

Preparation and Thermal Properties of Acrylic Polymers with Pendant Spirobis lactone Groups

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SYNOPSIS

A series of acrylic terpolymers containing varying concentrations of crosslinkable glycidyl, spirobis lactone, and hydroxyl pendant groups was prepared by radical chain polymerization. The glass-transition temperatures and weight average molecular weights of the terpolymers span broad ranges and can be independently selected by control of monomer composition. Cross-linking at 210°C was monitored by infrared spectroscopy. The rate and extent of reaction of spirobis lactone groups were found to be greater than those for glycidyl groups. The activation energies of the spirobis lactone and glycidyl reactions in the range between 160 and 210°C were calculated by Arrhenius treatment of the curing kinetics and found to be 31.0 ± 1.1 kJ mol⁻¹ and 59.1 ± 1.2 kJ mol⁻¹, respectively. The double ring opening reaction of the spirobis lactone groups has no effect on the volume of the cross-linked polymers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Shrinkage is an unavoidable consequence of conventional addition polymerization. Atoms in van der Waals contact as monomers must move closer to create covalent bonds. Shrinkage is particularly problematic in thermosetting polymers because it weakens polymeric resins and the composites in which they are used. Shrinkage also imparts internal stress that can create fissures in the resin, causing a stress concentration and premature failure of the bulk polymer. Shrinkage during the manufacture of molded objects causes the polymer to pull away from the walls of the mold, with the result that molded objects do not conform to the intended shape. In composite materials, shrinkage of the matrix resin causes it to retract from fillers and fibers, resulting in disruption of the intimate contact critical for efficient load transfer between matrix and reinforcement.

"Expanding monomers" designed to eliminate shrinkage during polymerization have been widely studied for their potential value in the development of advanced optical adhesives,¹ impression materi-

als, castings, strain-free composites,² potting and encapsulating resins, laminates, photoresists, and binders for solid propellants.³ For other applications, such as high-strength adhesives, strongly adhering coatings,⁴ dental restoratives,⁵⁻⁷ prestressed plastics, and bone cements, a slight expansion in volume would have great utility.

Bicyclic monomers are the most important of the expanding monomers. They polymerize through a double ring opening reaction in which two or more bonds are broken for each bond formed.⁸ Nearly 100 monomers of this type have been prepared and polymerized.⁹ For example, the change in volume during the reaction of an epoxy resin with a polyamide, normally -3% at room temperature, can be adjusted to zero or to values as high as +1% by the addition of suitable bicyclic monomers.¹⁰ However, bicyclic monomers react in a number of competing pathways; monomer structure and reaction conditions must be carefully controlled to ensure that double ring opening reactions dominate the polymerization. Even when the reaction mechanism is carefully controlled, however, volume change during polymerization is influenced more by thermal factors than by reaction mechanisms.⁹

Epoxy resins are important matrix polymers for composites. The resins are frequently cured with

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anhydrides, but this reaction can be accompanied by as much as 25% shrinkage.¹¹ Spirobisactones are analogues of anhydrides, for both are formed by the elimination of a molecule of water from a diacid, but a carbonyl group is involved in the formation of a spirobisactone and the carbonyl carbon becomes the atom shared by the two rings. Like anhydrides, bisactones are effective curing agents for epoxies; thermal properties of materials cured with spirobisactones are superior to those of materials cured with anhydrides, but shrinkage is 3.0–3.5%.¹² Our study¹³ of the reaction of spirobisactones with an epoxy resin demonstrated that bisactone rings react faster than epoxy rings, open early in the polymerization, and are consumed before the resin mass gels. The epoxy reactions become dominant only after the concentration of the bisactone group becomes very low. Thus expansion resulting from bond breaking in excess of bond forming serves only to enlarge the volume of the liquid phase. The liquid resin expands, but subsequent addition reactions cause the customary shrinkage and the value of the expanding monomer in controlling shrinkage is lost.

In order to obtain an unambiguous evaluation of the potential for double ring opening reactions to modulate volume change during polymerization, it is necessary to use a bicyclic monomer that reacts exclusively by a double ring opening pathway, and to ensure that this monomer reacts only after the polymer matrix has acquired resistance to flow. Because the polymer matrix resists flow, an increase in volume is directed to voids at the filler–resin interface or to voids in the polymer matrix. Contact between matrix and filler is enhanced and voids, which can serve as channels for the introduction of destructive agents, are reduced or eliminated.

The purpose of this work is to investigate the chemistry of linear acrylic polymers containing varying proportions of mutually reactive cross-linkable pendant groups, namely, glycidyl ethers, spirobisactones, and hydroxyl groups. Bisactones react explicitly by a double ring opening reaction. Conditions are controlled to ensure that the double ring opening occurs in a highly viscous matrix. This article describes the synthetic procedures, structural characterization, thermal properties, and kinetics of curing of the cross-linkable terpolymers.

EXPERIMENTAL

Materials

Thionyl chloride, 2-hydroxyethyl methacrylate (HEMA), glycidyl methacrylate (GMA), and tet-

rahydrofuran (THF) (all from Aldrich), dichloromethane (Fisher), and 2,2'-azobis(2-methylpropanitrile) (AIBN) (Kodak) were obtained at highest purity and used as received. Triethylamine (Fisher) was dried over 4-Å molecular sieves before use. 4-Carboxy-7,7'-dioxo-2,2'-spirobi(benzoc[*c*]tetrahydrofuran) was synthesized commercially (Polysciences, Inc.) by the method of Brady and Sikes¹³ and was used as received.

Characterization

Fourier transformed infrared (FTIR) spectra were obtained on a Perkin–Elmer Model 1800 spectrophotometer operating in the double-beam mode at a resolution of 2 cm⁻¹. Spectra of liquids were obtained on smears between KBr flats; solids were ground with KBr and pressed into pellets. Peak intensities are given as very strong (vs), strong (s), medium (m), and weak (w).

Proton magnetic resonance (¹H NMR) spectroscopy was performed on a Bruker MSL 300 spectrometer in a static magnetic field of 7.04 T and at a Larmor frequency of 300.1 MHz. Measurements were made with a 5-μs 90° pulse length on solutions in deuterated chloroform. For each signal, positions are given in parts per million (ppm) referenced to tetramethylsilane as standard, multiplicities are shown as singlet (s), doublet (d), or multiplet (m), and the number and identity of protons are listed.

Gel permeation chromatography (GPC) was performed using a Hewlett–Packard Series 1050 pump, two Altex μ-Spherogel columns (10³ and 10⁴ Å, respectively), and a Wyatt/Optilab 903 interferometric refractometer. Polystyrene standards with narrow molecular weight distributions were used to calibrate the instrument; THF was used as the mobile phase at a flow rate of 1.0 cm³ min⁻¹.

