Anionic Copolymerization of Bislactone End-Capped Diols with the Diglycidyl Ether of Bisphenol A

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Received May 14, 1990; Revised Manuscript Received July 16, 1990

ABSTRACT: Aromatic diols are converted to diesters by reaction with 4-carboxy-7,7′-dioxo-2,2′-spirobi(benzo[c]tetrahydrofuran) in the presence of dicyclohexylcarbodiimide and 4-(dimethylamino)pyridine. Under tertiary amine catalysis, the bislactone groups of these diesters react with commercially pure bisphenol A diglycidyl ether via a multiple ring-opening reaction forming cross-linked polymers with superior thermal properties. The progress of the reaction is followed by infrared spectroscopy, and the mechanism of the ring-opening reaction is determined. Thermal properties of all polymers and the surface properties of fluorine-containing polymers are reported.

Introduction

Polymers are produced when diglycidyl ethers react with polycyclic aromatic spirobislactones. In the latter molecules, two lactone rings share a common carbon atom, and both rings open during polymerization. Spirobislactones are similar to acid anhydrides in that they are formed from dicarboxylic acids by loss of water, but in bislactones a carbonyl group in the same molecule takes part in the dehydration. Both aromatic and aliphatic bislactones produce useful polymers.[1]

Bislactones cure glycidyl ethers in a manner similar to acid anhydrides.[2] The bislactone group reacts with nucleophilic groups in multiple ring-opening reactions to generate diester-substituted benzophenone moieties in the polymer backbone. Two bonds are broken for each bond formed. With a tertiary amine catalyst, bislactones are effective from 25 to 150 °C; in the absence of catalyst, bislactones do not react[1] with glycidyl ethers below 200 °C.

The reaction of oxiranes with anhydrides[3] is usually accompanied by a reduction in the volume of the reactants. For example, when the diglycidyl ether of bisphenol A is copolymerized with various acid anhydrides, the volume of the reactants decreases from 6 to 25%.[4] This shrinkage creates internal strain in the resin, which leads to diminished mechanical properties of the bulk polymer. In composites, the resin may retract from reinforcing fibers, creating loss of adhesion and forming voids or channels for the penetration of foreign substances.

Reactions in which two or more bonds are broken for each bond formed have been investigated as possible avenues to control the shrinkage inherent in polymerizations. Each of these reaction schemes involves multiple ring-opening steps, and strategies have been employed for cationic,[5] free-radical,[6] and anionic[7] polymerizations. Volume changes have been adjusted from the negative value characteristic of the polymerization to slightly positive values, depending on the nature and amount of the comonomer.

Bislactones and anhydrides extend the developing polymer chain but do not create cross-links in the polymer network. Reported here are the bulk properties of polymers produced from bifunctional bislactone comonomers, which can cross-link two developing polymer chains. Various telechelic monomers containing two bislactone functionalities have been prepared and reacted with a commercially pure diglycidyl ether of bisphenol A (DGEBA) to produce thermosetting polymers. Thermal properties of the resultant polymers have been determined, and the surface properties of polymers made from bislactones containing fluorine have also been measured.

Experimental Section

Materials. The liquid bisphenol A diglycidyl ether (DGEBA) was a commercial product (Epon 828, Shell) having $M_n = 376$ and an epoxide equivalent weight of 185–192. The material includes ca. 12% of higher oligomers that contain hydroxyl groups.[8] 2,4,6-Tris(dimethylaminomethyl)phenol ("tris") (K-54, Pacific Anchor or EH-30, Henkel), *p*-xylene (Aldrich, Fluka), phthalic anhydride (Aldrich), and diols were used as received. Solvents were dried over 4-Å molecular sieves before use.

