Copolymerization of Glycidol with Functionalized Phenyl Glycidyl Ethers

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ABSTRACT: Various copolymers of glycidol with phenyl-containing comonomers (glycidyl 2-methylphenyl ether, 2-biphenylyl glycidyl ether, 4-*tert*-butylphenyl glycidyl ether, methoxyphenyl glycidyl ether, and *p*-nitrophenyl glycidyl ether) were synthesized by cationic ring-opening polymerization, for possible use as nanoparticle coatings. The copolymerization involving *p*-nitrophenyl glycidyl ether produced *p*-nitrophenol as a byproduct. The copolymers were found to have relatively low average molecular weights and high polydispersities, with glass-transition temperatures in the −20 to +10°C range (approximately). © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1462–1466, 2005

Key words: amphiphiles; cationic polymerization; copolymerization; glycidol; hyperbranched

INTRODUCTION

This report is the fourth in a series of articles on the cationic ring-opening polymerization of glycidol (2,3-epoxy-1-propanol) and its copolymerization with epoxide comonomers, an industrially useful[1] process. In an earlier report in this journal,[2] the copolymerization of glycidol with a number of (mostly alkyl) epoxide comonomers was examined. This article extends the scope of this reaction to include copolymerization of glycidol with phenyl glycidyl ethers, with the aim of making a novel family of copolymers for possible use as nanoparticle coatings.

Many of the uses of nanoparticles, such as in analytical, medical, and biological applications, depend on their fluorescent properties,[3] which depend strongly on the particles' coating. Amphiphilic branched polymers have been found to make excellent coatings for nanoparticles,[4] which inspired this work on the synthesis of hyperbranched amphiphilic copolymers of glycidol with a number of different functionalized phenyl glycidyl ethers.

EXPERIMENTAL

Materials

4-*tert*-Butylphenyl glycidyl ether (TBGE), glycidyl 2-methylphenyl ether (GMPE), glycidol, and narrow

molecular weight polystyrene standards were obtained from Aldrich (Milwaukee, WI); boron trifluoride diethyl etherate (BF$_3$:OEt$_2$), *p*-methoxyphenyl glycidyl ether (MPGE), 2-biphenylyl glycidyl ether (BPGE), and *p*-nitrophenyl glycidyl ether (NPGE) were obtained from Across 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. Dichloromethane, the reaction solvent, was stored over 4-Å molecular sieves under nitrogen. GMPE was purified by distillation and NPGE was recrystallized from chloroform/hexane; other materials were used as received.

Synthesis

Polymerizations were carried out according to a previously published procedure[2] using 0.1 mol (6.7 mL) glycidol and 0.12 mol of a comonomer in dichloromethane. The progress of the reaction was monitored by GC-MS. After 21 hrs the reaction was quenched by adding 2 mL distilled water and stirring for an additional hour. Following rotary evaporation of most of the solvent, the mixture was transferred to a preweighed beaker and placed in a warm sand bath overnight to further remove residual solvents. The next day it was lyophilized to evaporate any remaining volatiles.

Analysis

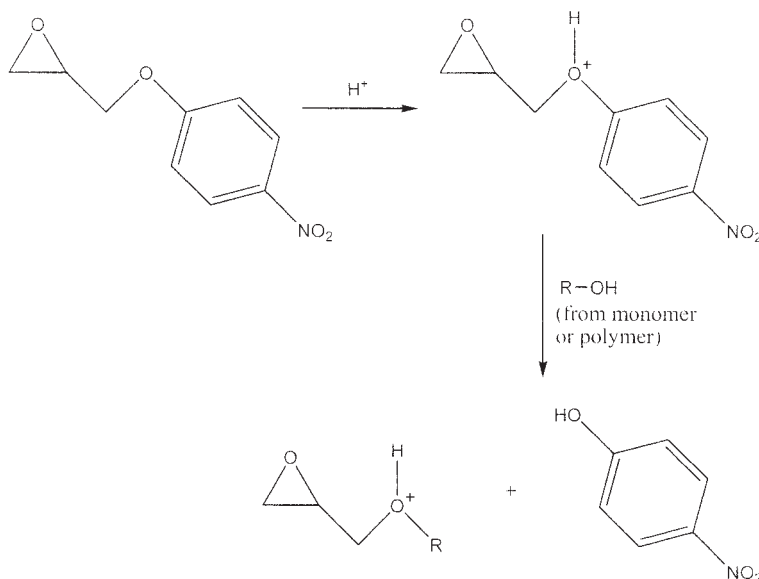Polymerizations were monitored using a Thermoquest (San Jose, CA) Trace 2000 GC with a Trace MS detec-