Thermal analysis was performed on a Perkin–Elmer Series 7700 Thermal Analyzer equipped with a DSC-7 module for differential scanning calorimetry (DSC), a TGA-7 module for thermogravimetric analysis (TGA), and a TMA-7 module for thermomechanical analysis (TMA). DSC, TGA, and TMA experiments were carried out under a stream of dry nitrogen at heating rates of 20, 10, and 5°C min⁻¹, respectively.

Gas chromatography–mass spectroscopy (GC–MS) was performed on a Hewlett–Packard 5890 Series II gas chromatograph equipped with a Hewlett–Packard 5971A quadrupole mass selective detector and controlled by a Hewlett–Packard 59970 MS ChemStation. Polymers were heated by a Chemical Data Systems Pyroprobe 2000 pyrolysis probe from

ambient to elevated temperature at $10^{\circ}\text{C min}^{-1}$. Volatile products were collected at -20°C at the head of a capillary column ($12\text{ m} \times 0.22\text{ mm i.d.} \times 0.33\text{-}\mu\text{m}$ film) containing HP-1 cross-linked methyl silicone gum as the stationary phase. Separation was achieved by heating the column at $20^{\circ}\text{C min}^{-1}$ to 240°C . Helium was used as the carrier gas at a flow rate of approximately $1.0\text{ cm}^3\text{ min}^{-1}$.

Synthesis

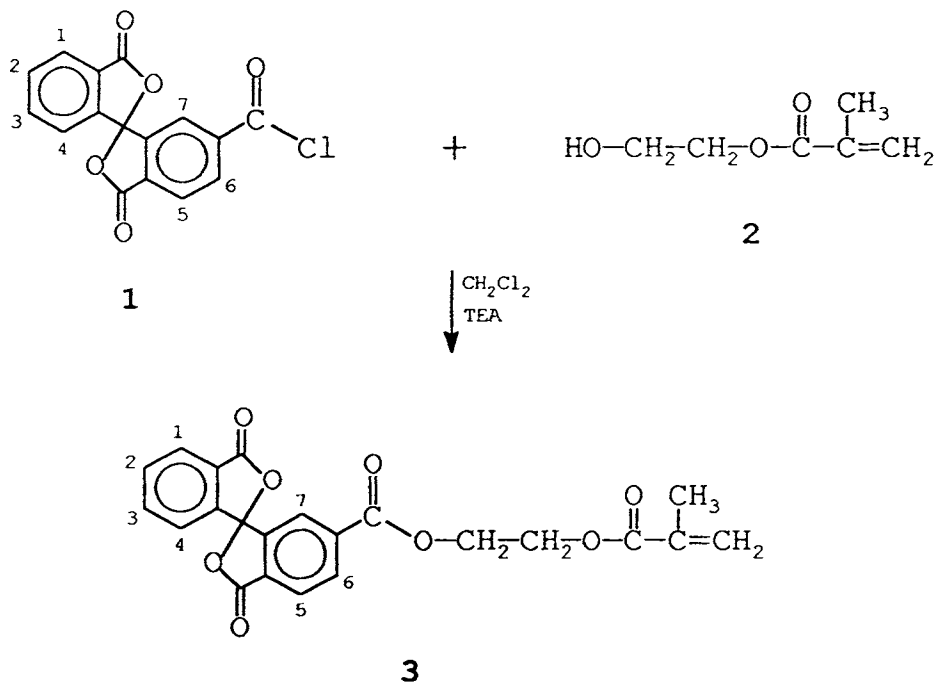
4-Chlorocarbonyl-7,7'-dioxo-2,2'-spirobi(benzo[c]tetrahydrofuran) (1)

The parent carboxylic acid (50.0 g, 0.169 mol) was added to 300 mL thionyl chloride and refluxed until it dissolved. The solution was filtered while hot through a medium porosity, sintered glass funnel. To the hot solution was added 25 mL carbon tetrachloride and about 100 mL *n*-hexane, and the product crystallized as the solution cooled. The resulting white needles were collected, washed with *n*-hexane, and dried in a desiccator under reduced pressure, yielding 51.0 g (0.162 mol, 96% yield): m.p. $180.0\text{--}183.5^{\circ}\text{C}$ at $1^{\circ}\text{C min}^{-1}$. IR 3060 (w), 1793 (vs), 1605 (w), 1468 (m), 1425 (w), 1341 (m), 1305 (s), 1289 (s), 1273 (m), 1248 (m), 1211 (s), 1190 (m), 1146 (s), 1089 (s), 1009 (s), 939 (s), 889 (s), 823 (m), 793 (m), 782 (m), 763 (w), 699 (s), 688 (m),

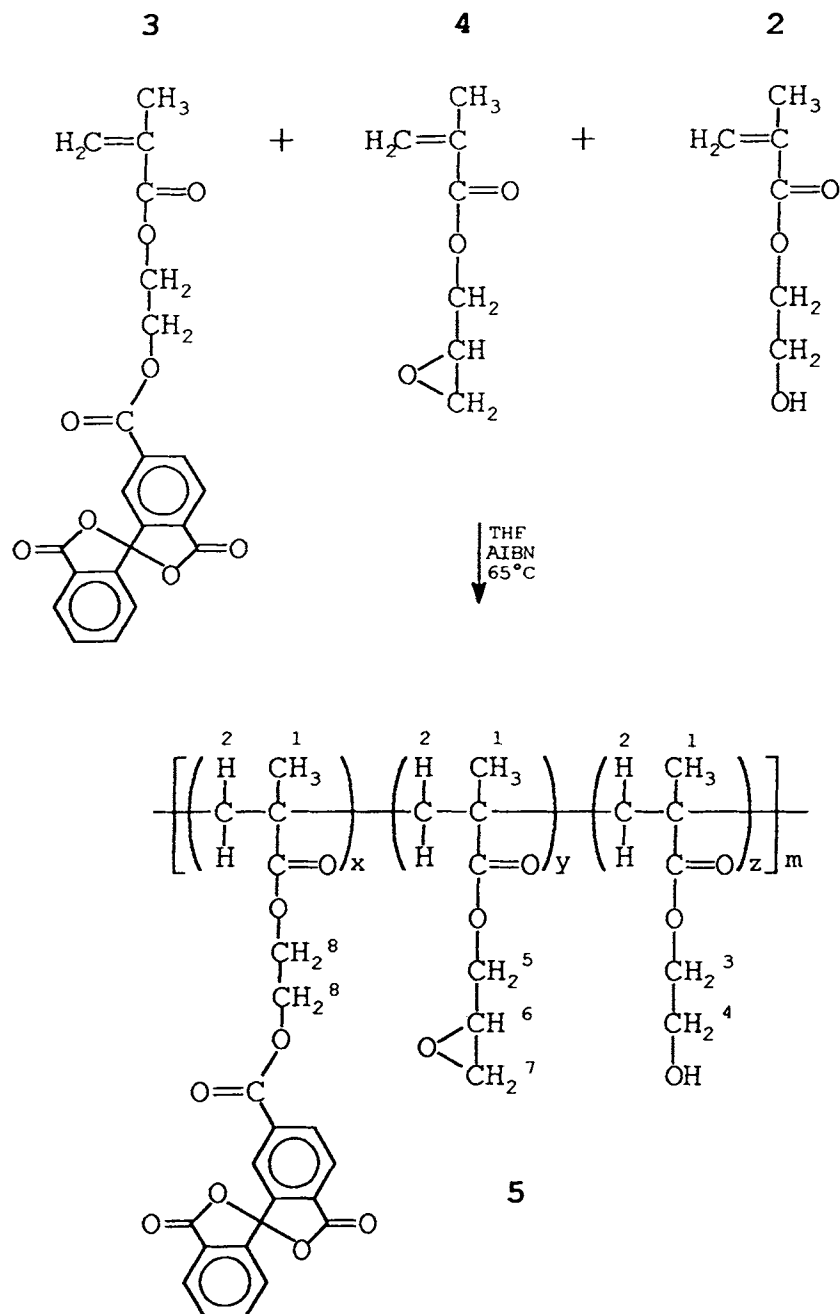
673 (w) cm^{-1} . $^1\text{H NMR}$ 7.28–7.30 ppm (m, 1, H^4), 7.78–7.80 (m, 2, H^2 , and H^3), 7.98 (s, 1, H^7), 8.07–8.10 (m, 1, H^1), 8.17–8.20 (d, 1, H^5), 8.46–8.49 (d, 1, H^6).