Characterization. Fourier transform infrared (FTIR) spectra were measured on a Perkin-Elmer Model 1800 spectrophotometer operating in the double-beam mode at a resolution of 2 cm^{-1}. Spectra of compounds **3** and **5-10** were obtained for films cast from acetone or methylene chloride on KBr flats and dried at 120 °C; spectra were obtained for polymers cured between KBr flats. Polymer surface characterization measurements were made in the single-beam mode using a Perkin-Elmer MIR (multiple internal reflectance) accessory with a KRS-5 crystal cut at 45°; a minimum of 500 scans were obtained and ratioed against background scans to give a resolution of 2 cm^{-1}. Peak intensities are given as very strong (vs), strong (s), medium (m), and weak (w). Thermal analysis was performed on a Du Pont Model 1090 thermal analyzer or a Du Pont Model 2100 Thermal Analyst using Model 910 differential scanning calorimetry (DSC), Model 982 dynamic mechanical analysis (DMA), and Model 951 thermal gravimetric analysis (TGA) modules. Resin samples were tested under nitrogen, and instruments were calibrated with indium and tin standards. Heating rates of 5 °C/min (DSC, DMA) or 10 °C/min (DSC, TGA) were used for powdered cured materials and for uncured resins under nitrogen purge in hermetically sealed pans. Under these conditions, FTIR and DSC are sensitive to 3% or more of uncured monomer. Surface energy measurements were made with an NRL contact angle goniometer, Model A-100, manufactured by Ramé-Hart, Inc., using distilled and deionized water. Samples for surface energy measurements were washed with solvent to remove mold release agent and lightly sanded to ensure a flat surface. Melting points were obtained with a Fisher Johns melting point apparatus and are uncorrected. Solutions were evaporated below 40 °C under diminished pressure.

2,5-Dimethylbenzophenone-2′-carboxylic Acid (3). This compound was made as shown in Scheme I by a modification of a procedure by Meyer.[9] Phthalic anhydride (**2**, 100 g, 676 mmol) was added to 550 mL of *p*-xylene in a 2-L flask equipped with a water-cooled condenser and was stirred until most of it dissolved.

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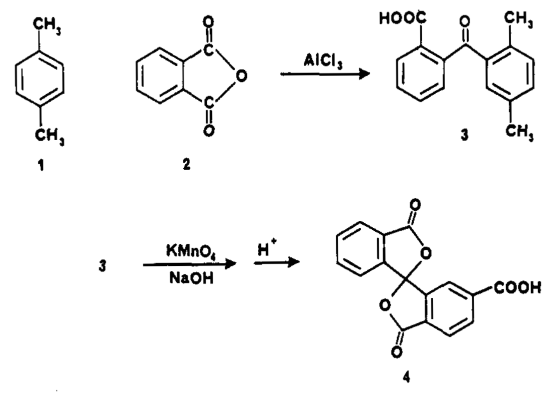
Scheme I

