol (**2b**) was added. To this mixture, 32.2 g (1.07 mol) of paraformaldehyde was added. The mixture was heated to $\approx 90^\circ\text{C}$, which gave rise to a homogeneous solution. After ≈ 2 h, 30 mL of hypophosphorous acid was added to discharge the brown color due to I_2 formation. The solution was allowed to stir overnight, which resulted in the precipitation of the product as a yellow crystalline solid, which was filtered, washed twice with water, and dried *in vacuo* (51 g, 80%). Recrystallization from EtOH/ H_2O (2/1 v/v) afforded **2d** as off-white crystals; m.p. = 207–208.5°C. $^1\text{H-NMR}$ in $CDCl_3$: $\delta = 4.58$ (s, 2H), 2.20 (s, 12H), 1.78 (s, 12H). The mass spectrum PI peak at $m/e = 298$.

Diglycidyl Ether of 4,4'-dihydroxy-2,6,2',6'-tetrabromo-3,5,3',5'-tetramethylbiphenyl (6b)

To 700 mL (8.95 mol) of epichlorohydrin, 300 g (538 mmol) of diol **2f** was added. The resulting slurry was heated to $\approx 80^\circ\text{C}$, at which point a homogeneous solution was obtained. To this was added, dropwise, 129 g (3 equiv) of 50% NaOH with concomitant precipitation of NaCl. After 1 h, another 2 equiv of 50% NaOH was added and the solution stirred at 80°C for another 1 h. The reaction mixture was then cooled to room temperature, and 300 mL of CH_2Cl_2 and 300 mL of H_2O were added with vigorous agitation. The organic phase was separated, washed with two 200 mL portions of H_2O , dried with anhydrous $MgSO_4$, filtered, and stripped to dryness on a rotary evaporator. The resulting off-white solid was collected by filtration, washed with EtOH, and dried *in vacuo* to yield 271 g (75%) of **6b**. The product was recrystallized from EtOH; m.p. = 190–192°C. Titration of **6b** gave epoxide equivalent weight = 337.2 g (theor = 335.0 g). $^1\text{H-NMR}$ in

$CDCl_3$: $\delta = 3.95$ (m, 4H), 3.40 (m, 2H), 2.83 (m, 4H), 2.42 (s, 12H).

Diglycidyl Ether of 4,4'-dihydroxy-2,6,2'-tribromo-3,5,3',5'-tetramethylbiphenyl (6a)

Compound **6a** was prepared in a manner identical to that of **6b** described above. The isolated yield was 66% of **6a** as a yellow solid. Recrystallization from EtOH afforded **6a** as pale yellow crystals; m.p. = 131–133°C. Titration of **6a** gave EEW = 297.7 g (theor = 295.6 g). $^1\text{H-NMR}$ in $CDCl_3$: $\delta = 6.80$ (s, 1H), 3.95 (m, 4H), 3.40 (m, 2H), 2.82 (m, 4H), 2.45 (s, 3H), 2.40 (s, 6H), 2.30 (s, 3H).

Polymer Synthesis

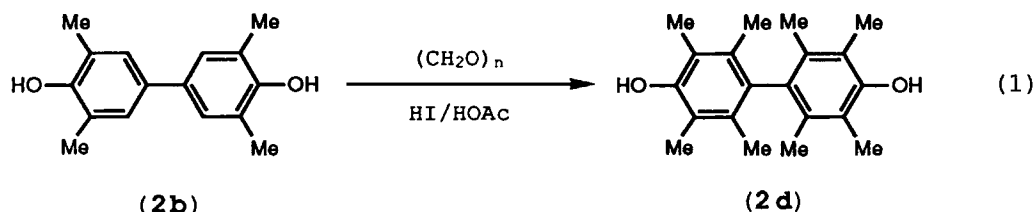
All polymers were prepared in an identical manner. The preparation of polymer **5f** is illustrative of the methodology employed. To a 100 mL resin kettle equipped with overhead stirring, a condenser, and a N_2 inlet, 4.807 g (10.04 mmol) of **2e**, 3.581 g (10.41 mmol) of purified diglycidyl ether of bisphenol-A (**4**), and 5 mL of distilled dipropylene glycol methyl ether was added. The reaction flask was padded with N_2 and heated to $\approx 100^\circ\text{C}$, at which point all monomers were dissolved and 5 drops of Al catalyst were added. The reaction temperature was allowed to rise to $\approx 180^\circ\text{C}$. Viscosity buildup was compensated for by additions of 1–2 mL of solvent in order to maintain stirring. After a period of 4 h, 250 mg of phenol was added in order to cap any residual epoxide end groups. The reaction solution was cooled to near room temperature and diluted with 20 mL of THF. The polymer was isolated by pouring the diluted reaction solution into excess MeOH in an explosion-proof blender. The polymer was redissolved in THF and reprecipitated into MeOH, filtered, and dried *in vacuo* at $\approx 150^\circ\text{C}$ for 20 h. The isolated yield of polymer **5f** was 6.6 g (79%). $^1\text{H-NMR}$ in d_6 -DMSO: $\delta = 6.95$ (m, 8H), 6.80 (s, 1H), 4.60 (m, 2H), 4.25 (m, 2H), 4.20 (m, 4H), 3.92 (m, 4H), 2.40 (s, 3H), 2.35 (s, 6H), 2.24 (s, 3H), 1.60 (s, 6H).

