Amphiphilic Copolymers of Glycidol with Nonpolar Epoxide Comonomers

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ABSTRACT: To explore the industrially used copolymerization of glycidol with other epoxide species, a series of copolymers of glycidol with various comonomers (epichlorohydrin, isopropyl glycidyl ether, 1,2-epoxybutane, propylene oxide, and glycidyl phenyl ether) has been synthesized by cationic ring-opening polymerization in dichloromethane, using boron trifluoride diethyl etherate as the initiator. The facile synthesis proceeded at room temperature under ordinary atmosphere. The air- and temperature-stable products—mostly clear, colorless, viscous liquids—are proposed to consist of a hyperbranched polyglycidol core (incorporating varying fractions of comonomer) with arms made from comonomer-derived repeat units. These copolymers had low molecular weights and rather broad molecular weight distributions. There was wide variation in the polarity of these copolymers, depending on the comonomer used, resulting in materials that were soluble in solvents ranging from benzene to water. The glass-transition temperatures observed for these copolymers also varied widely, ranging from −56 to 1°C. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2290–2299, 2001

Key words: amphiphilic; cationic; copolymerization; glycidol; hyperbranched

INTRODUCTION

This report is the second in a series examining the industrially useful[1] cationic copolymerization of glycidol (2,3-epoxy-1-propanol) with epoxide comonomers. In an earlier report,[2] the copolymerization of glycidol with epichlorohydrin, which is used to generate hydrophilic chromatographic coatings for nonpolar crosslinked polystyrene supports, was examined in some detail. This study explores the general features of this reaction, with the aim of making a family of copolymers with a range of hydrophobicity for use in, for example, coatings for hydrophobic interaction chromatography (HIC) media. In the course of this investigation, which resulted in just such a family of copolymers, insights were gained into the mechanism of polymerization and the structure of the resulting polymers. Moreover, a couple of other comonomers examined were found to be unsuitable for this polymerization, which made it possible to estimate the scope of the current method, in terms of the range of variability in epoxide monomer structure that can be tolerated by this polymerization technique. The polymerization of glycidol has also attracted considerable fundamental research attention during the past decade. The cationic ring-opening homopolymerization of glycidol is known to form hyperbranched polyethers replete with hydroxyl

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groups[3]; low-polydispersity hyperbranched polymers and copolymers of glycidol were also obtained recently by anionic polymerization techniques.[4–6]

EXPERIMENTAL

Materials

1,2-Epoxybutane, glycidol, and narrow molecular weight polystyrene standards were obtained from Aldrich (Milwaukee, WI); boron trifluoride diethyl etherate ($BF_3 : OEt_2$), cyclohexene oxide, epichlorohydrin, glycidyl phenyl ether, isopropyl glycidyl ether, propylene oxide, and styrene oxide were obtained from Acros Organics (Geel, Belgium). Acetone, dichloromethane, methanol, and HPLC-grade tetrahydrofuran (THF) were obtained from Fisher Chemicals (Rockville, MD). All reaction materials were reagent grade and stored under nitrogen. Monomers and dichloromethane, the reaction solvent, were stored over 4A molecular sieves.

Synthesis

Polymerizations were carried out at room temperature (22°C) in a glass three-neck 250-mL round-bottom flask fitted with a mechanical stirrer, condenser operating at 5°C with a $CaCl_2$ drying tube, and a thermometer. This reactor was dried with a heat gun under a gentle stream of dry nitrogen. To this dried flask, in air, were added 150 mL dichloromethane, 0.12 mol (7.7 mL) glycidol, and 0.17 mol of a comonomer. Polymerization was initiated by the addition of 1.6 mmol (200 μL) $BF_3 : OEt_2$. The reaction mixture was stirred vigorously throughout the course of the reaction.

The progress of the reaction was monitored by GC-MS as follows: a 100-μL aliquot was withdrawn at intervals from the reaction mixture and poured into 1 mL methanol, which effectively quenched the reaction, after which 1 μL of this methanol solution was injected into the GC-MS for measurement of monomer concentration. The polymerizations were allowed to run overnight for 23 h. In the copolymerization of glycidol with propylene oxide, the reaction was stopped after 2 h because both monomers were completely consumed by this time. In all cases, the reaction was stopped by the addition of 1 mL distilled water, followed by a couple of hours of vigorous stirring. At this point, the solvent, water, and residual monomer were removed by rotary evaporation for about 5 h under vacuum, keeping the reaction mixture immersed in a water bath at 60°C. The polymer was then placed in a freeze dryer (trap at ~ -50°C, pressure $\sim$ 5 Pa) for 1 day to remove any remaining traces of volatile contaminants. All polymers were stored tightly capped in clear glass bottles under ordinary atmosphere at room temperature.