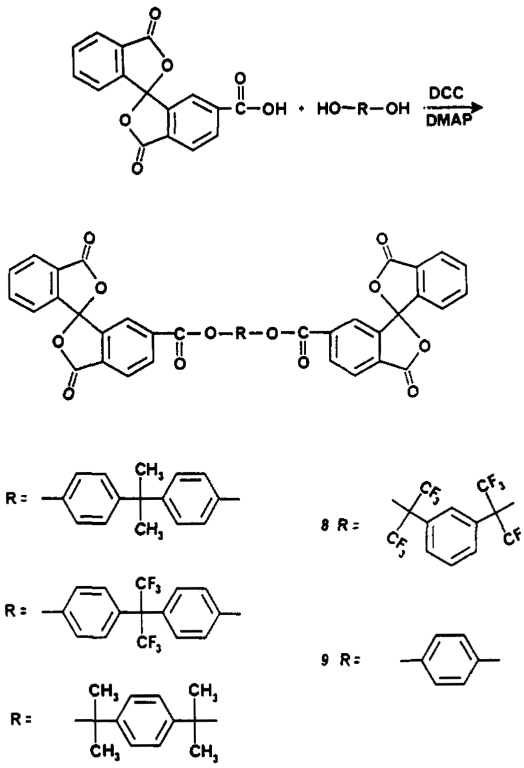


The solution was cooled in ice water, and powdered aluminum chloride (200 g, 1.50 mol) was added in one portion. The solution was warmed slowly until evolution of hydrogen chloride slackened, heated to 90 °C over 45 min, kept at this temperature for 2.5 h, and cooled in an ice bath. Ice was added slowly, followed by concentrated hydrochloric acid (150 mL), and the mixture was steam-distilled to remove unreacted *p*-xylene. Aluminum salts were removed by filtration and washed with cold water which was combined with the filtrate. Sodium carbonate (50 g) in 1 L of water was added, and the liquid was warmed rapidly and filtered while hot. Addition of 50% aqueous sulfuric acid (130 mL) precipitated the product as an oil that crystallized when cold. The product (140 g, 551 mmol, 82% yield), recrystallized from toluene, had the following properties: mp 140–145 °C (lit.[10] mp 147.5 °C); IR 3066 (m), 3021 (m), 2968 (m), 2925 (m), 2664 (w), 2545 (w), 1725 (s), 1695 (vs), 1672 (vs), 1610 (w), 1596 (m), 1575 (m), 1497 (m), 1450 (m), 1412 (s), 1380 (m), 1303 (vs), 1235 (m), 1213 (m), 1140 (w), 1123 (w), 1081 (w), 1037 (w), 951 (m), 903 (w), 859 (w), 797 (w), 754 (m), 727 (w), 687 (w), 649 (w), 613 (w) cm^{-1}.

4-Carboxy-7,7′-dioxo-2,2′-spirobi(benzo[*c*]tetrahydrofuran) (4). To a boiling solution of 3 (20.2 g, 80 mmol) in 5% aqueous sodium hydroxide (350 mL) was added dropwise a solution of potassium permanganate (49 g, 310 mmol) in 1.2 L of water, and the mixture was refluxed for 7–10 h. The cooled mixture was filtered to remove manganese dioxide and boiled to diminish its volume. Addition of 50% aqueous hydrochloric acid (50–70 mL) precipitated a mixture (20.0 g) of 4 and its related tricarboxylic acid as an oily solid, which was washed with water until the washings were neutral. The oven-dried product was suspended in 2-methoxymethyl ether (200 mL) and benzene (25 mL), and the solution was refluxed with Dowex 50X8-100 resin (H^+) (3–4 g) until evolution of water ceased (1–3 h); water of reaction was removed in a water separator. The mixture was filtered while still warm (40 °C) to remove the catalyst, and addition of the reaction solution to cold water (1 L) precipitated 4. The precipitate was filtered and washed repeatedly with cold water until all traces of solvent were removed, yielding 18.0 g (61 mmol, 76%) of white crystals: mp 285–293 °C (lit.[11] mp 230 °C); IR 3069 (br), 1810 (sh), 1796 (s), 1700 (s), 1623 (w), 1606 (sh), 1495 (w), 1468 (w), 1420 (w), 1343 (w), 1293 (m), 1287 (m), 1242 (m), 1215 (m), 1105 (w), 1089 (m), 1007 (m), 922 (s), 867 (m), 781 (m), 755 (m), 719 (m) cm^{-1}. Anal. Calcd for $C_{16}H_8O_6$: C, 64.87; H, 2.72. Found: C, 64.85; H, 2.76.

General Procedures for End Capping. Esterifications were accomplished as shown in Scheme II using a modification of a procedure by Jones.[12] Acid 4 (2.2 molar equiv) was dissolved in dry tetrahydrofuran (50–100 mL) in a 500-mL flask fitted with a drying tube; a diol (1 molar equiv), 4-(dimethylamino)pyridine (DMAP, 1 molar equiv), and dicyclohexylcarbodiimide (DCC, 2 molar equiv) were added and dissolved. The mixture was stirred at room temperature for 7 h and filtered to remove precipitated 1,3-dicyclohexylurea (DCU), and THF was removed by flash evaporation. The residue was dissolved in dichloromethane, washed with water, dilute aqueous hydrochloric acid, and water, dried over calcium sulfate, and filtered. The solvent was removed under diminished pressure to yield the solid end-capped monomer. Monomers contained traces (1–2%) of DCU that could not be removed by multiple recrystallizations from dichloromethane–methanol or from ethyl acetate.

Scheme II



End-Capped Diol (5) from 2,2-Bis(4-hydroxyphenyl)propane (Bisphenol A). Acid 4 (2.47 g, 8.3 mmol) and bisphenol A (860 mg, 3.8 mmol) yielded 2.31 g (2.9 mmol, 78%) of an off-white amorphous solid: mp 152–158 °C; IR 3060 (w), 3034 (w), 2970 (m), 2931 (m), 2857 (m), 1792 (vs), 1741 (s), 1646 (m), 1601 (s), 1505 (m), 1467 (m), 1343 (m), 1309 (s), 1276 (s), 1256 (m), 1227 (vs), 1204 (vs), 1173 (s), 1089 (s), 1066 (s), 1009 (s), 928 (s), 883 (m), 748 (m), 701 (m) cm^{-1}.