4-[2-(Methacryloxy)ethoxycarbonyl]-7,7'-dioxo-2,2'-spirobi(benzo[c]tetrahydrofuran) (3)

Esterification was accomplished as shown in Scheme 1. HEMA (2, 9.48 mL, 0.075 mol) in dichloromethane (125 mL) was added dropwise to a stirred solution of 1 (23.7 g, 0.075 mol) and triethylamine (13.1 mL, 0.094 mol) in dichloromethane (450 mL) and allowed to react for 24 h. The resulting mixture was then washed with water, 10 wt % aqueous hydrochloric acid, 2.5 wt % aqueous sodium bicarbonate, and again with water. The organic phase was dried over calcium carbonate and concentrated to half its volume by flash evaporation. The calcium carbonate was removed by filtration, and while the solution was warmed on a hot plate, 100 mL of methanol and about 200 mL of *n*-hexane was added. Gradual cooling of this solution led to the formation of very pale yellow crystals that were filtered, washed with *n*-hexane, and dried at room temperature under reduced pressure, yielding 27.0 g (0.066 mol, 88%): m.p. $139.5\text{--}142.0^{\circ}\text{C}$ at $1^{\circ}\text{C min}^{-1}$. IR 3072 (w), 2960 (w), 1791 (vs), 1734 (m), 1712 (m), 1638 (w), 1470 (w), 1438 (w), 1343 (w), 1328 (w), 1309 (m), 1292



Scheme 1



Scheme 2

(w), 1274 (s), 1260 (w), 1246 (w), 1233 (m), 1211 (m), 1185 (m), 1170 (m), 1112 (w), 1089 (m), 1031 (w), 1011 (w), 949 (w), 926 (s), 898 (w), 884 (w), 703 (w) cm^{-1} . $^1\text{H NMR}$ 1.89 ppm (s, 3, $-\text{CH}_3$), 4.45–4.61 (d, 4, $-\text{CH}_2-\text{CH}_2-$), 5.56 and 6.07 (s, 2, $=\text{CH}_2$), 7.26–7.29 (m, 1, H^4), 7.75–7.78 (m, 2, H^2 , and H^3), 7.91 (s, 1, H^7), 8.05–8.08 (m, 1, H^1), 8.09–8.12 (d, 1, H^5), 8.37–8.40 (d, 1, H^6).

Acrylic Terpolymers (5)

Linear terpolymers were prepared as shown in Scheme 2; the example that follows is for the preparation of terpolymer **5e**. A solution of **3** (4.36 g, 0.011 mol, 22 mol %), GMA (**4**, 4.97 g, 0.035 mol, 70 mol %), and HEMA (**2**) (0.52 g, 0.004 mol, 8 mol %) in THF (75 wt %) was stirred at 65°C. The

initiator AIBN (0.15 mol %) was added and the reaction was allowed to continue for 24 h. The terpolymer was precipitated by the addition of warm methanol, washed with *n*-hexane, and dried under reduced pressure, to give **5e** as a white powder (8.96 g, 91%). IR 3543 (w), 3063 (w), 2998 (m), 2954 (m), 1794 (vs), 1732 (vs), 1606 (w), 1485 (w), 1468 (w), 1450 (w), 1388 (w), 1341 (w), 1310 (m), 1278 (s), 1259 (m), 1234 (s), 1210 (m), 1171 (s), 1151 (s), 1091 (m), 1010 (m), 967 (w), 932 (s), 908 (m), 850 (w), 754 (m), 702 (w), 691 (w) cm^{-1} . $^1\text{H NMR}$ 0.88 ppm (s, 3, H^1), 1.84–1.89 (m, 2, H^2), 2.61–2.80 (d, 1.14, H^7), 3.19 (s, 0.57, H^6), 3.73–7.77 (m, 0.63, H^4), 4.29 (s, 1.20, H^3 , and H^5), 4.52 (s, 1.6, H^8), 7.33–8.40 (m, 2.80, bislactone aromatic protons).

