Photopolymerization of an Expanding Monomer with an Aromatic Dioxirane

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ABSTRACT: The objective was to study the photocationic polymerization of an expanding monomer, 1,5,7,11-tetraoxaspiro[5.5]undecane (TOSU), and an aromatic dioxirane, bisphenol A diglycidyl ether (BADGE). Both homopolymerizations and binary polymerizations were conducted. The homopolymer, poly(TOSU), was found to be a linear poly(carbonate), which was soluble in acetone. Poly-(BADGE) products contained ether linkages in addition to primary and secondary alcohol functionalities. Binary polymerization products varied depending on the irradiation time and length of dark cure. ^{13}C-NMR analysis of binary polymerizate products revealed peaks not seen in homopolymer spectra consistent with the formation of copolymer linkages. Mass spectrometry data revealed peaks consistent with oligomers that contained both TOSU and BADGE mer units. The structures of key reaction products were proposed. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 62–71, 2004

Key words: MALDI-TOF; NMR; expanding monomers; cationic polymerization; dioxiranes

INTRODUCTION

Most thermoset resins shrink about 2–6% during polymerization.[1] The premature failure of polymer-based composites is usually caused by poor adhesion between the filler and the matrix or from voids and cracks caused by polymerization shrinkage. If a material were to expand upon polymerization, it would be able to fill gaps and bind to substrates much more effectively. Such materials would have applications as high-performance adhesives, sealants, and coatings. They could be used as precision castings and dental composites and in other applications where high-strength composites are required. One way to make low-shrinkage/low-stress materials has been to incorporate spiroorthocarbonates, spiroortho esters, and other strained bicyclic monomers.[2–5] In one case, a volumetric expansion of 17% was reported.[6] Spiroorthocarbonates and spiroorthoesters have been used as volume-control additives when copolymerized with epoxies, improving bonding strength and other physical properties.[7–9] However, others have failed to duplicate these improvements and it has been suggested that the observed reduction in shrinkage may be due to a lowering of the epoxy glass transition temperature rather than a volumetric expansion.[10,11] The literature on spiroorthocarbonates and other expanding monomers in oxirane resin systems has been reviewed.[12,13]

More recently, copolymerization between a dioxirane and a 1,5,7,11-tetraoxaspiro[5.5]undecane (TOSU) (using boron trifluoride monoethylamine and elevated temperature) was shown to have zero shrinkage.[14] The mechanism of polymerization was the generation of an acid from the boron trifluoride monoethylamine, similar to that described previously for similar polymerizations of oxiranes using BF_3-based compounds.[15]

To develop low-shrinkage, reduced-stress resins it is necessary to understand how dioxiranes and expanding monomers interact in cationically reacting systems. To do this, a simple model system consisting of an aromatic dioxirane (bisphenol A diglycidyl ether, BADGE) and an unsubstituted spiroorthocarbonate (TOSU) was chosen. BADGE is representative of aromatic dioxiranes that are used as base resins, and there are many studies describing the NMR analysis of its polymerization.[16–18] TOSU was chosen because it can only polymerize via spirocyclic ring opening. The structures of the BADGE and TOSU monomers are shown in Table I.

The polymerization of BADGE with TOSU has been previously studied[19] using an aryl sulfonium salt initiator at 120–150°C, resulting in copolymerization. In the current study, the polymerization was conducted using a visible light photoacid initiator system and a

TABLE I
Monomer Structures

Name and abbreviation	Structure
Bisphenol A diglycidyl ether (BADGE)	
1,5,7,11-Tetraoxaspiro[5.5]undecane (TOSU)	

conventional dental curing lamp. The chemistry and use of photoacid initiators, photosensitizers, and electron donor compounds in cationic resin systems have been previously described.[20,21]

Cationic polymerizations of BADGE (also known as the diglycidyl ether of bisphenol A, or DGEBA) and other oxiranes have been widely studied for decades using infrared and ^{13}C-NMR spectroscopy.[16–18,22] Both techniques can monitor the disappearance of oxirane and other functional groups in monomers, along with the appearance of hydroxyl, ether, carbonyl, and other groups in polymers. Matrix-assisted laser desorption and ionization time of flight (MALDI-TOF) mass spectrometry has recently been used in the characterization of synthetic polymers.[23,24] It is especially useful for analyzing polymers, which cannot be volatilized by other ionization methods.

Computational methods based on quantum mechanics have recently been applied to determine activation energies and enthalpies of polymerization for a variety of monomers.[25–27] These calculations can help predict which reactions are most favored energetically.

The objective of this study was to test the hypothesis that TOSU and BADGE can copolymerize using a visible light photoinitiation system. NMR was used to analyze the homopolymerization products of BADGE and TOSU and to compare them to the spectra obtained from binary polymerization products. MALDI-TOF determined the molecular weight ranges of selected polymerizate products. Structures of key polymeric products were proposed, based on previously published spectra of the reaction between BADGE and a model compound, butanediol.[19]

EXPERIMENTAL

Materials

The monomer, BADGE, (EPON Resin 825) was from Resolution Performance Products, (Houston, TX). TOSU was synthesized at Midwest Research Institute by transesterification of 1,3-propanediol in the presence of *p*-toluenesulfonic acid. The photoinitiator system consisted of phenyl-[*p*-(2-hydroxytetradecyloxy-)phenyl]iodonium hexafluoroantimonate, PI (Gelest,

Inc., Tullytown, PA); camphorquinone (CQ; Aldrich, Milwaukee, WI); and ethyl 4-dimethylaminobenzoate (EDMAB; Fisher Scientific, Pittsburgh, PA). Chromatographic grade silica, dichloromethane, ethyl acetate, and chloroform were from Fisher Scientific. Chloroform-*d* or $CDCl_3$, 99.8 atom %, containing 1% tetramethylsilane (TMS), was from Aldrich.