End-Capped Diol (6) from 2,2-Bis(4-hydroxyphenyl)-hexafluoropropane (Bisphenol A6F). Acid 4 (3.68 g, 12.4 mmol) and bisphenol A6F (1.89 g, 5.6 mmol) yielded 4.31 g (4.8 mmol, 86%) of an off-white amorphous solid: mp 160–163 °C; IR 3065 (w), 2932 (w), 2857 (w), 1794 (vs), 1748 (s), 1653 (w), 1607 (w), 1511 (m), 1468 (m), 1324 (m), 1309 (m), 1276 (s), 1256 (s), 1216 (vs), 1177 (vs), 1089 (s), 1066 (m), 1010 (m), 928 (s), 884 (m), 747 (m), 735 (m), 702 (m) cm^{-1}.

End-Capped Diol (7) from 1,4-Bis(2-hydroxy-2-propyl)-benzene. Acid 4 (11.63 g, 39.3 mmol) and the diol (3.63 g, 18.7 mmol) yielded 11.9 g (15.9 mmol, 85%) of a white amorphous solid: mp 123–126 °C; IR 3058 (w), 3032 (w), 2978 (w), 2931 (m), 2855 (w), 1792 (vs), 1714 (s), 1623 (m), 1513 (w), 1468 (m), 1365 (m), 1343 (m), 1312 (s), 1281 (vs), 1259 (m), 1236 (vs), 1213 (m), 1173 (m), 1085 (s), 1013 (m), 921 (s), 875 (m), 756 (m), 697 (m) cm^{-1}.

End-Capped Diol (8) from 1,3-Bis(2-hydroxy-2-hexafluoropropyl)benzene. Acid 4 (18.05 g, 61.0 mmol) and the fluorinated *meta* diol[13] (11.3 g, 27.6 mmol) yielded 21.7 g (22.5 mmol, 82%) of an off-white, amorphous powder: mp 118–123 °C; IR 3104 (w), 2977 (w), 2876 (w), 1792 (s), 1745 (s), 1607 (w), 1488 (w), 1467 (m), 1431 (w), 1364 (w), 1343 (w), 1306 (w), 1275 (w), 1252 (w), 1215 (m), 1187 (m), 1160 (m), 1131 (w), 1090 (m), 1025 (m), 1010 (m), 964 (m), 917 (m), 877 (m), 867 (m), 785 (w), 769 (w), 742 (w), 722 (w), 714 (w), 696 (m) cm^{-1}.

End-Capped Diol (9) from Hydroquinone. Acid 4 (17.0 g, 57.4 mmol) and hydroquinone (3.0 g, 27.3 mmol) yielded 4.87 g (7.3 mmol, 27%) of a white amorphous powder: mp 148–152 °C; IR 3063 (w), 3031 (w), 2930 (m), 2854 (m), 1791 (vs), 1742 (s), 1648 (m), 1606 (m), 1510 (m), 1289 (m), 1263 (m), 1210 (s), 1122 (s), 1079 (s), 1010 (m), 894 (s), 855 (m), 730 (m), 684 (m) cm^{-1}.

Polymerization Conditions. Degassed bisphenol A diglycidyl ether (100 molar equiv) and a comonomer (20–30 molar equiv) were thoroughly mixed in 30- to 50-g batches, with warming as necessary to effect solution; tris catalyst (5 molar equiv) was added after the solution cooled to room temperature. The solution was centrifuged at 2200 rpm to remove entrained air, poured into silicone molds treated with a mold release agent (MS-136 fluorocarbon release agent, Miller-Stephenson), and cured in a forced-draft oven at 80–225 °C for 18–96 h. Curing conditions for each mixture were determined after study of the reaction mixture by DSC. A typical curing cycle consisted of 12–18 h at 125 °C, slow cooling to room temperature, removal of the sample from the mold, and a cure of 4–8 h at 155 °C followed by 4 h at 225 °C.

Results and Discussion

The spirobislactone end-capping group 4 was synthesized by a three-step procedure. Phthalic anhydride (2) reacted with *p*-xylene (1) in the presence of aluminum chloride to produce 2,5-dimethylbenzophenone-2′-carboxylic acid (3). Oxidation by potassium permanganate yielded a triacid which was cyclized to 4 by refluxing with an acid ion-exchange resin in 2-methoxyethyl ether and removing the water of reaction.