Curing Conditions

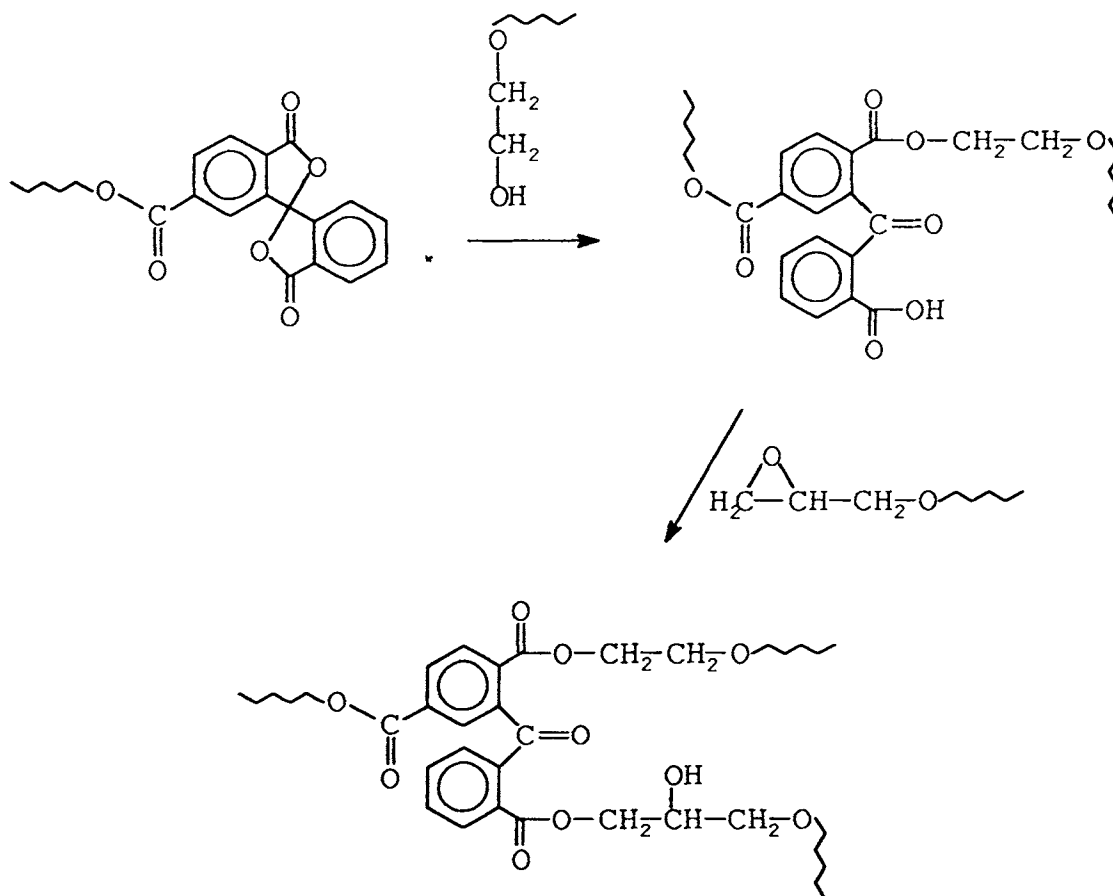
The terpolymers were cross-linked by heating at 210°C for 48 h. Additional curing experiments were carried out at 160 and 185°C for terpolymer **5e**. Prior to curing, the polymer samples, either as pow-

der or cast from solution, were dried under reduced pressure (<0.5 mmHg) for at least 12 h at room temperature. The curing reaction is summarized in Scheme 3.

RESULTS AND DISCUSSION

Design Considerations and Molecular Weights of Terpolymers

A series of acrylic terpolymers having bislactone, epoxy, and hydroxyl functionalities were synthesized in order to explore their chemistry in detail. The design of the polymers began with the establishment of limits for the concentration of each functional group. In order to fully explore the limits of the chemistry of these terpolymers, the concentration of each group was allowed to span as wide a range as possible. The concentration of the hydroxyl group was chosen to be between 3 and 12 mol %. As the initiator of polymerization, a low concentration of



Scheme 3

the hydroxyl group was considered sufficient; excessively high concentrations were avoided because they would lead to the formation of water-sensitive hydrogel-like materials that would be unsuitable for demanding applications. The concentration of the bislactone function needed to span a wider range in order to delimit its effect upon volume change during polymerization. Thus, to characterize volume change behavior over the widest possible range of polymer compositions, the concentration of this group was fixed between 5 and 40 mol %. The epoxy group, which is the dominant cross-linking group, formed

the remainder of the functionality of the polymer; thus its concentration fell in the range of 48–92 mol %. All possible compositions of terpolymers made from monomers in these concentrations fall within the parallelogram shown on the tricoordinate plot in Figure 1.

Eleven polymers (5a–5k) that systematically cover the range of all possible compositions were chosen and synthesized as described above; the monomer ratios are given in Table I and are plotted in Figure 1. Each polymer was characterized by FTIR and ^1H NMR spectroscopy, and the spectral