Methods

Polymerization techniques

A summary of reaction conditions for four polymerizations is given in Table II. Polymerizations (single runs) were carried out in glass scintillation vials (Fisher Scientific) with magnetic stirring. Reaction mixtures were prepared just prior to testing. Mixtures containing about 2.0 g of monomer(s) and 0.08 g of the photoinitiator system were irradiated using a 3*M* XL2500 dental curing light (3MESPE Dental Products, St. Paul, MN) with an 11-mm-diameter light guide tip 12 cm above the sample surface. Light intensity (4 mW/cm^2) was measured with an EFOS Cure Rite visible light-curing meter (Model 8000; EFOS, Inc., Mississauga, Ontario, Canada). Binary polymerizations were conducted at 65–70°C to maintain the solubility of TOSU in BADGE. Binary polymerization mixtures contained 60 mol % BADGE and 40 mol % TOSU. The photoinitiator system levels in all cases were: PI/CQ/EDMAB = 3/1/0.1 wt % based on the weight of the monomer(s). Some polymerizations included a period of dark cure. Selected binary polymerizations were quenched by the addition of 4.2 g of

TABLE II
Summary of Reaction Conditions

Reaction	Run No.	Irradiation (min)	Dark cure (min)	Temp. (°C)
TOSU homopolymerization	1	1.5	2.5	140
BADGE homopolymerization	2	2.83	0.67	65–70
Binary polymerization	3	10	1	65–70
Binary polymerization	4	9.5	9	65–70

silica gel (250–400 mesh, 60 Å; Fisher Scientific) and stored at -10 to -20°C with desiccant prior to analysis.

Separation of monomers from polymer

Unreacted monomers were separated from polymers on a 4.5 × 50 cm column packed with silica and preequilibrated with 9:1 CH_2Cl_2:ethyl acetate (v : v). After the monomers were removed with 1800 mL of this eluent, the mobile phase was switched to acetone to elute the polymeric materials. The acetone was evaporated off and the polymer residue (viscous liquid) was redissolved in $CDCl_3$ with 1% TMS to obtain NMR spectra.

NMR analysis

NMR spectra were obtained on a Varian 400-MHz NMR, equipped with a broadband, tunable probe, a SunSparc computer, and VNMR software. Proton NMR spectra were obtained at 399.791 MHz, using a 90° pulse width and a 5-s. pulse delay. Carbon-13 spectra were obtained using a 45° pulse width and a 1-s. pulse delay. Eight transients were collected for proton and 256 transients were collected for ^{13}C-NMR spectra, with proton decoupling. To determine the number of protons attached to each carbon, attached proton test and distortionless enhancement through polarization transfer (DEPT) spectra were obtained.

Molecular weight characterization

The molecular weight ranges of selected soluble polymeric products were characterized using MALDI-TOF mass spectrometry. The samples were analyzed using an Applied Biosystems Voyager-DE STR MALDI-TOF mass spectrometer (Applied Biosystems, Framingham, MA). The samples were internally calibrated using matrix-related masses. Samples were prepared in ethyl acetate or tetrahydrofuran. Dithranol was used as the matrix and was prepared at 20 mg/mL in tetrahydrofuran. The sample and matrix were mixed at 1 : 1 (v/v) or 1 : 5 (v/v) and 0.8 μ to 1.0 μL of the mixture was applied to a gold-plated MALDI plate with shallow wells. Delayed extraction reflectron spectra were acquired in the positive ion mode with an acceleration voltage of 20 kV, an extraction delay time of 200 ns, and a grid voltage of 65%. About 100 laser shots were fired to acquire the spectra and processing was done with Applied Biosystems Data Explorer (version 4.0) software.

Computational energetics

The AM1 method[25] was used for reaction energetics calculations (heat of reaction, ΔH_{rxn}; activation energy, E_{act}) as implemented in the program AMPAC with Graphical User Interface (Semichem, Shawnee Mission, KS). ΔH_{rxn} was computed as the difference between the heat of formation (ΔH_f) of the products and the ΔH_f of the van der Waals complex formed by the reactant molecules. E_{act} was computed as the difference between the ΔH_f of the transition state and the ΔH_f of the van der Waals complex formed by the reactant molecules. The application of these methods to related expanding monomer and oxirane cationic polymerization systems has been previously described.[26,27] Proton affinities (PA) were calculated by a previously reported method.[28]

RESULTS AND DISCUSSION

Homopolymerization of TOSU

Homopolymerization of TOSU (Run No. 1, Table II) produced a linear poly(carbonate) that was readily soluble in acetone and chloroform. A reaction temperature of 140°C was necessary to keep the neat monomer in the melt state during irradiation. The ^{13}C-NMR spectrum of poly(TOSU) is shown in Figure 1. The peak assignments are compared to those of the TOSU monomer in Table III. The peak due to the spiro carbon in the monomer at 113.44 ppm was not present in the polymer. As the spiroorthocarbonate ring opened, it was converted to a carbonate carbonyl with a chemical shift of 155 ppm. The –CH_2O– peak in monomeric TOSU at 62.02 ppm was shifted after the reaction. In the homopolymer spectrum, peaks at 64–67 ppm were due to internal –CH_2O– groups and those at 58.45 ppm were due to terminal –CH_2OH groups. This is similar to the spectrum of poly(ethylene glycol) in which the internal –CH_2O– groups produce different chemical shifts (depending on whether they are due to the dimer, trimer, or higher molecular weight oligomers) and a single peak near 58 ppm for the terminal –CH_2OH carbons.[15] Finally, the internal –CH_2- groups in the TOSU monomer produced a peak at 23.79 ppm, which shifted to 28.1–30.8 ppm in the poly(TOSU).