RESULTS AND DISCUSSION

Monomer Synthesis

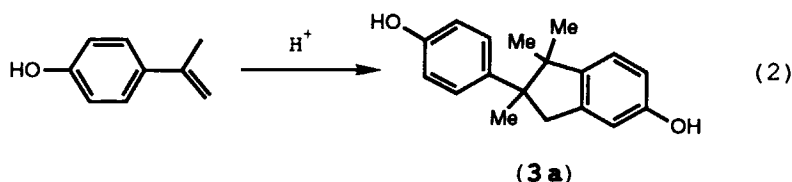
All monomers were synthesized according to procedures well documented in the literature^{3–5,7} with the exception of diols **2d**, **3a**, **3b**, and **3c**. 4,4'-Octamethylbiphenol (**2d**) was prepared in 70–80% yield by reductive C-alkylation of 4,4'-tetramethyl-

biphenol (**2b**) with formaldehyde and hydroiodic acid using glacial acetic acid as solvent [eq. (1)]. A

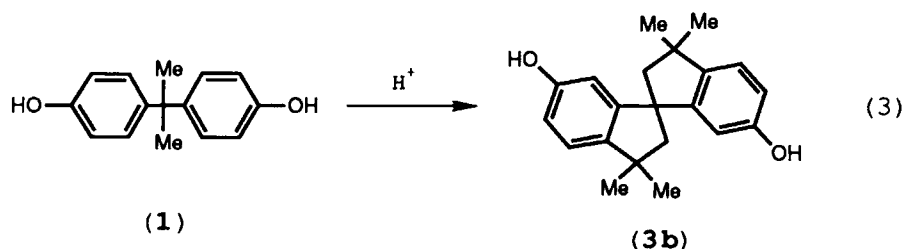


similar procedure was reported previously for the exhaustive C-methylation of phenol and other aromatic compounds⁹:

Indanediphenol (**3a**) was prepared by acid-catalyzed dimerization and subsequent cyclization of isopropenylphenol^{5,6} [eq. (2)]:



Spirobiindanediphenol monomers **3b** and **3c** were formed directly from bisphenol-A (**1**) or tetramethylbisphenol-A by reaction with sulfonated polystyrene ion-exchange resin (acid form) in hot toluene⁷ [eq. (3)]:



Polymer Synthesis

The poly(hydroxy ethers) synthesized for this study include copolymers **5**, derived via reaction of bisphenol-A diglycidyl ether with several sterically rigid aromatic diols (Table I), as well as two homopolymers (**7**) prepared from rigid diols and their corresponding diglycidyl ethers (Table II). Both **5** and **7**, compositions of which were confirmed by their ¹H-NMR spectra, were formed in hot (150–180°C) dipropylene glycol methyl ether containing a catalytic amount of the phosphonium salt, Et-Ph₃P⁺OAc⁻. Presumably, the phosphonium cation coordinates with the epoxide oxygen atom, thus activating the epoxide group toward nucleophilic attack. Also, the acetate anion, in simple equilibrium