Figure 1 Proposed mechanism for formation of *p*-nitrophenol during the attempted polymerization of NGPE and glycidol with BF_3:OEt_2.

tor, equipped with a Restek Rtx-5MS capillary column of length 15 m and ID 0.25 mm, with helium as the carrier gas. ^{1}H- and ^{13}C-NMR spectra were recorded using a Varian (Palo Alto. Ca) Mercury Plus 300-MHz spectrometer operating at 300 and 70 MHz, respectively. A 0.250-g sample of each copolymer was dissolved in 1 mL CD_6Cl_3 for NMR analysis. Infrared spectra of thin films of polymer smeared on KBr disks were taken with a Perkin–Elmer (Norwalk, CT) System 1760 FTIR. Differential scanning calorimetry (DCS) was performed on a Mettler (Columbus, OH) DSC 30 equipped with a low-temperature cell. The temperature range analyzed was -150 to 50°C, at a heating rate of 10°C/min. Polymer molecular weight was measured by gel permeation chromatography (GPC) with a Waters (Milford, MA) GPC system (515 HPLC pump, 717plus autosampler, 2410 refractive index detector, column heater module, Millennium32 software, and two Waters HR 4E columns. 30°C). HPLC grade THF was used as the mobile phase, and narrow molecular weight distribution polystyrene standards of molecular weights 212,400, 29,300, 3680, and 760 g/mol were used for molecular weight calibration.

RESULTS AND DISCUSSION

Polymerization

Each of the comonomers MPGE, TBGE, BPGE, GMPE, and NPGE were copolymerized with glycidol. Upon addition of initiator, the reaction temperature rose to about 40°C in a few minutes accompanied by the formation of a clear, colorless, viscous precipitate of hyperbranched polyglycidol, as usual. The glycidol was almost completely consumed during this initial phase and the comonomer was subsequently consumed much more slowly. The polyglycidol precipitate initially formed slowly redissolved as the comonomer added to the ends of the polyglycidol chains. As before, the structure of these copolymers is a polar polyglycidol core with nonpolar polyether arms. All polymers were obtained in high yields (average yield 92%).

There was one exception to the above-described sequence of events, which occurred with NPGE. In this case, an exothermic reaction took place as usual upon addition of BF_3:OEt_2, but with the formation of an intense yellow (still clear) solution. In less than 1 min the solution became cloudy and opaque. As the reaction proceeded, the opaqueness of the solution lessened while the intense yellow color increased. By the end of the reaction, the solution was transparent yellow with an orange insoluble layer at the bottom of the reaction flask. The yellow color was probably a result of the formation of *p*-nitrophenol as shown in Figure 1.