The ^{1}H-NMR spectrum of poly(TOSU) was also different from that of the TOSU monomer. The internal –CH_2– groups were shifted from 1.7 ppm in the monomer to 1.9 ppm in poly(TOSU). The chemical shift for the –CH_2O– groups in the monomer is converted to two different types of –CH_2O– groups in the poly(TOSU). One is adjacent to the carbonyl and appears at 4.05 ppm and the other is two carbons away from the carbonyl and appears at 3.65 ppm.

Homopolymerization of BADGE

When BADGE was homopolymerized (Run No. 2, Table II), 58% of it was converted into a crosslinked polymer that was not soluble in acetone or chloro-
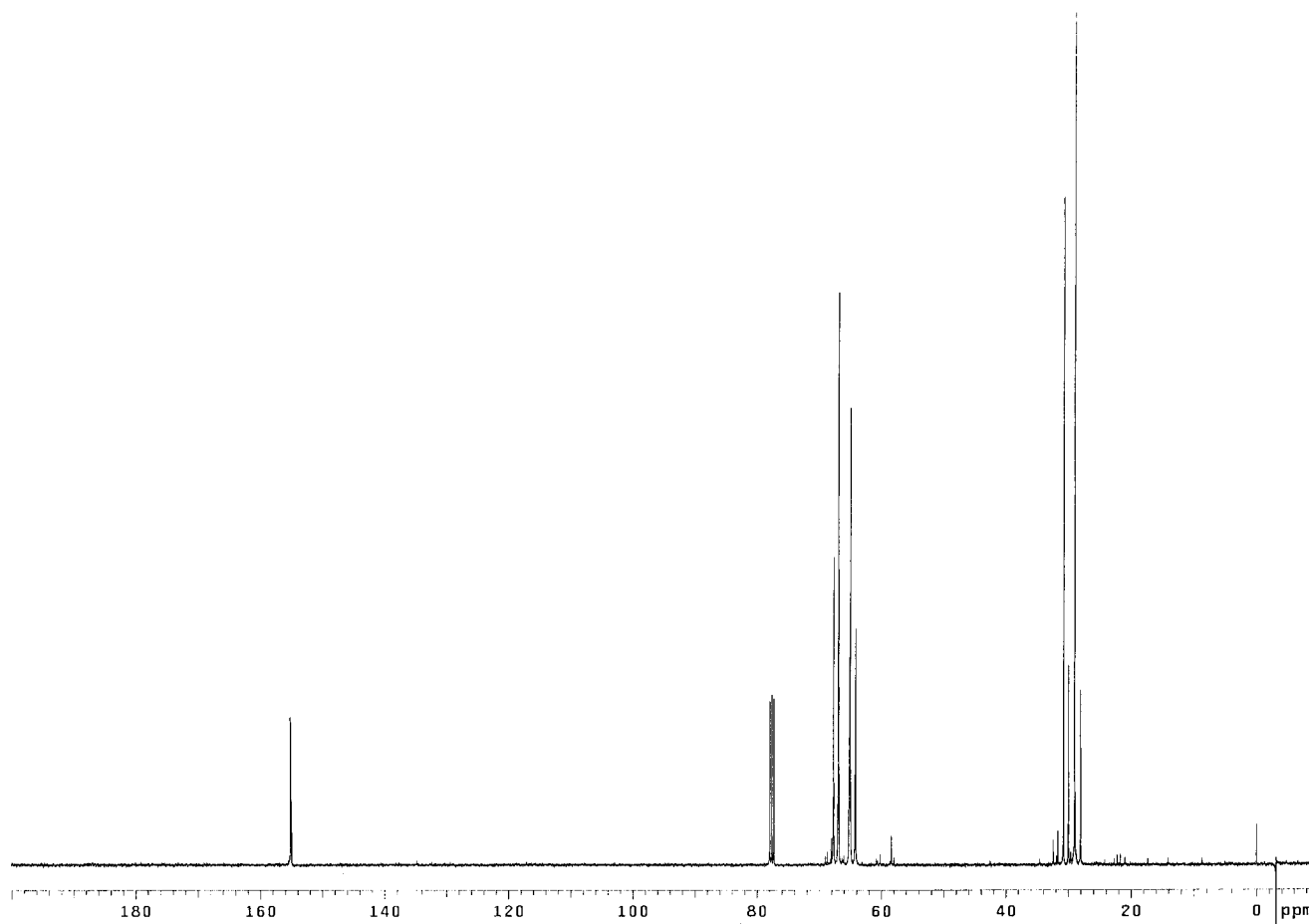
Figure 1 ^{13}C-NMR of poly(TOSU)—full spectrum (0–200 ppm).

form. The reaction was carried out at 65–70°C to be comparable to binary polymerizations. The soluble portion contained unreacted BADGE monomer and some poly(BADGE). The complete ^{13}C-NMR spectrum of soluble poly(BADGE) after unreacted monomer was removed is shown in Figure 2. The spectrum was very similar to previously reported spectra of poly-(BADGE).[19–21] However, there were two smaller peaks (60.6 and 77.6 ppm), due to terminal –CH$_2$OH and R-CHOR, respectively. These were produced by a reaction at the secondary alcohol of the BADGE re-

peating unit, or –mer. The larger peak at 68.9 ppm was produced by reaction at the primary alcohol of the BADGE –mer. Assignments for major peaks are shown in Table IV. It should be noted that the top structure is characteristic of higher molecular weight oligomers. The middle structure shows a minor reaction product, in which the secondary alcohol has reacted to form an ether. The bottom structure is characteristic of lower molecular weight oligo(BADGE), which is terminated with oxiranes that produce peaks at 44.2 and 49.9 ppm.