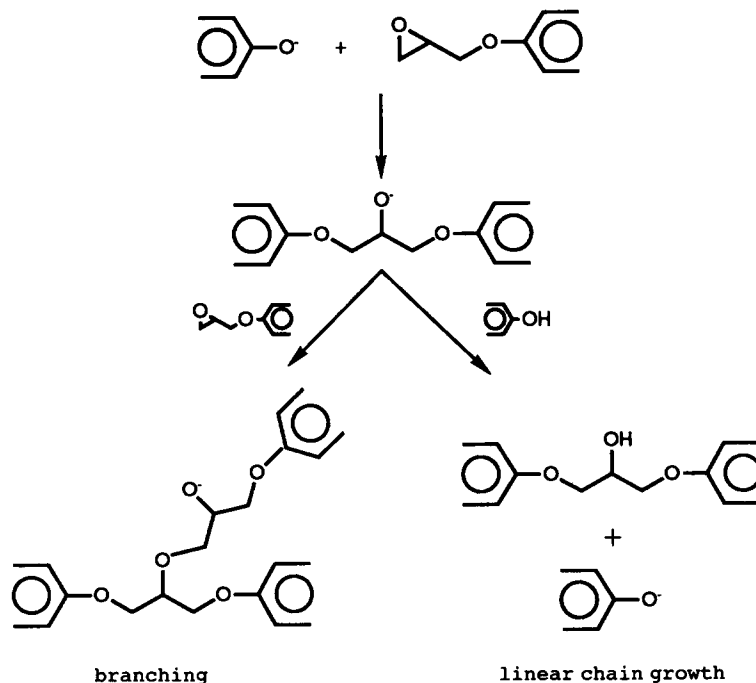
with the large excess of diphenol, probably generates a very small initial concentration of phenate anion, which serves as a stronger nucleophile than does the diphenol itself.

The preparation of high molecular weight poly(hydroxy ethers) from bisphenols and diglycidyl ethers is not as straightforward as is the synthesis of most other step-growth polymers. Not only is the usual rigorous purity of monomers and solvent required, but the stoichiometry of the polymerization must be adjusted to compensate for a small degree of branching due to reaction of intermediate alkoxide, generated along the polymer backbone, with residual epoxide functionality (see Scheme 1). The selectivity of the phenol/epoxide reaction with re-

spect to linear chain growth vs. branching has been examined previously.¹⁰ Typically, high molecular weight products are obtained when excesses (1–5%) of diglycidyl ether are employed; for preparations of **5** and **7**, we found excesses of 2–4% to be optimum. We also learned that relative weight-average molecular weights of the polymers, which ranged from 60,000 to 149,000, can be maximized by initially allowing the monomers to polymerize at high concentration (60–70% solids), followed by gradual dilution, in order to maintain effective stirring and temperature control as the polymerization proceeds and bulk viscosity increases. Residual epoxide end groups, which can lead to thermally induced cross-linking even in high molecular weight phenoxy thermoplastics, were consumed by treatment of the polymers with phenol prior to their isolation (see Experimental).

Polymer Characterization

Bisphenol A-based poly(hydroxy ether) **5a**, a commercially available thermoplastic (Union Carbide Corp.), exhibits $T_g = 100^\circ\text{C}$ and is completely amorphous. Replacement of half of the bisphenol A nuclei in **5a** (via the pathway shown in Table I) with more rigid biphenylene, indanediphenylene, and spirobiindanediphenylene linkages yielded copolymers **5b**, **5h**, and **5i** with progressively increased chain stiffness reflected by T_g 's of 109, 121, and 131°C , respectively. The torsional mobility of biphenyl-containing **5b** was further diminished by sterically congesting the area around backbone ether linkages^{1d} through introduction of *ortho*-methyl groups (**5c**, $T_g = 118^\circ\text{C}$) or a combination of *ortho*-methyl and *tert*-butyl substituents (**5d**, $T_g = 126^\circ\text{C}$; Table I):

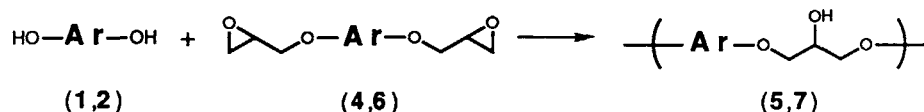


Scheme 1

Similarly, the T_g of **5i**, based on spirobiindanediphenol, was increased substantially from 131 to 147°C by preparation of the tetramethyl analog (**5j**, Table I), despite the relatively low molecular weight (MW) (47,000) of copolymer **5j** compared with the MW of the other **5**.

Additional increases in T_g within the series of copolymers listed in Table I were realized by allow-

ing hepta- and octa-substituted biphenols to polymerize with diglycidyl ether **4**. The octamethyl biphenyl segment in **5e** limits motion around both phenylene-ether and phenylene-phenylene bonds, resulting in a T_g (152°C) that is 34° higher than that of polymer **5c** (see above) in which the methyl substituents restrict mobility only around the ether linkages. Poly(hydroxy ether) **5g**, containing the