Polymerization of spiro end-capped comonomers with the diglycidyl ether of bisphenol A was carried out by mixing the comonomers into warm DGEBA, cooling the mixture to room temperature, and adding the tertiary amine catalyst. Mixtures were poured into molds, cured at elevated temperatures until solid, and then removed from the mold for final curing at higher temperatures. Changes in the volume of the resin mixtures during polymerization were not measured. The progress of the polymerization reaction was also followed by FTIR spectroscopy, which proved to be a sensitive probe of molecular structure, especially in the carbonyl region. Proton NMR spectroscopy was not used because the aromatic multiplets and methyl singlets are not definitive, and first-order coupling constants cannot be readily obtained from the spectra.

Infrared Spectroscopy. Resins curing between KBr flats were scanned at intervals throughout the reaction. The infrared spectra of the copolymers contain bands near 3500 (hydroxyl), 1790 (bislactone carbonyl), 1730 (benzoate ester), 1675 (diaryl ketone), and 915 cm^{-1} (oxirane ring).

During the first 7 h of the reaction of DGEBA with 5 at room temperature, bands at 3500 and 1792 cm^{-1} diminished, the band at 1729 cm^{-1} became more broad and strong, a shoulder at 1718 cm^{-1} denoting the formation of aryl carboxylic acid groups appeared, and a new band emerged at 1675 cm^{-1}. During the next 200 h, bands at 3500 and 1675 cm^{-1} became stronger, bands at 1792 and 915 cm^{-1} disappeared, and the band at 1729 cm^{-1} became stronger and sharper as carboxylic acids were esterified. FTIR spectra in the carbonyl region are shown in Figure 1.

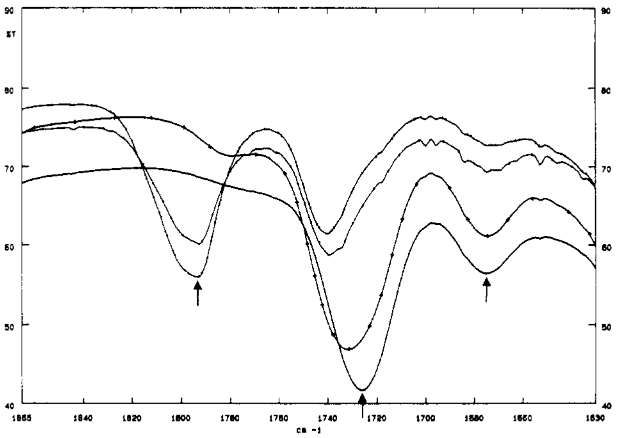


Figure 1. FTIR spectra in the carbonyl region of a mixture of DGEBA (100 parts) and end-capped bisphenol A (5) (7 parts) kept between KBr flats at room temperature for 1 (– ••), 6.5 (– • –), 90 (+++), and 200 h (—) after mixing. Arrows denote the diminishing bislactone carbonyl band (1792 cm^{-1}) and the growing ester (1730 cm^{-1}) and diaryl ketone (1675 cm^{-1}) bands.

This behavior indicates that the copolymerization proceeds in two steps as shown in Scheme III. At first, bislactone rings are opened by reaction with hydroxyl groups in DGEBA or with oxirane rings activated by the tertiary amine catalyst. Nucleophilic attack at a carbonyl carbon in the bislactone group forms a new bond to this carbon and cleaves a C–O single bond in each lactone ring, converting the bicyclic lactone to an acid- and ester-bearing benzophenone moiety in the polymer backbone. By rotation about single bonds before the copolymer gels, this moiety may uncoil and assume more extended, space-filling conformations. In a second step, carboxylic acids react with oxirane groups to produce ester and hydroxyl functionalities. The oxirane reaction becomes dominant only when the concentration of bislactones becomes relatively low, for nucleophiles evidently react with bislactones faster than with oxiranes. This cycle is repeated until the reaction is complete. The copolymerizations of 6–9 with DGEBA proceeded in a similar fashion; relevant IR carbonyl frequencies are listed in Table I and are related to the structural segments denoted in Scheme III.