Analysis

The GC-MS used to monitor the polymerizations was a Thermoquest (San Jose, CA) Trace 2000 GC with a Trace MS detector, equipped with a Restek Rtx-5MS capillary column (length 15 m; i.d. 0.25 mm). Helium was used as the carrier gas. ^{1}H– and ^{13}C–NMR spectra were recorded using a Bruker/IBM WP270SY spectrometer (Bruker Instruments, Billerica, MA) operating at 270.1 and 67.9 MHz, respectively. The former were obtained in $CDCl_3$ ($\sim$ 70 mg polymer per mL of solvent) and the latter in CD_2Cl_2 ($\sim$ 250 mg polymer per mL of solvent). Infrared spectra of thin films of polymer smeared on KBr disks were taken with a Perkin–Elmer System 2000 FTIR (Perkin Elmer Cetus Instruments, Norwalk, CT). Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC 2920 (TA Instruments, New Castle, DE) connected to a liquid nitrogen cooling accessory and running the Thermal Advantage instrument control program. The temperature range analyzed was -120 to 40°C, at three different heating rates: 5, 10, and 20°C/min. Temperature calibration was done using deuterated ammonium dihydrogen phosphate, which undergoes a phase transition at -31°C. TA Universal Analysis software was used to determine the polymers' glass-transition temperatures, chosen to be the inflection points in the samples' thermograms at each of the three heating rates. Gel permeation chromatography (GPC) provided a relative measure of polymer molecular weight, and was carried out on a Waters GPC system (515 HPLC pump, 717plus autosampler, 2410 refractive index detector, and column heater module; Waters Instruments, Milford, MA). The column bank consisted of a pair of Waters HR 4E columns, maintained at 30°C along with the detector, and the entire system was controlled by the Millennium32 software package, which was also used for data reduction. HPLC-grade THF was used as the mobile phase, and polystyrenes 44000, 13700, 3680, and 760 were used for molecular weight

calibration. The polymer concentration used for GPC analysis was 5 mg/mL.

RESULTS AND DISCUSSION

Synthesis

Using the above-described synthetic method, seven different copolymerizations were attempted, using glycidol and one of each of the following comonomers: cyclohexene oxide, epichlorohydrin (ECH), 1,2-epoxybutane (EB), glycidyl phenyl ether (GPE), isopropyl glycidyl ether (IGE), propylene oxide (PO), and styrene oxide. Addition of $BF_3 : OEt_2$ to the reaction mixture promptly initiated polymerization. Because the polymerization was strongly exothermic, presumably as a result of the tremendous amount of strain energy released during epoxide ring-opening, the reaction mixture consistently reached reflux within 1 min, achieving temperatures of about 43–45°C. This part of the synthesis was accompanied by the formation of a clear, colorless, viscous precipitate that settled on the sides of the flask and on the stirrer blade. For this reason, a mechanical stirrer had to be used instead of a magnetic stir bar. Periodic GC-MS analysis of the reaction mixture revealed a precipitous decline in the concentration of glycidol during this time. Within the first 10 min of the reaction, the glycidol was almost completely consumed, whereas the comonomer concentration decreased to varying degrees. The reaction mixture subsided to room temperature over the course of about 1 h, as the comonomer began to be consumed slowly over a time span ranging from several hours to 1 day.

The monomer consumption profiles are shown in Figure 1. The precipitate was observed to disappear slowly, so that at the end of the reaction period a clear, colorless solution was obtained. Rotary evaporation and subsequent freeze drying of the various reaction mixtures yielded polymers in the form of clear, colorless, viscous liquids; however, poly(GPE-*co*-glycidol) was a translucent tacky gum. All polymers were obtained in near-quantitative yield (average yield 98%, minimum 95%). No further purification was performed because no additional steps are needed for these materials to be useful in actual chromatographic coatings applications.

The complete disappearance of glycidol during the initial stages of the reaction, accompanied by a relatively slower decrease in comonomer concentration, was a clear indication that the viscous precipitate formed was composed mostly of the extremely polar polyglycidol, which is known to be insoluble in dichloromethane.[2] The cationic polymerization of glycidol with $BF_3 : OEt_2$ in dichloromethane occurs with a very high degree of branching,[3] so it can be assumed that the polyglycidol precipitate in this reaction was hyperbranched. Subsequently, as the nonpolar comonomer added on to the termini of the polyglycidol chains in the precipitate, an amphiphilic copolymer was formed, which was soluble in dichloromethane. The complete dissolution of the final product in dichloromethane was evidence that a copolymer was formed, and not simply a mixture of homopolymers of glycidol and the comonomer, although concurrent formation of small amounts of homopolymer cannot be ruled out. The structure of these copolymers is surmised to consist of a hyperbranched, polar polyglycidol core (which

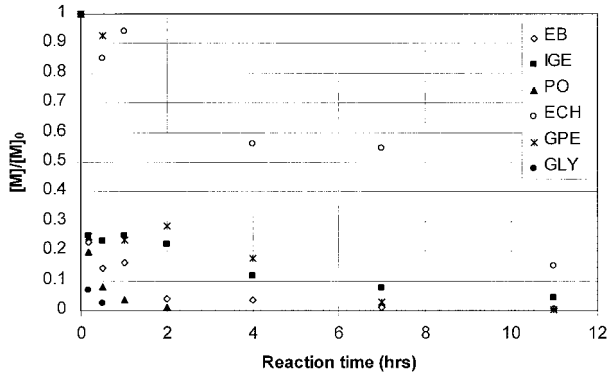

Figure 1 Monomer concentration [M] relative to starting monomer concentration $[M]_0$ as a function of reaction time. GLY = glycidol.