Spectra

^{13}C-NMR spectra of the various polymers are shown in Figure 2. All spectra were referenced against the CD_2Cl_2 quintet at 54.0 ppm. Peaks in the 60–85 ppm range are from CH or CH_2 from the polymer main chains and bonded to hydroxyl or ether oxygens, and also peaks from –CH_2—O—phenyl carbons of comonomer. Branching in these polymers is con-
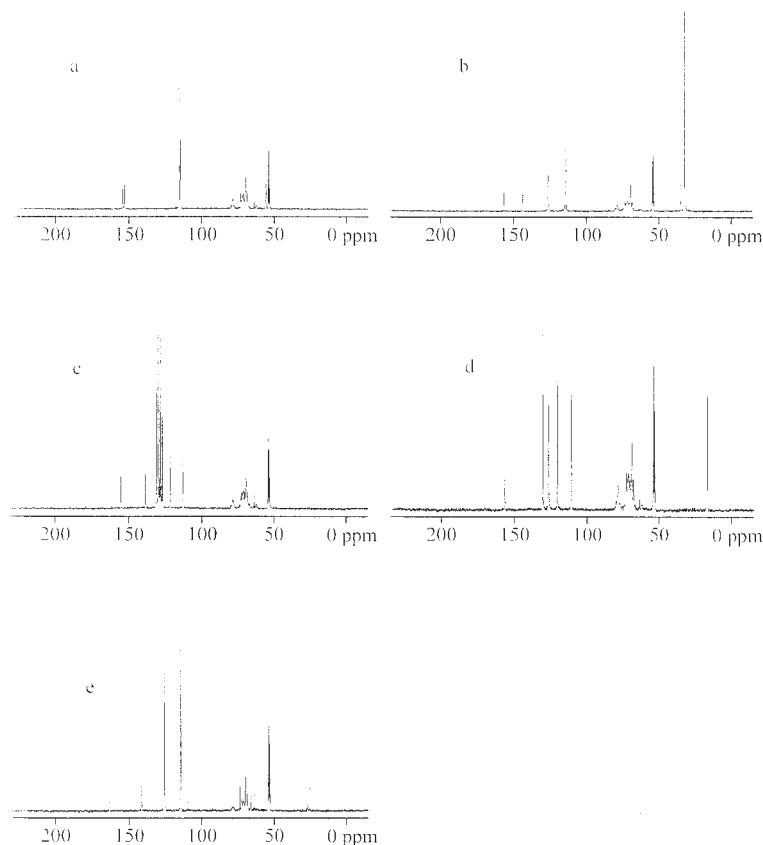
Figure 2 ^{13}C-NMR spectra of (a) poly(MPGE-*co*-glycidol), (b) poly(TBGE-*co*-glycidol), (c) poly(BPGE-*co*-glycidol), (d) poly(GMPE-*co*-glycidol), and (e) poly(NPGE-*co*-glycidol).

firmed by the presence of resonances at 79.0 ppm and 69.5–71.2 ppm from dendritic carbons is polymer.[2] Because all spectra contained side groups phenyl carbons, they all contained peaks ranging between 111 and 164 ppm. In Figure 2(a), the methyl carbon resonance of poly(MPGE-*co*-glycidol) can be seen as a peak at 56.2 ppm. The *t*-butyl carbon resonances from poly (TBGE-*co*-glycidol in Figure 2(b) can be seen at 31.8 and 34.5 pp. Because there are no other alkyl side groups carbons associated with poly(BPGE-*co*-glycidol), no other peaks were expected or seen in Figure 2(c). For the poly(GMPE-*co*-glycidol) copolymer in Figure 2(d), the methyl carbon has a peak at 16.6 ppm. In the poly(NPGE-*co*-glycidol), there were again no alkyl side group carbons to give rise to any additional peaks in Figure 2(e), besides those already discussed.

Proton NMR spectra of these polymers are shown in Figure 3. The series of peaks between 2.9 and 5.0 ppm correspond to main-chain methine and methylene protons. The hydroxyl protons are evident in all spectra by a rather broad, symmetric, and featureless peak occurring between 2.6 and 3.4 ppm. In some cases, the hydroxyl peak overlaps significantly with the methine and methylene protons. All phenyl hydrogens are downfield between 6.8 and 8.2 ppm. Side-group protons from alkyl hydrogens are as follows: Figure 3(b)

shows a singlet for the *t*-butyl hydrogens at 1.3 ppm, and the methyl hydrogens of the poly(GMPE-*co*-glycidol) can be seen at 2.2 ppm in Figure 3(d).

Finally, Figure 4 displays the FTIR spectra of all polymers between 4000 and 500 cm^{-1}. The FTIR spectra are as expected with a broad hydroxyl band at about 3400 cm^{-1}, and aryl C—H stretched at about 3000 cm^{-1}, clearly visible in a few of the spectra, but obscured by the O—H stretch in others.

The spectral data discussed above corroborate the structures proposed for these copolymers, and clearly discernible peaks for the side groups (with the exception of the *p*-nitrophenyl group in NPGE) in various spectra indicate that they are not involved in side reactions during polymerization.