Table II Synthesis and Characterization of Poly(hydroxy ether) Homopolymers

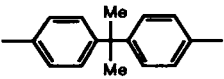
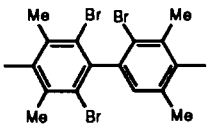
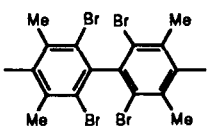
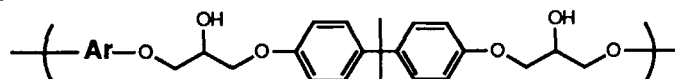
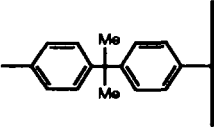
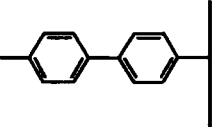
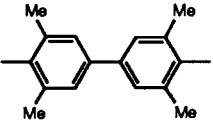
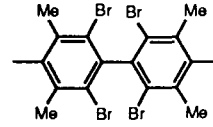
Diol No.	Diglycidyl Ether No.	—Ar—	Polymer No.	MW × 10 ⁻⁴	T _g (°C)
1	4		5a	9.6	100
2e	6a		7a	6.0	198
2f	6b		7b	8.9	242

Table III Physical Properties^a of Poly(hydroxy ethers)

Ar				
Polymer no.	5a	5b	5c	5g
Yield strength (MPa)	62.1	56.6	58.6	73.1
(psi)	(9,000)	(8,200)	(8,500)	(10,600)
Break strength (MPa)	51.7	49.7	50.3	71.7
(psi)	(7,500)	(7,200)	(7,300)	(10,400)
Ultimate elongation (%)	6	65	8	8
Tensile modulus, MPa	1860	1720	2210	2760
(psi)	(270,000)	(250,000)	(320,000)	(400,000)
Notched ^b Izod impact strength, J/m (ft-lb/in.)	160 (3)	1175 (22)	107 (2)	53 (1)

^a Determined for 0.125 in.-thick compression-molded samples.^b Notch radius = 0.010 in.

2,6,2',6'-tetrabromo-3,5,3',5'-tetramethyl-biphenylene species, is sterically analogous to **5e** (bromo groups and methyl substituents have similar steric bulk) but softens at a higher temperature ($T_g = 171^\circ\text{C}$). Evidently, T_g in **5g** is enhanced through intermolecular polar interactions unavailable to octamethylated **5e**; similar behavior has been observed for amorphous polycarbonates derived from tetrabromo- ($T_g = 265^\circ\text{C}$) and tetramethylbisphenol-A ($T_g = 207^\circ\text{C}$).¹¹ Copolymer **5f**, incorporating 3,5,3',5'-tetramethyl-2,6,2'-tribromobiphenyl segment exhibits $T_g = 157^\circ\text{C}$, a value that might be greater were **5f** (MW = 70,000) of comparable molecular weight to **5g** (MW = 149,000).

Poly(hydroxy ethers) with exceptionally high T_g were generated by polymerizations of 4,4'-dihydroxy-2,6,2'-tribromo-3,5,3',5'-tetramethylbiphenyl (**2e**) and 4,4'-dihydroxy-2,6,2',6'-tetrabromo-3,5,3',5'-tetramethylbiphenyl (**2f**) with their corresponding diglycidyl ethers (**6a,b**, Table II).

Thus, homopolymers **7a** and **7b** have backbones that combine significant steric restrictions to torsional mobility with likely interchain polar interactions to achieve T_g of 198 and 242°C . These values are remarkably high for an uncross-linked phenoxy system but will be of only limited value, at least for thermoplastic applications, since they dictate processing temperatures ($> 300^\circ\text{C}$) at which the materials begin to degrade.

In contrast, copolymers **5** (Table I) can be readily compression-molded at about 100°C above their T_g with no evidence for cross-linking or decomposition. Standard (ASTM) tensile specimens of **5b**, **5c**, and **5g** display yield and break strengths of 56.6–73.1 MPa and 49.7–71.7 MPa, values generally comparable to those of known homopolymer **5a** (Table III). Like **5a**, methylated **5c** and bromine-containing **5g** show little elongation at break (6–8%), but polymer **5b**, incorporating unsubstituted biphenyl linkages, exhibits ductile failure (65% elongation) along with surprisingly good impact resistance, evidenced by an Izod strength of 1175 J/m, a value

surpassing even that of polycarbonate (854 J/m).¹² Other **5** examined during this study are considerably more brittle (Table III) and have higher moduli (1860–2760 MPa) than does copolymer **5b** (1720 MPa, Table III).

The authors are grateful to the Dow Central Research Polymer Testing Laboratory for the determination of physical properties and to Dr. Abel Mendoza for providing samples of 4,4'-tetrabromotetramethylbiphenol (**2f**) and 4,4'-tribromotetramethylbiphenol (**2e**).

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