TABLE III
Structures and ^{13}C-NMR Chemical Shifts of TOSU and poly(TOSU)

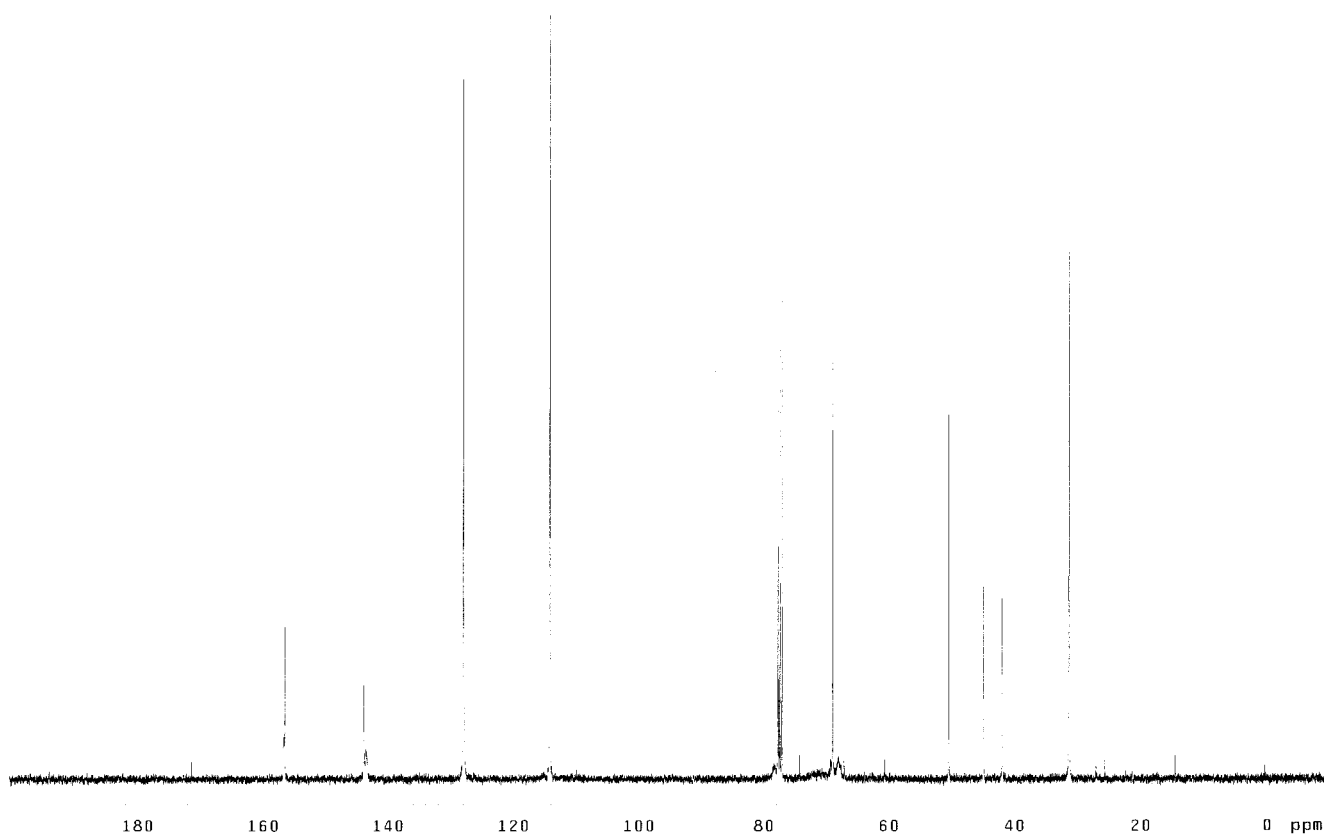| Structure	^{13}C-NMR Chemical Shifts
	1. 23.79 ppm 2. 62.02 ppm 3. 113.44 ppm
	1. 28.1–30.8 ppm 2. 64.2–67.1 ppm (internal -CH$_2$O-) 3. 58.45 ppm (terminal -CH$_2$OH) 4. 154.9–155.2 ppm

Figure 2 ^{13}C-NMR of poly(BADGE)—full spectrum (0–200 ppm).

For a similar homopolymerization with reduced irradiation time (1.25 min), a small amount of material eluted after the unreacted BADGE, but before the poly(BADGE) during separation. Its spectrum contained peaks at 68.9–69.0 ppm, due to the production of carbons from the group -OCH$_2$-CHOH-CH$_2$O- and peaks at 44.2 and 49.9 ppm due to oxiranes. This indicated that a reaction occurred between BADGE

TABLE IV
Structures and ^{13}C-NMR Chemical Shifts of poly(BADGE)