Scheme III

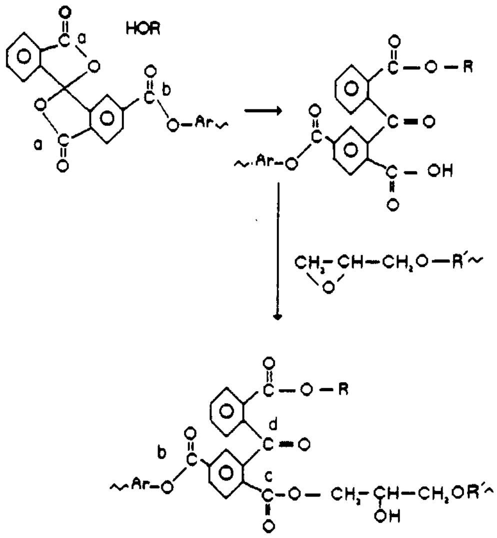


Table I
Carbonyl Absorption Frequencies of Copolymers[a]

comonomer	ν(CO), cm^{-1} a	b	c	d
5	1792	1741	1729	1675
6	1793	1741	1729	1675
7	1793	1724	1729	1675
8	1793	1768	1729	1669
9	1793	1740	1729	1675

[a] Carbonyl groups a, b, c, and d are defined in Scheme III.

Thermal Properties. Mixtures of an end-capped diol, DGEBA, and tertiary amine catalyst were examined by DSC from room temperature to 250 °C. Each mixture displayed two exotherms (Figure 2). An exotherm occurring between 135 and 150 °C was observed only in samples that exhibited a bislactone carbonyl absorption band in their FTIR spectra and therefore was assigned to the bislactone ring-opening reaction. A smaller, broader exotherm, appearing between 185 and 201 °C, was assigned

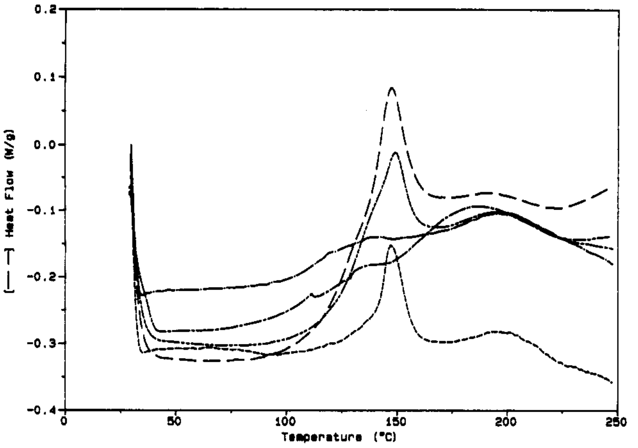


Figure 2. Differential scanning calorimetry curves for copolymers: 5 (– – –), 6 (– - -), 7 (– - –), 8 (– • –), and 9 (- - -).

Table II
Thermal Properties of Copolymers

comonomer	DSC exotherms, °C	T_g by DSC, °C	T_d by TGA, °C
5	147,195	120	392
6	150,192	125	390
7	135,185	110	410
8	140,190	60	380
9	147,201	104	400

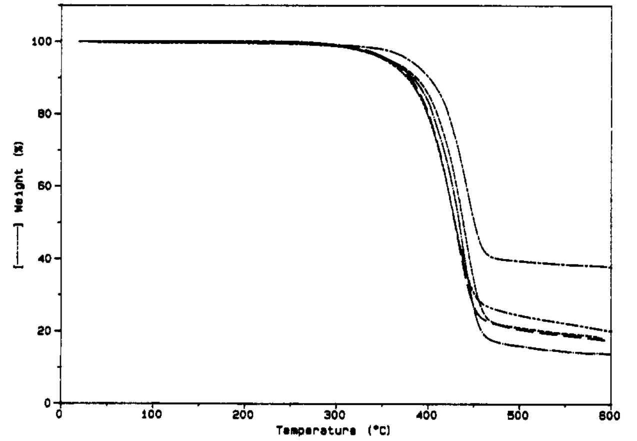


Figure 3. Thermogravimetric analysis curves for copolymers: 5 (– – –), 6 (– - -), 7 (– - –), 8 (– • –), and 9 (- - -).

to the reaction of an oxirane ring with a carboxylic acid group.[14]

Glass transition temperatures measured by DSC (Table II) for the polymers from the linear diols 5–7 and 9 were in the range 104–125 °C. The end-capped meta-substituted diol 8 gave a polymer with a T_g of 60 °C, reflecting the decreased efficiency of chain packing and resulting decreased cross-linking caused by the influence of the meta substitution of the diol. The polymerization of 9 required a longer time; the polymer was particularly brittle and glassy, and its T_g of 104 °C reveals a reduced extent of reaction due to the functional groups becoming isolated in the gelled resin matrix. The onset of decomposition (T_d) for all polymers, as measured by TGA and shown in Figure 3, was between 385 and 415 °C, reflecting the high aromatic content of the polymers.