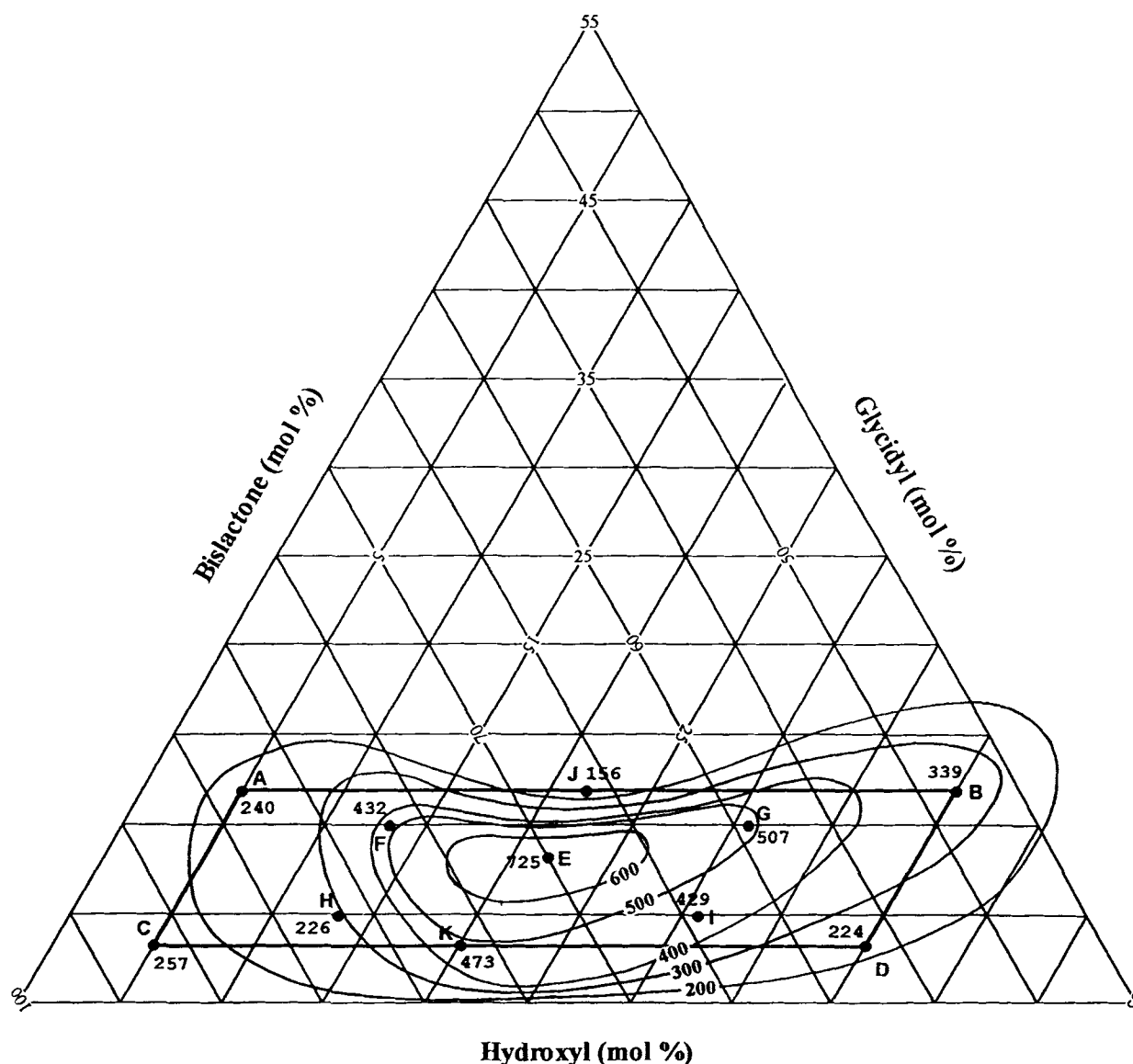


Figure 1 Tricoordinate contour plot relating M_w to terpolymer composition. Contours show $M_w \times 10^{-3}$.

Table I Physical Properties of Terpolymers

Sample	GMA/BLT/HEMA ^a (mol %)	T_g^b (°C)	$M_w^c \times 10^{-3}$ (g mol ⁻¹)	PDI ^d
5a	83/5/12	54	240	3.10
5b	48/40/12	95	339	2.30
5c	92/5/3	53	257	3.30
5d	57/40/3	107	224	3.00
5e	70/22/8	53	725	8.20
5f	77/13/10	51	482	4.20
5g	59/31/10	89	507	4.70
5h	82/13/5	75	226	3.10
5i	64/31/5	105	429	5.40
5j	66/22/12	69	156	4.50
5k	77/20/3	59	473	4.20

^a Monomers: GMA, glycidyl methacrylate (4); BLT, bislactone ester of hydroxyethyl methacrylate (3); HEMA, hydroxyethyl methacrylate (2).

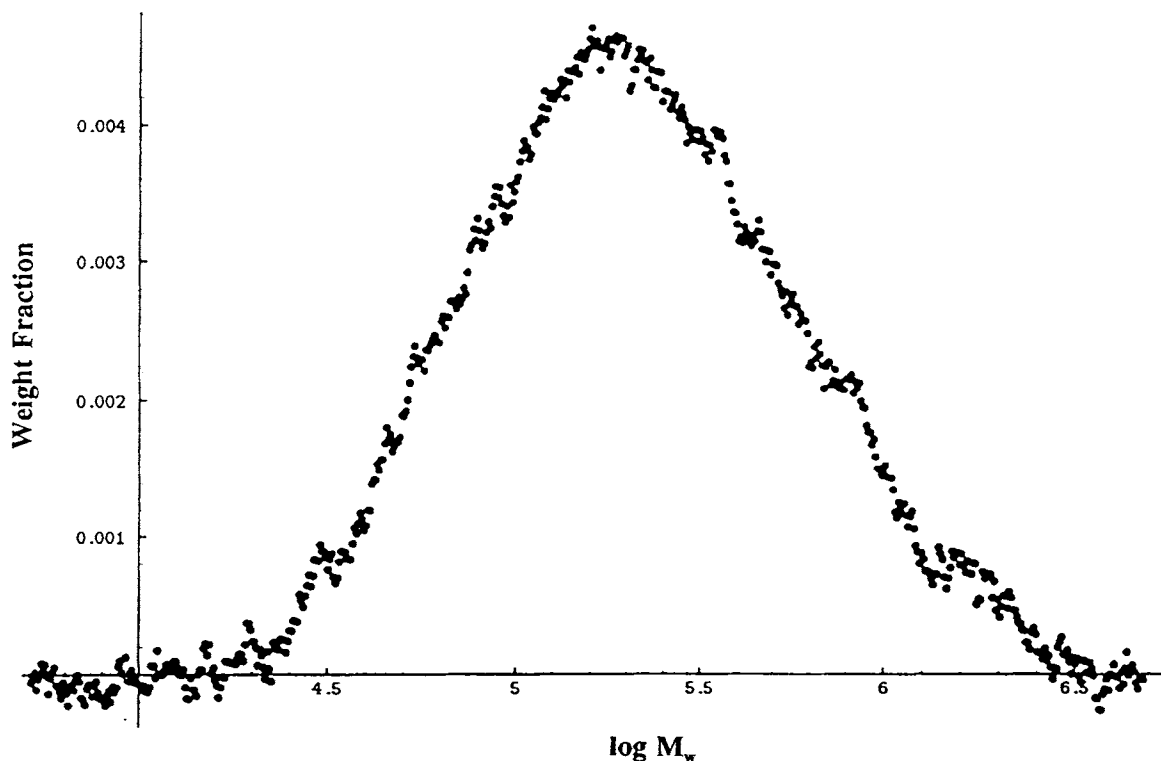
^b Measured by differential scanning calorimetry (DSC).

^c Measured by gel permeation chromatography (GPC) using polystyrene standards.

^d Polydispersity Index = M_w/M_n .

data obtained were consistent with a random structure for the terpolymers. The molecular weight distribution of each polymer was determined by GPC and the data are summarized in Table I. Each of the terpolymers has a relatively high molecular weight

and a polydispersity index ($PDI = M_w/M_n$) from 3.0 to 8.2, as expected for high-conversion radical-chain polymerizations. The PDI of **5b** was lower than average at 2.3; its molecular weight distribution is shown in Figure 2. The PDI of terpolymer **5e** was

**Figure 2** Molecular weight distribution of terpolymer **5b**.

the highest of all polymers at 8.2, as expected for the polymer with the highest molecular weight ($725,000 \text{ g mol}^{-1}$).

The relationship between weight average molecular weight (M_w) and terpolymer composition is depicted graphically in Figure 1. Terpolymer **5e**, composed of midrange amounts of the three monomers, had the highest M_w , at $725,000 \text{ g mol}^{-1}$. Compared to terpolymer **5e**, small changes in the concentration of the hydroxyl species resulted in large decreases in the M_w . A more gradual decrease in M_w was observed when the concentration of either the bislactone or glycidyl species was varied from its value in terpolymer **5e**.