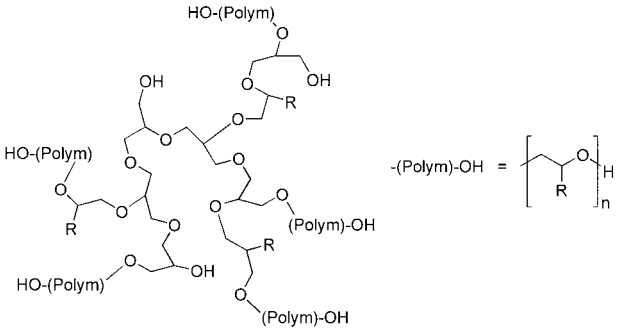

Figure 2 Proposed structure of copolymers, showing a hyperbranched polyglycidol core incorporating a few comonomer units, and having nonpolar arms consisting of comonomer.

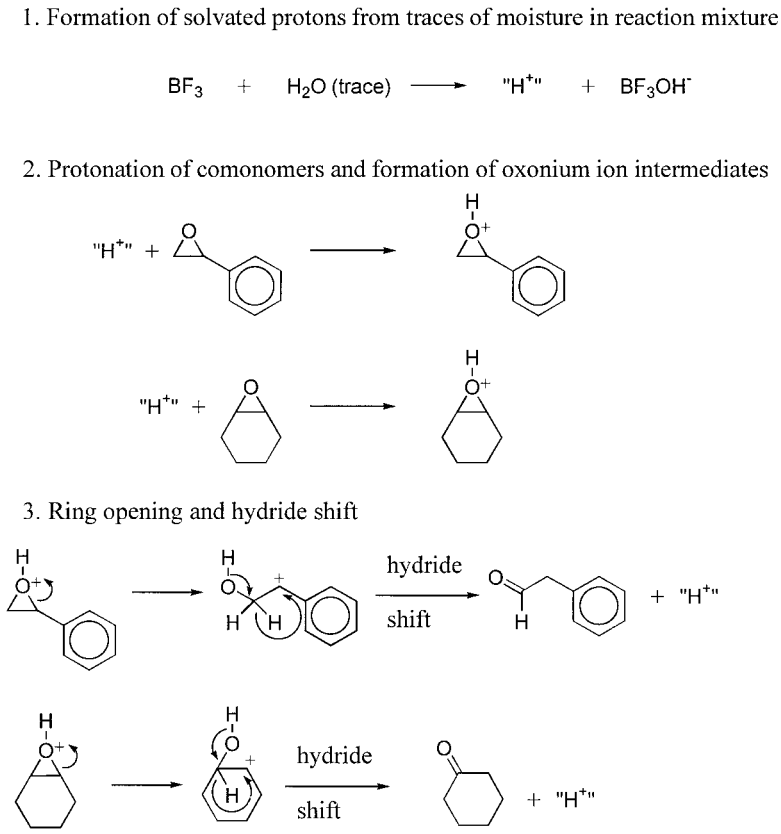

Figure 3 Proposed mechanism for formation of carbonyl compounds during the attempted polymerization of styrene oxide and cyclohexene oxide with $BF_3 : OEt_2$.

may contain some comonomer units), from which emanate nonpolar arms formed exclusively from the comonomer. A representative structure is shown in Figure 2.

There were three exceptions to the just-described sequence of events, which occurred with cyclohexene oxide, styrene oxide, and PO. In the case of cyclohexene oxide and styrene oxide, an exothermic reaction took place as usual upon addition of $BF_3 : OEt_2$, but without the formation of a precipitate or any significant reduction in the glycidol concentration. However, GC-MS analysis of the reaction mixtures indicated the formation of carbonyl derivatives of each of these two monomers, presumably by the hydride shift mechanism shown in Figure 3. Styrene oxide undergoes this side reaction arising from the stability of the benzyl cation intermediate in Figure 3, whereas the cyclohexene oxonium ion rearranges because of steric hindrance at the α-carbon, which prevents efficient polymerization. No polymeric material was isolated from either of these two reaction mixtures; cyclohexene oxide and styrene oxide did not, therefore, copolymerize with glycidol under these conditions. In the case of PO, no precipitate was formed at any stage in the reaction, indicating the incorporation of a significant fraction of PO units along with glycidol in the hyperbranched core of the copolymer.

Based on the preceding observations, one may generalize that 1,2-epoxyalkanes, glycidyl ethers, halogenated epoxide compounds (analogous to epichlorohydrin), and ethylene oxide itself would be amenable to the copolymerization described here. Conversely, epoxide compounds with aryl moieties attached (e.g., styrene oxide derivatives) and cycloalkene oxides would probably not serve well as comonomers because of the facile formation of carbonyl compounds in lieu of polymerization under these reaction conditions.