Surface Properties. The contact angle between distilled, degassed water and the copolymer surface was determined for each copolymer and is listed in Table III. Nonfluorinated polymers gave values between 75 and 78°. The fluorinated *meta* diol derivative 8 caused a pronounced rise in the contact angle to 91° when used at a concentration of 21 mol of 8 to 100 mol of DGEBA.

Table III
Contact Angles with Distilled Water[a]

comonomer[b]	contact angle, deg	comonomer[b]	contact angle, deg
5	75	7	77
6	78	8	91
6[c]	99	9	77

[a] Average of five determinations; standard deviation 3°. [b] 100 mol of DGEBA:20–30 mol of comonomer unless otherwise noted. [c] 100 mol of DGEBA:72 mol of 6.

The contact angle of the surface of the bisphenol A6F derivative 6 was 78° when 33 mol of 6 was copolymerized with 100 mol of DGEBA, but when the molar ratio was raised to 72:100, the contact angle increased to 99°. FTIR spectra of this sample were obtained in the transmission mode and in the multiple internal reflectance (MIR) mode for the top and bottom surfaces. The most useful diagnostic bands for the trifluoromethyl group are[15] 1350–1120 and 770–690 cm^{-1}, but the former region is crowded with aryl ester C–O stretching bands, and the latter region contains out-of-plane C–H bending bands of aromatic rings. The spectra of the surfaces are similar, but the transmission spectrum differs from those of the surfaces. The surfaces lack bands at 3500 (hydroxyl) and 3030 cm^{-1} (aromatic C–H stretch), and bands at 1730 (aryl ester carbonyl), 1667 (diaryl ketone carbonyl), and 1290 cm^{-1} (aryl ester C–O bend) are weaker. The spectra suggest that polar hydroxyl, ester, and aromatic groups adopt positions in the interior of the polymer, thereby allowing the trifluoromethyl groups to congregate preferentially at the surfaces.

Conclusions

Aromatic diols have been end-capped with bislactone groups and the resulting monomers reacted with DGEBA to produce polymers. Nucleophilic attack at a bislactone carbonyl group opens both lactone rings and produces a carboxylic acid that reacts with glycidyl ethers, forming esters and secondary alcohols. As in other reactions of diglycidyl ethers, other competing reactions may also take place. The resulting polymers are stable at 380 °C or higher, and those polymers containing fluorine show high contact angles with distilled water as a result of preferential concentration of trifluoromethyl groups on the surface of the polymer.

Acknowledgment. A.M.S. thanks the Office of Naval Technology for an ONT Postdoctoral Fellowship, administered by the American Society for Engineering Education. Financial support from the Office of Naval Research is gratefully acknowledged.

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Registry No. 1, 106-42-3; **2**, 85-44-9; **3**, 60288-22-4; **4**, 129684-58-8; **5**, 130055-01-5; (**5**)(Epon 820) (copolymer), 130055-02-6; **6**, 129557-56-8; (**6**)(Epon 828) (copolymer), 130932-98-8; **7**, 130055-03-7; (**7**)(Epon 828) (copolymer), 130055-04-8; **8**, 129557-58-0; (**8**)(Epon 828) (copolymer), 130932-99-9; **9**, 130055-05-9; (**9**)(Epon 828) (copolymer), 130055-06-0; DCC, 538-75-0; DMAP, 1122-58-3; bisphenol A, 80-05-7; bisphenol A6F, 1478-61-1; 1,4-bis(2-hydroxy-2-propyl)benzene, 2948-46-1; 1,3-bis(2-hydroxy-2-hexafluoropropyl)benzene, 802-93-7; hydroquinone, 123-31-9; water, 7732-18-5; Epon 828, 25068-38-6.