Molecular weight and thermal properties

Average molecular weights $\bar{M}_n$ and $\bar{M}M_w$ were determined by GPC, against polystyrene standards. Each copolymer was analyzed in duplicate by GPC, and the averaged results are shown in Table I. For poly(TBGE-*co*-glycidol) and poly(BPGE-*co*-glycidol), there were two distinct peaks observed, indicative of two different molecular weight fractions in these materials. In general, polymer molecular weights were low and
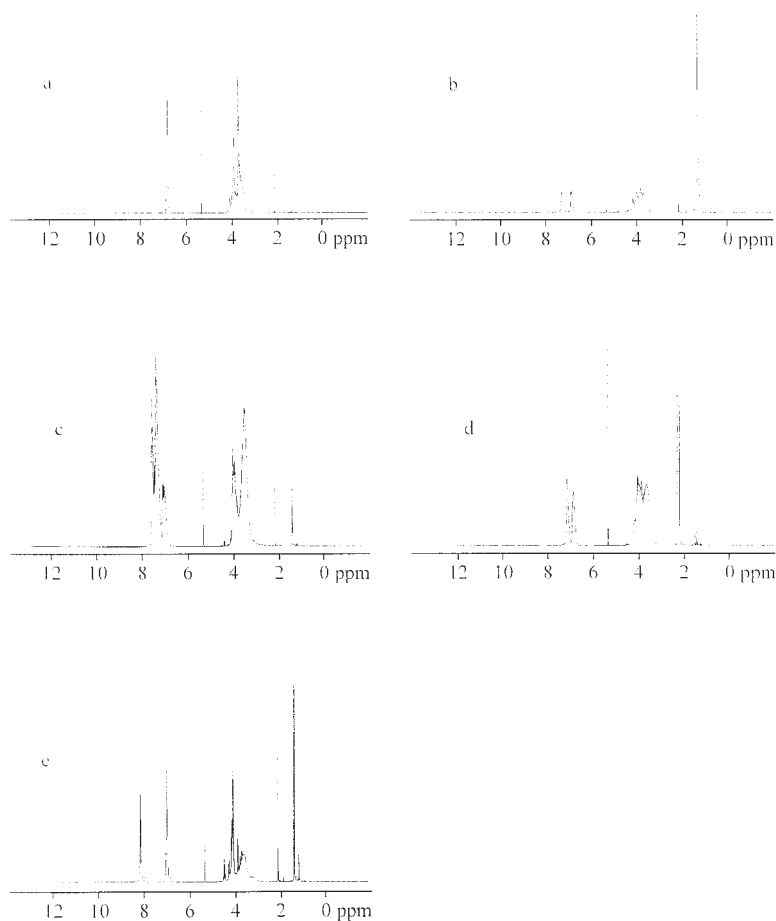
Figure 3 ^{1}H-NMR spectra of (a) poly(MPGE-*co*-glycidol), (b) poly(TBGE-*co*-glycidol), (c) poly(BPGE-*co*-glycidol), (d) poly(GMPE-*co*-glycidol), and (e) poly(NPGE-*co*-glycidol).

polydispersities were high, as previously observed for similar systems.[2]

The glass-transition temperatures (T_g) of all copolymers were measured by DSC. Sample thermograms

of poly(MPGE-*co*-glycidol) and poly(BPGE-*co*-glycidol) scanned at a heating rate of 10°C/min are displayed in Figure 5. in which the T_g is identified as the inflection point in the curves. These are representative
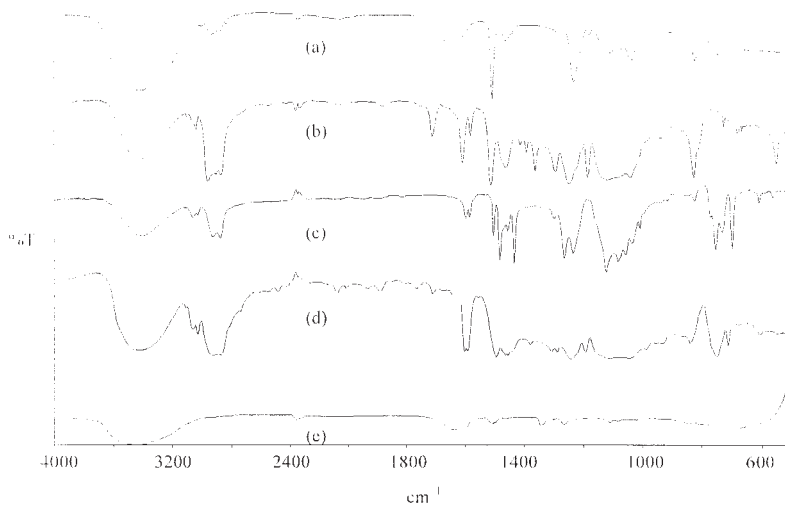