Structure

^{13}C–NMR spectra of the various polymers are shown in Figure 4, and features common to all spectra are discussed first. The quintet centered at 54.0 ppm corresponds to CD_2Cl_2 and is used as an internal reference. The peaks from about

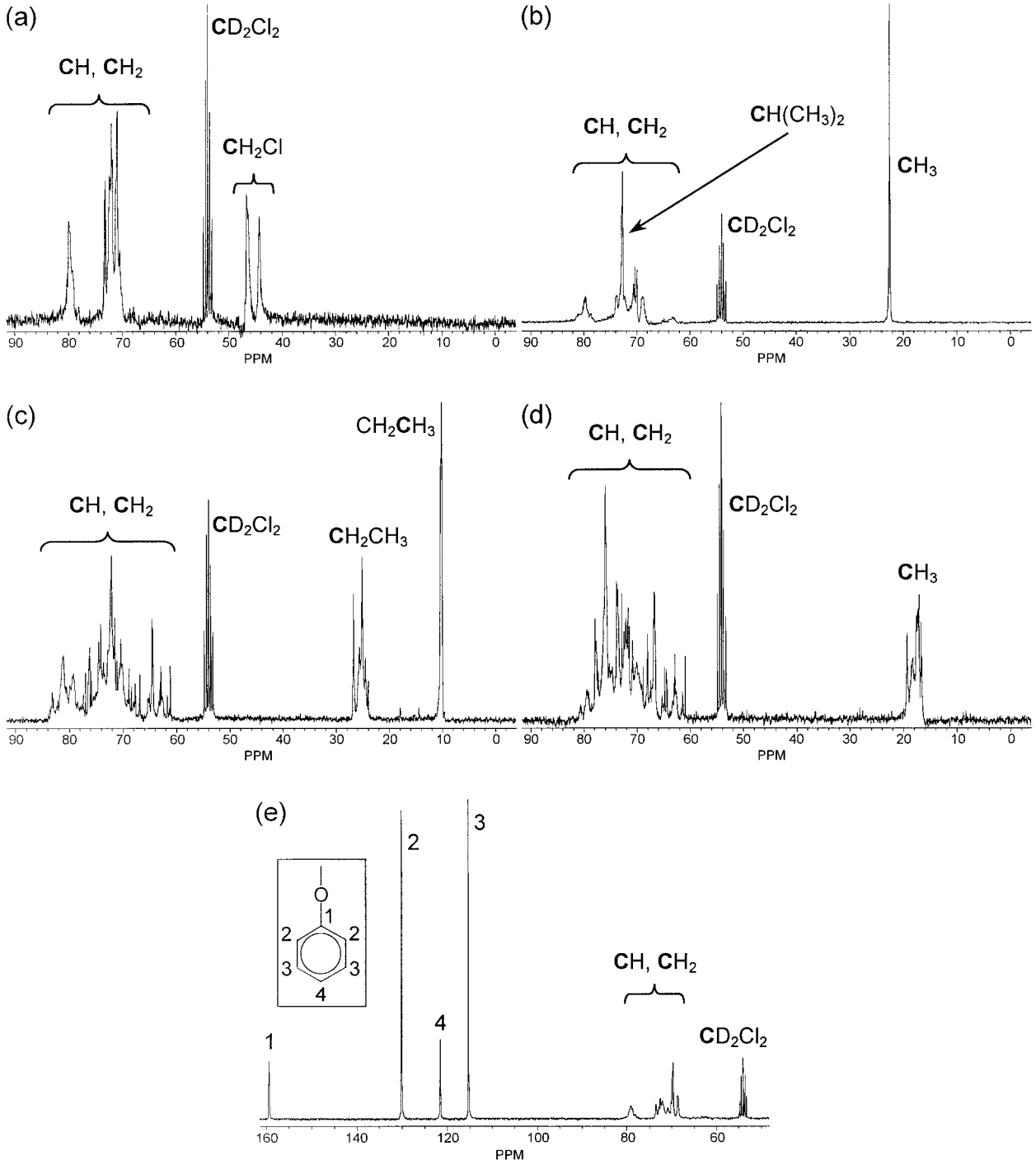

Figure 4 ^{13}C–NMR spectra of (a) poly(ECH-*co*-glycidol), (b) poly(IGE-*co*-glycidol), (c) poly(EB-*co*-glycidol), (d) poly(PO-*co*-glycidol), and (e) poly(GPE-*co*-glycidol). Note the different scale in (e) to accommodate phenyl carbon resonances, numbered in inset.

60–85 ppm in the spectra correspond to various methine or methylene carbons lying along the polymer main chains and bonded to hydroxyl or ether oxygens.[3,4,7] The resonances at 79.5 ppm and those between 72.0 and 73.5 ppm, seen in all spectra, indicate the presence of dendritic carbons[4] in these polymers, which is important evidence of branching in the polymer structure.