Structures	^{13}C-NMR Chemical Shifts
poly(BADGE)	1. 31.0 ppm 2. 41.2 ppm 3. 68.9 ppm 3′. 60.6 ppm (terminal -CH$_2$OH) 4. 113.6 ppm 5. 127.2 ppm 6. 143.9 ppm 7. 156.0 ppm
	1. 60.6 ppm (terminal -CH$_2$OH) 2. 77.6 ppm
	1. 44.2 ppm 2. 49.9 ppm 3. 68.9 ppm
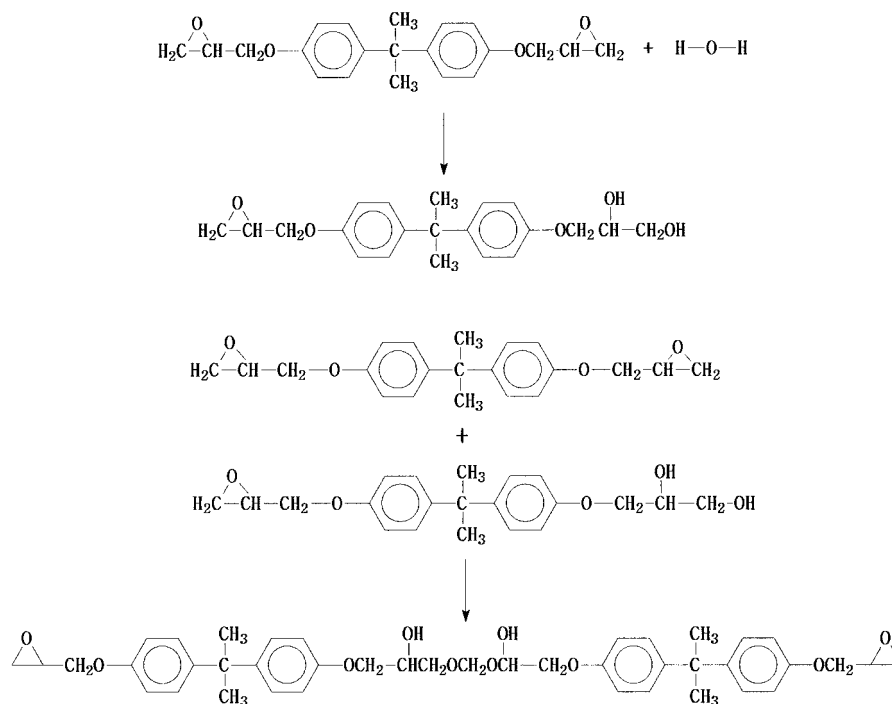
Figure 3   Reactions between BADGE and water and between BADGE and hydrolyzed BADGE.

180   160   140   120   100   80   60   40   20   0   ppm
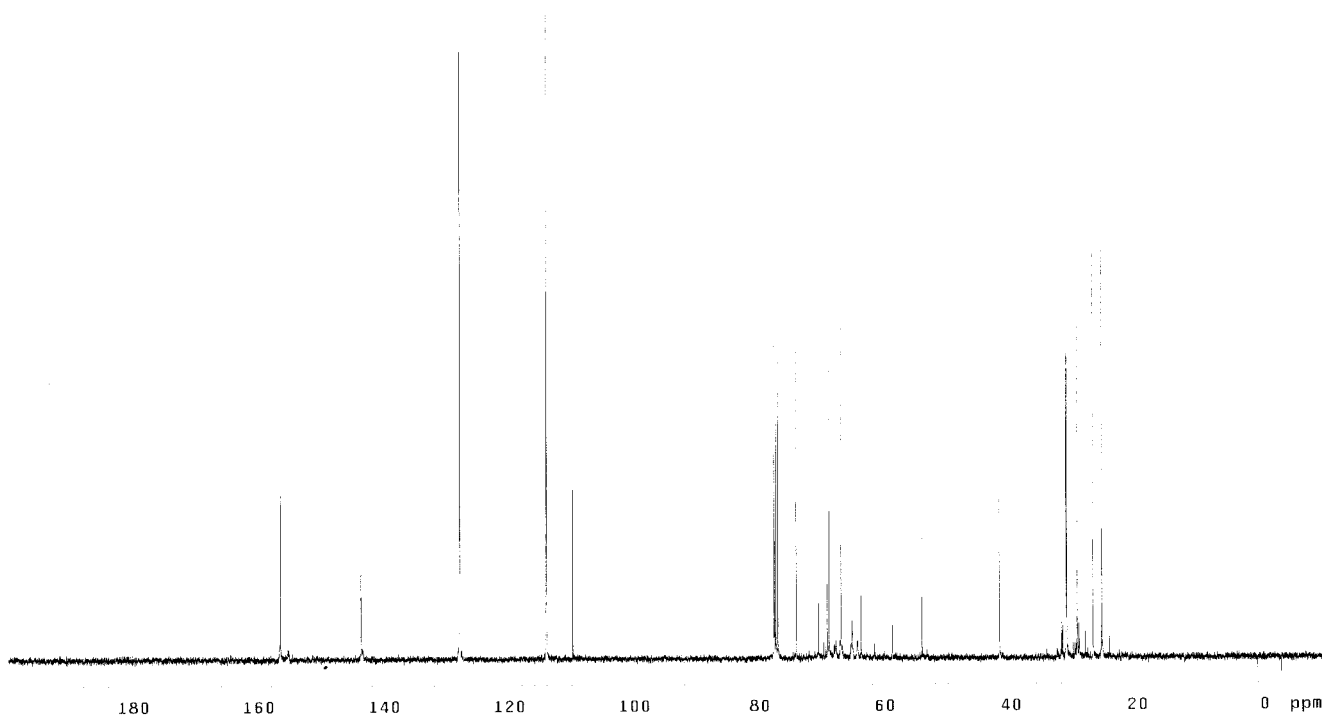
Figure 4 ^{13}C-NMR of copoly(TOSU/BADGE), soluble portion, 9-min photoirradiation and 9-min dark cure—full spectrum (0–200 ppm).