Kinetics of Curing

The reactions of the epoxy and bislactone functional groups were monitored by FTIR spectroscopy at 160,

185, and 210°C for 48 h. For example, FTIR spectra of terpolymer **5e** at various times during cross-linking at 210°C are shown in Figure 3. The carbonyl stretch of the bislactone group at 1795 cm^{-1} was used to follow its double ring opening reaction, and the asymmetrical ring stretch of the oxirane ring at 850 cm^{-1} was used to monitor the reaction of the glycidyl groups. The absorptivity of each band was measured at various times throughout the curing process and was normalized by dividing it by the absorptivity of the asymmetric carbon-hydrogen stretching band at 2965 cm^{-1} , which is unaffected by the various reactions during curing. The absorptivity of the bislactone band decreased rapidly during curing and that of the glycidyl band decreased at a much slower rate. A new band appeared at 1675 cm^{-1} and is assigned to the carbonyl stretching of the diaryl ketone formed in the ring opening reaction of the bislactone.

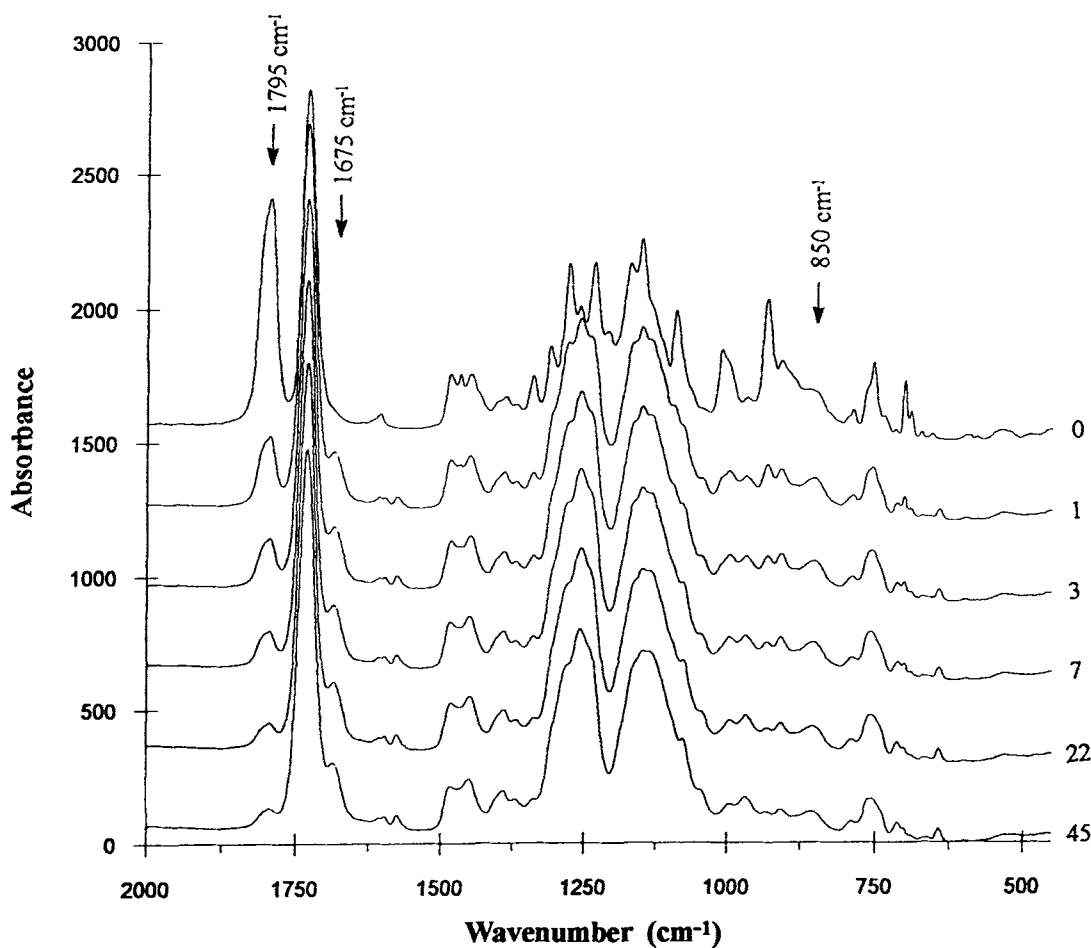


Figure 3 FTIR spectra of terpolymer **5e** cross-linked at 210°C for various times (in hours).

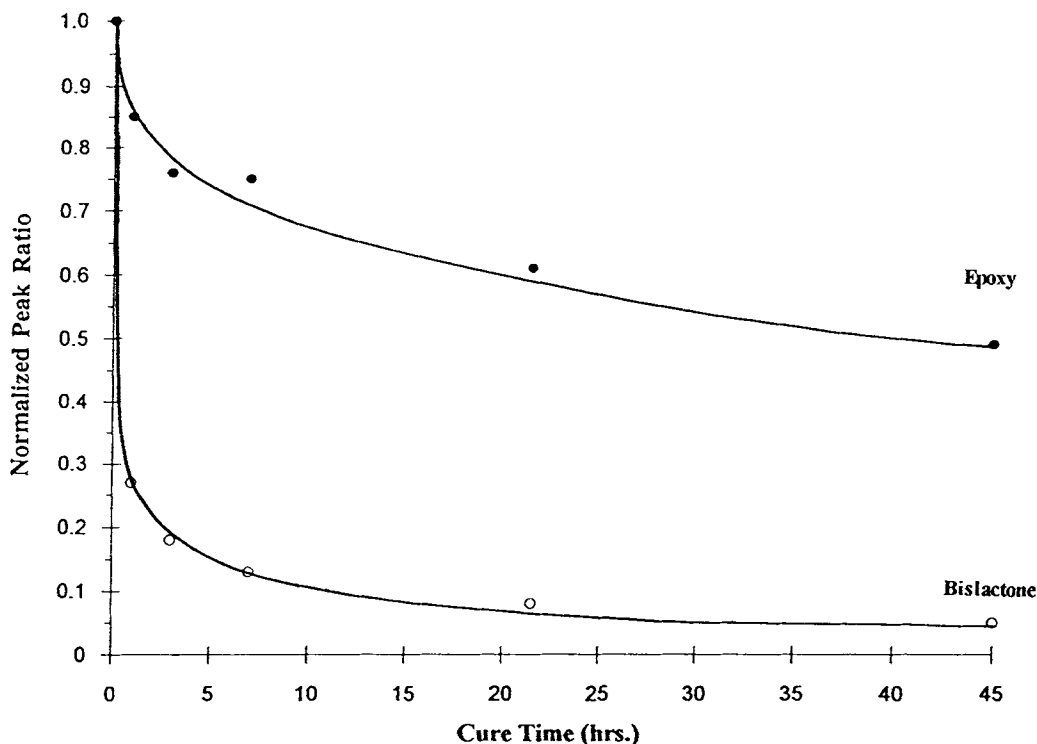


Figure 4 Plot of normalized peak height ratio against curing time at 210°C for (●) glycidyl and (○) bislactone functional groups in terpolymer **5e**.