Resonances ascribed to side-group carbons usually show up well outside the 60–85 ppm range inhabited by the main-chain carbons, and are often considerably sharper. DEPT spectra (not shown), which can discriminate between CH, CH_2, and CH_3 carbons, were used to assign major side-group peaks. In Figure 4(a), the chloromethyl carbon resonance of poly(ECH-*co*-glycidol) can be seen as a pair of peaks at 44.5 and 46.8 ppm. The strong methyl resonance of the isopropyl side group in poly(IGE-*co*-glycidol) is visible at 22.5 ppm in Figure 4(b), and the sharp spike at 72.6 ppm, although overlapping with the main-chain regime, can be assigned to the isopropyl CH resonance.[8] The absorbances attributed to the methylene and methyl carbons of the ethyl side groups in poly(EB-*co*-glycidol) can be unambiguously located in Figure 4(c) as a set of peaks at 24–28 ppm and a sharp peak at 10.2 ppm, respectively. As expected, there is only a single feature in the spectrum of poly(PO-*co*-glycidol) corresponding to the methyl side group, and this can be seen in Figure 4(d) as a cluster of peaks centered at 18 ppm. Finally, the sharp peaks attributed to the aromatic carbons of the side groups in poly(GPE-*co*-glycidol) can be seen between 115 and 160 ppm, and are numbered according to the inset in Figure 4(e). The methylene carbon resonances of the side groups in the two glycidyl ether species IGE and GPE were not discernible. It is presumed—not unreasonably, given that these carbons are attached to oxygens—that they lie within the envelope of similar main-chain carbon resonances between 60 and 85 ppm.

Proton NMR spectra shown in Figure 5 corroborate the structural information obtained by ^{13}C–NMR, and also allow one to observe the hydroxyl groups so important to the amphiphilic properties of the polymers. The hydroxyl protons are evidenced in all spectra by a rather broad, symmetric, and featureless peak occurring between 2.6 and 3.4 ppm. Another feature common to all spectra is the presence of a wide, fused series of peaks located between 3.2 and 4.1 ppm, corresponding to main-chain CH and CH_2 protons. Side-group protons, once again, can be differentiated from main-chain and hydroxyl protons for the most part. In Figure 5(a), the chloromethyl protons of poly(ECH-*co*-glycidol) generate a large spike at about 3.6 ppm within the main-chain region of the spectrum. The methyl protons of the isopropyl side group in poly(IGE-*co*-glycidol) are seen to display a partially resolved doublet centered at 1.13 ppm in Figure 5(b), and a multiplet attributed to the methine proton[8] of the same side group can be seen centered at 3.56 ppm. Figure 5(c) shows the ethyl side groups of poly(EB-*co*-glycidol) absorbing at about 1.5 ppm (CH_2) and 0.9 ppm (CH_3), with peak areas in the expected 2 : 3 ratio, whereas Figure 5(d) shows the presence of only methyl side-group protons in poly(PO-*co*-glycidol) absorbing at about 1.1 ppm. The spectrum of poly(GPE-*co*-glycidol) is shown in Figure 5(e), and can be seen to contain sharp solvent impurity peaks at 5.25 ppm (CH_2Cl_2) and 7.24 ppm ($CHCl_3$).

Infrared spectroscopy provides subsidiary structural information complementing that obtained by NMR, especially with regard to the functional groups present in the polymers. Figure 6 displays the FTIR spectra of all polymers between 4000 and 400 cm^{-1}. The features common to these spectra are the strong, broad O—H stretching band at about 3410 cm^{-1}; asymmetric and symmetric CH_2 stretching bands (combined with the symmetric CH_3 stretching band, when methyl groups are present) at 2924 and 2876 cm^{-1}, respectively[9]; and the broad, intense stretching vibrations of the ether C—O—C system at about 1100 cm^{-1}. The strong C—Cl stretching vibration in poly(ECH-*co*-glycidol) is seen at 747 cm^{-1} in Figure 6(a).[8] All three methyl group-containing polymers also show a sharp peak at 2970 cm^{-1} in Figure 6(b), (c), and (d) originating from the asymmetric C—H stretch of this group.[9] The geminal methyl substituents of the isopropyl functional group in poly(IGE-*co*-glycidol) also give rise to the medium-intensity, nearly equal doublet at 1382 and 1370 cm^{-1} in Figure 6(b). The spectra in Figure 5(b) and (e) show one or more shoulders on the main-chain ether stretching peak ascribed to the presence of additional ether linkages in these two polymers' side groups. Just to the high-frequency side of the alkyl C—H stretching vibrations in Figure 6(e) can be seen a couple of aryl C—H stretching vibrations at 3062 and 3040 cm^{-1} from the phenyl rings[9] in poly(GPE-*co*-glycidol). Close examination of this spectrum shows a set of four small bands in the overtone region ($\sim$ 2000 to 1600 cm^{-1}) characteristic of monosubstituted phenyl rings,[8,9] as are the peaks at 885, 755, and 692 cm^{-1} in the aromatic fingerprint region.[8]

In summary, both NMR and FTIR data are consistent with the proposed structures for the synthesized polymers: highly branched polyether chains replete with hydroxyl groups and side groups from the comonomers. From the preceding spectral data, it does not appear that any of the