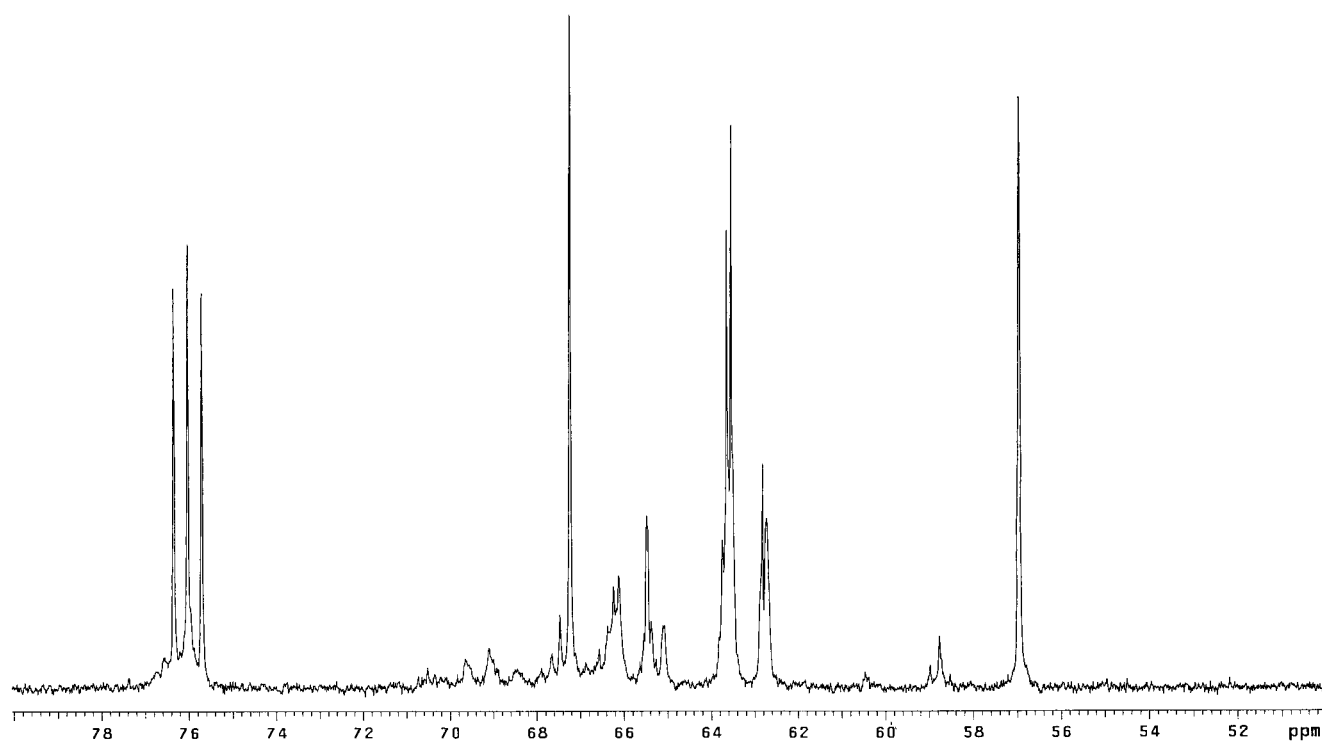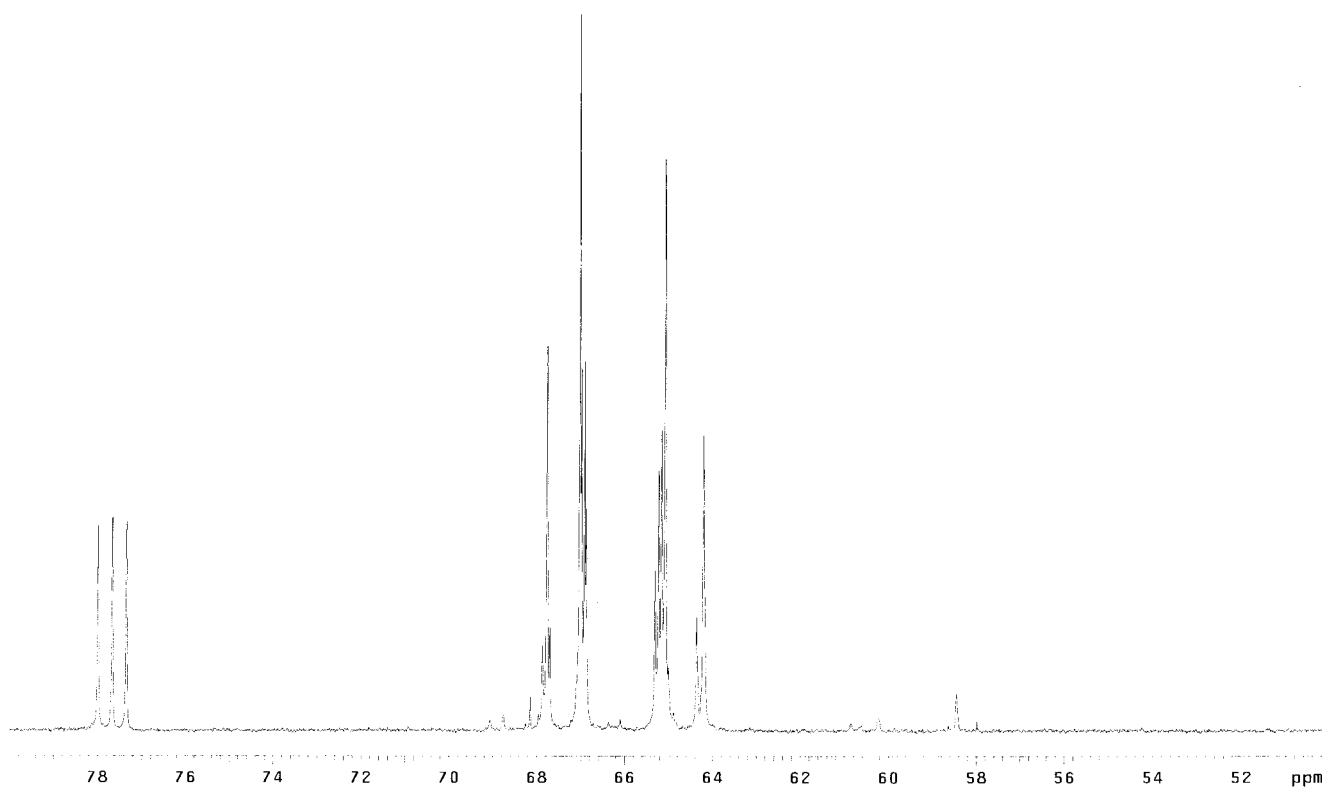