Figure 4 FTIR spectra of (a) poly(MPGE-*co*-glycidol), (b) poly(TBGE-*co*-glycidol), (c) poly(BPGE-*co*-glycidol), (d) poly(GMPE-*co*-glycidol), and (e) poly(NPGE-*co*-glycidol).

TABLE I
Average Copolymer Molecular Weights and Polydispersities

Polymer	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	Polydispersity index
Poly(MPGE-co-glycidol)	9.0×10^2	8.1×10^2	9.1
Poly(TBGE-co-glycidol)	1.2×10^3	4.3×10^4	35
Poly(BPGE-co-glycidol)	4.9×10^2	3.2×10^3	6.6
Poly(GMPE-co-glycidol)	1.4×10^3	3.6×10^4	26
Poly(NPGE-co-glycidol)	8.7×10^2	9.6×10^3	12

TABLE II
Glass-Transition Temperatures of Various Polymers as Measured by DSC[a]

Polymer	T_g (°C)
Poly(MPGE-co-glycidol)	−18
Poly(TBGE-co-glycidol)	−16 and 0.5
Poly(BPGE-co-glycidol)	−15 and 11
Poly(GMPE-co-glycidol)	−16
Poly(NPGE-co-glycidol)	−15

[a] Listed values were obtained from thermograms scanned at 10°C/min.

of the thermograms of the other polymers. The T_g's of all copolymers can be found in Table II, and all are well below ambient temperature. This is consistent with the flexible nature of the polyether main chains of these substances.[5] Poly(TBGE-co-glycidol) and poly(B-PGE-co-glycidol) were again different from the other copolymers. Rather than a single "step", there was a double "step" transition. This is in conformity with the GPC data, which suggested that there were two polymer fractions (low and high molecular weight) produced during those syntheses.

CONCLUSIONS

The BF$_3$-catalyzed cationic ring-opening polymerization reaction of glycidol with various comonomers, which we have been examining, has been extended to included several phenyl glycidyl ethers. The reaction easily produces novel, interesting copolymers with hyperbranched structure, although of low molecular weight and relatively high polydispersity. The resulting copolymers were characterized spectroscopically and thermally, and behave generally as expected. These copolymers may be useful for coatings, such as for nanoparticles and other surfaces.
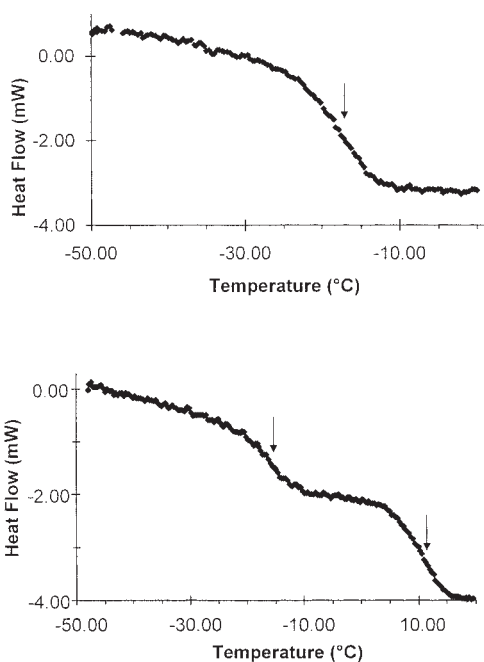
Figure 5 Sample DSC trace of (a) poly(MPGE-co-glycidol), and (b) poly(BPGE-co-glycidol), at 10°C/min, showing glass transitions (inflection points) marked by arrows.

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