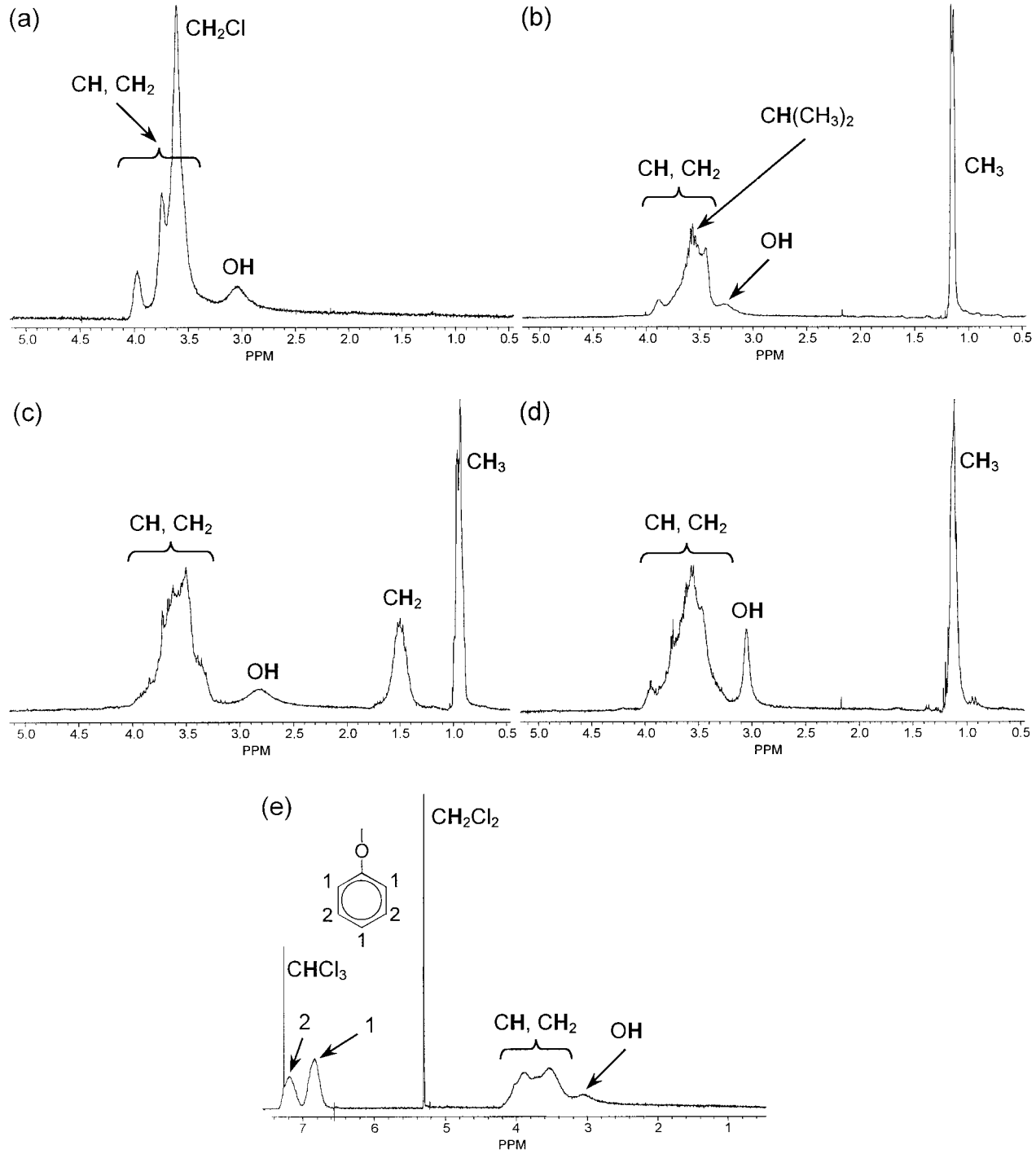

Figure 5 ^{1}H–NMR spectra of (a) poly(ECH-*co*-glycidol), (b) poly(IGE-*co*-glycidol), (c) poly(EB-*co*-glycidol), (d) poly(PO-*co*-glycidol), and (e) poly(GPE-*co*-glycidol). Note the expanded scale in (e) to accommodate phenyl proton resonances, numbered in inset.

side groups of the comonomers participate in the reaction in any way.

Properties

GPC analysis of the polymers yielded broad, irregularly shaped chromatograms, whereas the four narrow molecular weight distribution polystyrene standards were well resolved with the column set used. A sample elution profile of a polymer [poly(EB-*co*-glycidol) in this case] and of the standards are shown in Figure 7(a) and (b), respectively. The calibration curve from these