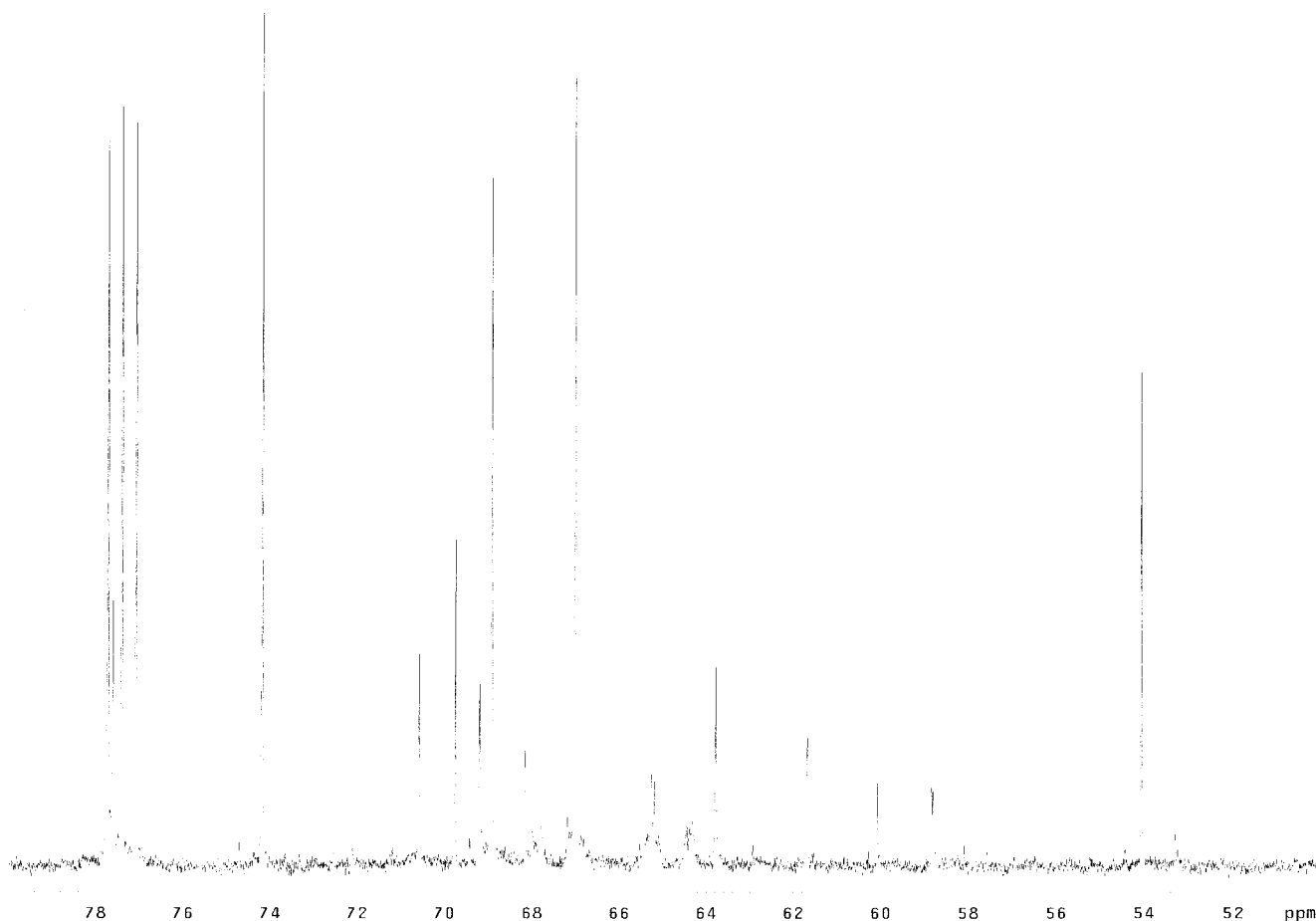**Figure 5** ^{13}C-NMR of poly(BADGE)—expanded spectrum (50–80 ppm).