Figure 4 shows the normalized FTIR absorbances of the bislactone and epoxy groups in terpolymer **5e** plotted against the curing time at 210°C. In this example, the bislactone concentration (originally 22%) and the epoxy concentration diminish with similar rates, and the bulk of the reaction is completed within 24 h. In terpolymers having a lower content of bislactone (5–13 mol %), the double ring opening reaction is essentially complete after 1 h of curing but the reaction of epoxy rings is slower. When the concentration of bislactone becomes very low, the double ring opening reactions occur so rapidly that they are complete before the terpolymers cross-link sufficiently to form a gelled network. Consequently, any change in volume during the double ring opening reaction of the bislactone group in these terpolymers occurs in the liquid phase and does not influence the properties of the cured polymer.

In polymers containing 22 mol % of bislactone groups or less, all of these groups react during cross-linking at 210°C. However, in compositions containing more than 30 mol % of bislactone, no more than about 25 mol % reacts. Because the molecular weight of monomer **3** is about three times that of

monomers **4** or **5**, 25 mol % of **3** corresponds to about 50 wt % of **3** in the polymer. This amount of bislactone reacts with about 17 wt % of glycidyl monomer **4** and most of the hydroxyl monomer **5** (1–4 wt %). Thus, at 25 mol % bislactone, the functional groups in approximately 70 wt % of the polymer have reacted, and the remaining reactive sites are isolated within the gelled polymer where they cannot react further. Figure 5 is a plot of the normalized absorption of the band at 1792 cm⁻¹ before and after reaction at 210°C. The plot shows a linear relationship between content and reactivity of bislactone groups up to about 25 mol % and demonstrates that this level is the maximum effective loading of bislactone groups in this type of terpolymer.

Activation energies for the cross-linking reactions of the bislactone and epoxy groups were obtained through an Arrhenius treatment of the IR data.¹⁴ The kinetics of cross-linking reactions follow the general formula:

$$-\frac{d[C]}{dt} = k[C]^{\alpha} \quad (1)$$

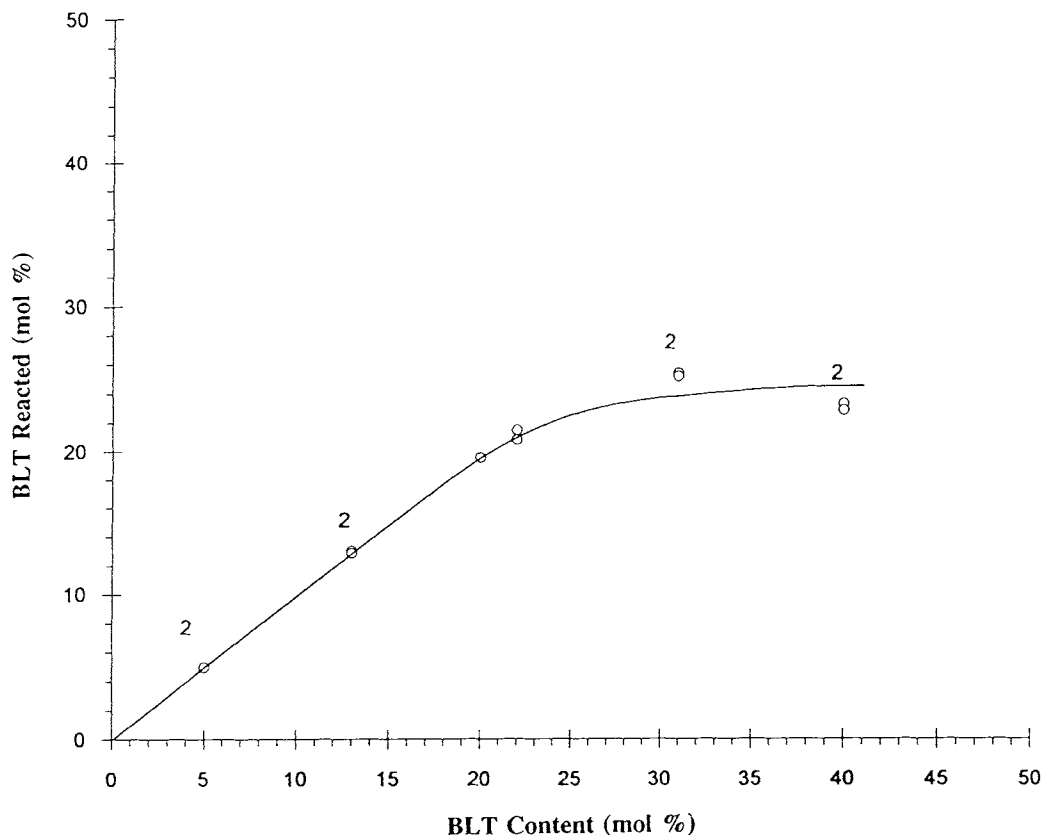


Figure 5 Plot of bislactone groups reacted after 210°C curing against bislactone groups present in the uncured terpolymers. A "2" denotes identical or nearly identical values for different monomers.

in which $[C]$ is the concentration of a reacting functional group, t is time, k is the rate constant of the reaction, and α is the order of the reaction with respect to that functional group. To determine the kinetics of reaction, this equation was converted to logarithmic form:

$$-\ln \frac{d[C]}{dt} = \ln k + \alpha \ln [C]. \quad (2)$$

For kinetic analysis, a double-logarithmic plot of the reaction rate ($d[C]/dt$) against the concentration $[C]$ is expected to yield a straight line that has a slope equal to the order of the reaction α and an intercept on the y -axis equal to the logarithm of the rate constant k .

The average intensity of infrared absorption bands after correction for background absorption was used as a measure of concentration. The carbonyl stretching band at 1795 cm^{-1} was used for the spirobislactone, and the asymmetrical ring stretching band at 850 cm^{-1} was used for the epoxy group.

The average intensity of the absorption band during the time interval was used as the concentration of the functional group, and the rate of change of concentration with respect to time was determined by dividing the decrease in absorbance by the time between measurements. Data for the reaction of the bislactone group at three temperatures are shown in Table II. These data were fitted to a straight line by linear regression analysis; these lines are shown in Figure 6, and values obtained from them are given in Table III.