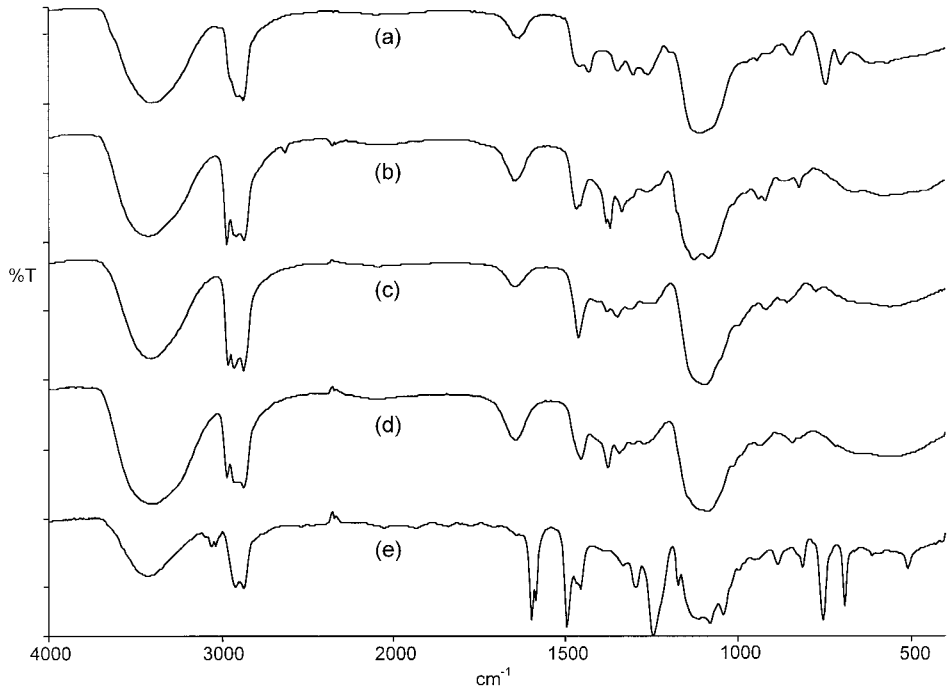

Figure 6 FTIR spectra of (a) poly(ECH-*co*-glycidol), (b) poly(IGE-*co*-glycidol), (c) poly(EB-*co*-glycidol), (d) poly(PO-*co*-glycidol), and (e) poly(GPE-*co*-glycidol).

standards was highly linear, with a correlation coefficient of 0.996. Small, sharp peaks were noticed in all chromatograms at the very low molecular size end of the GPC trace, between about 400 and 200 g/mol (~ 19 to 20 min retention time; the negative peaks beyond 20 min correspond to elution of solvent). These peaks probably correspond to small cyclic structures, which are known to form in such cationic polymerizations,[10] and are excluded from the molecular weight calculations to follow. Each polymer was analyzed in triplicate by GPC, the averaged results of which are shown in Table I. Because of the differences in chemical and physical structure between the linear polystyrene calibrants and the hyperbranched polymer products, these data are best viewed as a relative measure of polymer size and polydispersity. Other investigators[4] found that GPC generally gives higher molecular weight values for such hyperbranched polyglycidols than those obtained by, say, vapor phase osmometry.

A simple solubility test was conducted to determine the relative polarity of the various copolymers. About 50 mg of each polymer was added in a test tube at room temperature (22°C) to 1 mL of each of the following solvent sets, listed in order of increasing dielectric constant ϵ (roughly, polarity): hexane, $\epsilon = 1.89$; benzene, $\epsilon = 2.28$; dichloromethane, $\epsilon = 9.08$; acetone, $\epsilon = 20.7$; methanol,

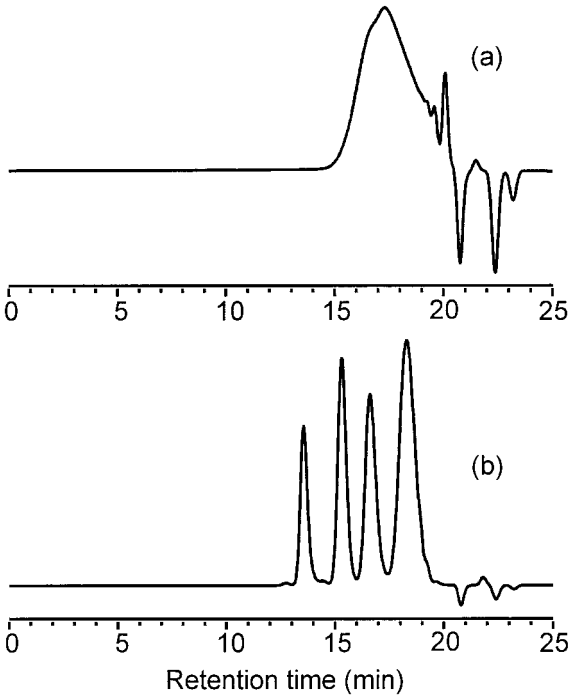

Figure 7 Sample GPC traces of (a) poly(EB-*co*-glycidol) and (b) narrow distribution polystyrene standards of MWs of 44,000, 13,700, 3680, and 760 (corresponding to the four peaks from left to right). The *y*-axis shows the detector response on an arbitrary scale.

Table I Average Polymer Molecular Weights and Polydispersity Indices from GPC Measurements

Polymer	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	Polydispersity Index
Poly(ECH-*co*-glycidol)	4279	73514	17.1
Poly(IGE-*co*-glycidol)	2893	9240	3.19
Poly(EB-*co*-glycidol)	1258	2593	2.06
Poly(PO-*co*-glycidol)	1191	2327	1.95
Poly(GPE-*co*-glycidol)	5834	48039	8.23

ϵ = 33.6; and water, ϵ = 80.4. Each solution was agitated violently for some minutes with a vortexer and allowed to stand for several hours, with occasional further shaking. The results are summarized in Table II, in which it can be deduced that the polymers form a graded set of materials of increasing polarity, reading down the first column in the table. The variation of polarity is remarkable, ranging from solubility in benzene to solubility in water.