Figure 6 ^{13}C-NMR of poly(TOSU)—expanded spectrum (50–80 ppm).

Figure 7 ^{13}C-NMR of copoly(TOSU/BADGE), soluble portion, 9.5-min photoirradiation and 9-min dark cure—expanded spectrum (50–80 ppm).

and water to form hydrolyzed BADGE. The hydrolyzed BADGE then reacted with a molecule of BADGE that had not been hydrolyzed to produce the internal -OCH$_2$-CHOH-CH$_2$O- and the oxirane end groups, as shown in Figure 3.

These results are very similar to those obtained for the superacid-catalyzed reaction between BADGE and hydrolyzed BADGE, in which the same product was observed.[22]

Binary polymerizations

The MALDI-TOF mass spectrum of the main oligomeric fraction from the BADGE/TOSU mixture irradiated for 10 min (Run 3, Table II) indicated that there were species with molecular weights up to ~3000. This sample was quenched just prior to the gel point. Peaks consistent with BADGE -mers up to $n = 6$, as well as several peaks consistent with BADGE (n)/ TOSU(m) comers ($n = 1$ to 7; $m = 2$ to 5), were found. Other peaks with masses which differed by multiples of ~340 (BADGE monomer) were also observed but could not be matched with expected -mer multiples. The ^{13}C-NMR spectrum had new peaks that did not

occur in the spectrum of either homopolymer, which indicated that copolymer had been formed. That is, there were peaks from 154.9 to 155.2 ppm, due to carbonate carbons, and peaks from 64.5 to 67.8 ppm, due to the formation of ether bonds between BADGE and TOSU -mers.

Longer dark cure (Run No. 4, Table II) resulted in some crosslinking and a partially insoluble product. The ^{13}C-NMR spectrum of the acetone-soluble portion (65 wt %) of the polymeric product is shown in Figure 4. There were no peaks at 23.79, 62.02, or 113.44 ppm, due to unreacted TOSU, or at 44.96 and 50.42 ppm, due to unreacted oxiranes. There were some peaks that were seen in spectra of the homopolymers. However, there were several peaks that did not appear in the spectra of either poly(BADGE) or poly(TOSU). There were peaks at 64.51, 65.26, and 67.80 ppm, due to –CH$_2$-O-CH$_2$- groups formed when oxiranes on BADGE reacted with the terminal –OH of oligomeric TOSU to form copolymer linkages. The peaks were broad, which is typical of crosslinked polymers with long spin–spin relaxation times.[14] Some homopolymer of BADGE was formed, as indicated by the sharper peak at 68.9 ppm, similar to that reported previously.[20]
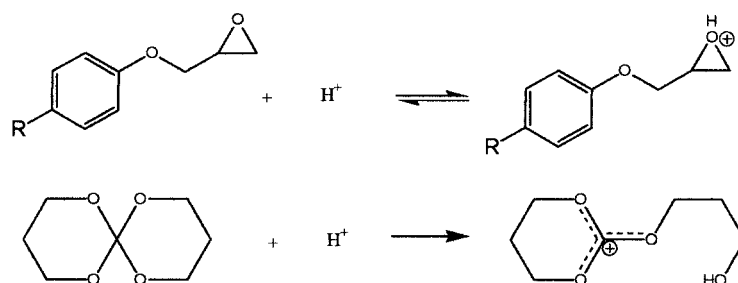
The region between 50 and 80 ppm contained several peaks of interest. This region for poly(BADGE), poly(TOSU), and copoly(TOSU/BADGE) is shown in Figures 5, 6, and 7, respectively. This region for the soluble portion of copoly(TOSU/BADGE), [Run 4, Table II], shown in Figure 7, contained several peaks that are were not in the spectra of either poly(TOSU) or poly(BADGE). They include a large peak at 74.20 ppm, due to a carbon with two attached protons (from the DEPT spectrum). It is probably due to a reaction between the secondary alcohol of oligo(BADGE) and a terminal –CH₂OH carbon from oligo(TOSU). The other unique peaks in this spectrum (from 54.06 to 70.59 ppm), are probably due to a reaction between the primary alcohol in oligo(BADGE) and a terminal –CH₂OH carbon from oligo(TOSU).

In a previous study by others, BADGE was reacted with 1,4-butanediol.[19] It was shown that the normal reaction product produced a peak at about 69 ppm, similar to that seen in the present study for the normal reaction between BADGE and poly(TOSU). The abnormal reaction product produced a peak at about 78 ppm, similar to that seen for the abnormal products formed when BADGE reacted with the terminal –OH groups in either poly(BADGE) or poly(TOSU). However, this abnormal product was a minor component of the polymer mixture with shorter irradiation times, but became a more significant component after longer polymerizations. This behavior was described previously.[29,30]

Computational energetics calculations

E_{act} and ΔH_{rxn} and PA were calculated for processes associated with the BADGE/TOSU polymerization system giving the following results (kcal/mol): TOSU ring protonation (PA = 189.6); BADGE oxirane ring protonation (PA = 181.8); BADGE homopolymerization (E_{act} = 1.5; ΔH_{rxn} = -13); TOSU homopolymerization (E_{act} = 30; ΔH_{rxn} = 13); and BADGE/TOSU copolymerization (E_{act} = 33; ΔH_{rxn} = 17). The calculations indicate first that TOSU has a greater proton affinity than does BADGE. As a result, it is thought that protons generated by the photoacid preferentially coordinate with nucleophilic TOSU ring sites. A sec-

ond consideration involves the ring opening process of the cyclic ethers. While the mechanism of BADGE oxirane protonation reversibly forms an oxonium cation,[32] protonation of the TOSU monomer results in irreversible ring opening and carbocation formation, due to the strong stabilizing effect of the three remaining carbonate oxygens. The combination of these two effects likely results in the TOSU monomer absorbing most if not all of the protons created by the photoinitiator system. ¹³C-NMR peaks indicative of possible copolymer ether linkages may have resulted from the reaction between hydroxyl groups (formed via TOSU ring-opening/homopolymerization) and BADGE oxiranes groups.

CONCLUSION

It has been demonstrated that TOSU and BADGE are polymerizable using a visible light photoinitiation system. For poly(TOSU), the ¹³C-NMR spectra indicated the formation of a polymer containing both a carbonate and an ether. Soluble poly(BADGE) produced peaks in the ¹³C-NMR spectrum that indicated the formation of a polymer containing –CHOH– and ether groups, similar to those obtained by other polymerization methods.[29] For binary polymerizations, new peaks appeared in the ¹³C-NMR spectrum that did not appear in the spectra of the homopolymers, indicating copolymer linkages.

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