Differential scanning calorimetry detected a prominent glass transition in all polymers. A sample thermogram of poly(IGE-*co*-glycidol) scanned at a heating rate of 10°C/min is displayed in Figure 8, in which the T_g is identified as the inflection point in the curve. The thermograms of the other polymers were similar. All polymers also showed a steady linear decrease in T_g as the heating rate decreased from 20 to 5°C/min, and the "true" T_g's were taken to be the extrapolated values at a zero heating rate. These are listed in increasing order in Table III. As can be seen in this table, most polymers showed T_g's well below 0°C, which is to be expected for such polymers as a result of the flexibility of their polyether backbones.[11] One notable exception to the trend of generally low T_g's is poly(GPE-*co*-glycidol), which showed the highest transition temperature of all

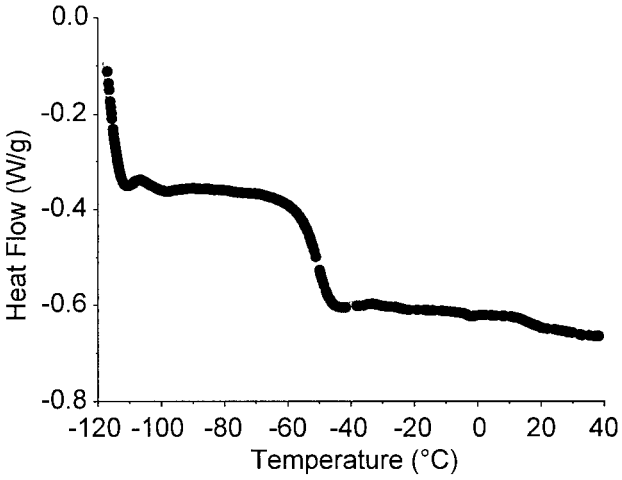

Figure 8 Sample DSC trace of poly(IGE-*co*-glycidol) at 10°C/min, showing a distinct glass transition in the central region of the curve (slope change). The exothermic direction is up on the *y*-axis and the sharp rise in the curve near −120°C is an artifact of the instrument, which appears on all thermograms.

at 1°C, most likely because the bulky phenyl side groups restrict main-chain motions.

The spectra, molecular weights, physical appearance, and other characteristics of the polymers did not change noticeably on storage for over 2 months, despite exposure to air and light. Noting that they are subjected to temperatures of up to 60°C during the recovery stage without harm, one can assume that these polymers are air-, light-, and temperature-stable materials.

It seems clear that the hydrophobicity of these copolymers can be controlled by the appropriate choice of comonomer. Structural control may possibly be achieved by sequential addition of monomers, for example, by allowing the polyglycidol cores to form first, and then adding the comonomer to force formation of block hyperbranched copolymers. Given that glycidol is almost fully

Table II Solubility of 50 mg of Polymers in 1 mL of Various Solvents at 22°C[a]

Polymer	Hexane	Benzene	Dichloromethane	Acetone	Methanol	Water
Poly(GPE-*co*-glycidol)	I	S	S	S	I	I
Poly(IGE-*co*-glycidol)	I	S	S	S	S	I
Poly(EB-*co*-glycidol)	I	S	S	S	S	I
Poly(ECH-*co*-glycidol)	I	I	S	S	S	I
Poly(PO-*co*-glycidol)	I	I	S	S	S	S

[a] The dielectric constant (and thus the polarity) of the solvents increases from left to right, varying from 1.89 for hexane to 80.4 for water. The polymers are arranged in order of increasing polarity from top to bottom. I = insoluble; S = soluble.

Table III Glass-Transition Temperatures (T_g) of Various Polymers as Measured by DSC, in Order of Increasing T_g Values[a]

Polymer	T_g (°C)
Poly(EB-*co*-glycidol)	−56
Poly(IGE-*co*-glycidol)	−54
Poly(PO-*co*-glycidol)	−51
Poly(ECH-*co*-glycidol)	−29
Poly(GPE-*co*-glycidol)	1

[a] The values listed were extrapolated to a zero heating rate from thermograms scanned at 20, 10, and 5°C per minute.

polymerized within about 10 min from the start of the reaction, this simple modification of reaction procedure would likely add very little to the total polymerization time. These and other experiments to determine the effects of solvent, temperature, and initiator on the polymerization are under way, as are investigations into the possibility of using other types of cationically polymerizable monomers besides epoxides to generate copolymers.

CONCLUSIONS

The straightforward cationic polymerization route discussed in this report is capable of generating stable hyperbranched polyethers with tunable polarity, which are soluble in solvents ranging from benzene to water, and exhibiting T_g's from −56 to 1°C. The structure of the copolymers is thought to consist of a polar polyglycidol core incorporating some comonomer, and radiating arms composed entirely of comonomer repeat units. The reaction proceeds at room temperature in ordinary atmosphere and goes to a very high degree of completion, producing polymers of low molecular weight and broad molecular weight distribution, as well as some small cyclic by-products and possibly homopolymers also. The choice of comonomer plays an important role in determining the polarity and thermal properties of the resultant copolymer. It appears that cycloalkene oxides and epoxides with aromatic rings attached are not suitable for this method of polymerization that can be carried out, however, with glycidyl ethers, halogenated epoxide compounds, and 1,2-epoxyalkanes.

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