The order of reaction α for the spirobislactone falls by a factor of about 2.5 over the temperature range studied, indicating that the rate of depolymerization for this group approaches the rate of polymerization as the temperature rises. Above 210°C there will be a ceiling temperature at which these rates are equal. At that temperature the addition and removal of spirobislactone groups on the developing polymer backbone will be in equilibrium, and the net rate of polymerization will be zero.

The rate constants for an isothermal reaction de-

Table II Kinetic Measurements of Spirobis lactone Reactivity

Curing Temperature (°C)	Curing Time (h)	Normalized IR Absorbance	$\ln(d[C]/dt)$	$\ln d[C]$
160	0	1.00		
	1	0.89	-2.207	-0.057
	3	0.83	-3.506	-0.151
	7	0.79	-4.605	-0.211
	24	0.73	-5.654	-0.274
	30	0.71	-5.704	-0.328
	48	0.69	-6.802	-0.356
	185	0	1.00	
1		0.76	-1.427	-0.128
3		0.66	-2.995	-0.342
7		0.58	-3.912	-0.478
24		0.49	-5.241	-0.625
30		0.47	-5.704	-0.734
48		0.44	-6.397	-0.787
210		0	1.00	
	1	0.72	-1.272	-0.151
	3	0.66	-2.813	-0.416
	7	0.52	-3.912	-0.580
	24	0.40	-5.241	-0.777
	30	0.37	-5.704	-0.955
	48	0.34	-6.497	-1.036

terminated over a range of temperatures can be used to determine the activation energy of the reaction in that temperature range. Providing that the reaction can be described by an Arrhenius relationship, the activation energy (E_{Act}) is given by:

$$\ln k = \frac{-E_{\text{Act}}}{RT} + A \quad (3)$$

where R is the gas constant ($8.315 \text{ J mol}^{-1} \text{ K}^{-1}$), T is temperature (K), and A is a constant. A plot of $\ln k$ against $1/T$ is expected to give a straight line with a slope of $-E_{\text{Act}}/R$ and an intercept of A . From plots of this type, the activation energy for reaction of the bis lactone group was found to be $31.0 \pm 1.1 \text{ kJ mol}^{-1}$, and that for the reaction of the epoxy group was found to be $59.1 \pm 1.2 \text{ kJ mol}^{-1}$.

Thermal Analysis

The thermal properties of the linear uncross-linked terpolymers were investigated by DSC and TGA. Data obtained during rapid heating for $<1 \text{ h}$ at 10 or $20^\circ\text{C min}^{-1}$ differs from that obtained during iso-

thermal heating at $160\text{--}210^\circ\text{C}$ for many hours primarily because only a small amount of cross-linking occurs during a thermal analysis experiment.

The glass-transition temperatures (T_g) of the terpolymers measured by DSC fell in the range of $50\text{--}110^\circ\text{C}$, are listed in Table I, and are plotted in Figure 7. The concentration of the hydroxyl species had little effect on the T_g of the terpolymers and, in general, samples with higher T_g s contained greater concentrations of bis lactone groups and lower levels of glycidyl groups. By superposition of Figures 1 and 7, it can be seen that the molecular weight and T_g of these polymers can be independently controlled by judicious selection of the monomer content.

A large broad endotherm was present in the DSC traces of the terpolymers. These endotherms occurred between 215 and 275°C and differed significantly in magnitude, breadth, and shape. The DSC heating curve for terpolymer **5e** is representative and is shown in Figure 8. FTIR spectra of samples heated to temperatures just below and just above the endotherms show that the endotherms were not caused by curing reactions, but were caused by depolymerization of the terpolymers. This was confirmed by GC-MS experiments and by TGA that

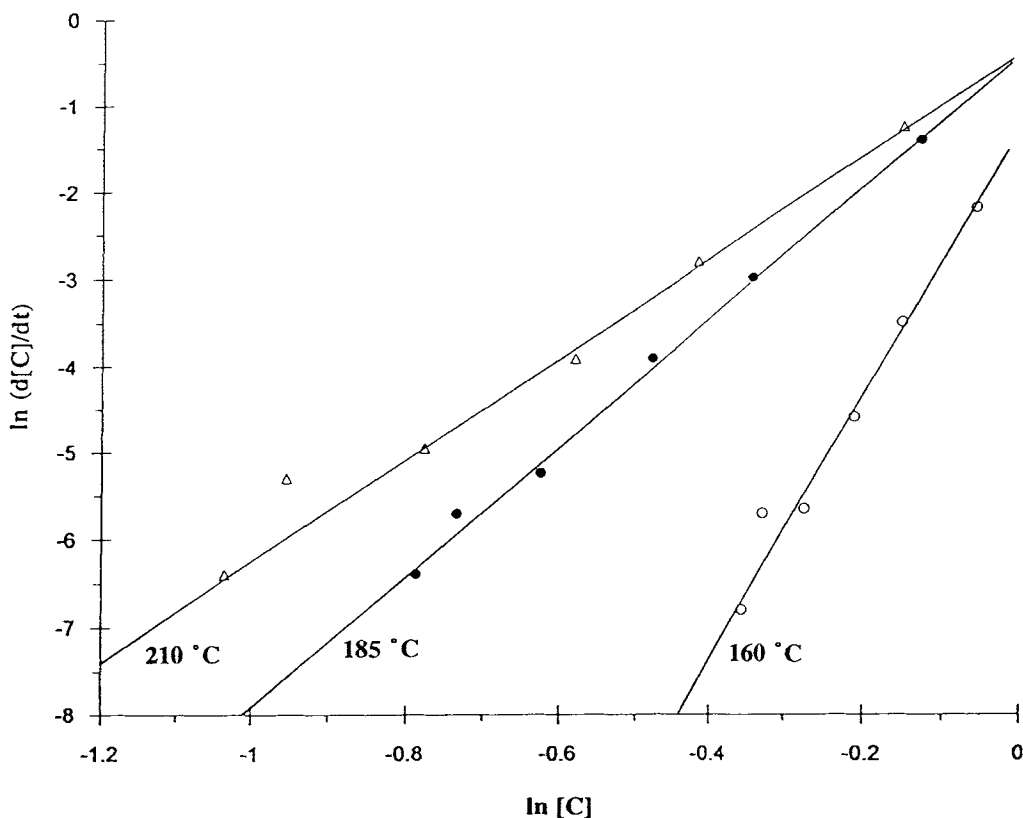


Figure 6 Bislactone reaction data at (○) 160°C, (●) 185°C, and (△) 210°C plotted in the form of eq. (2).

revealed that residual monomers evaporated between 100 and 200°C.

The thermal stability of the terpolymers was investigated by TGA. When the temperature was raised from ambient to 600°C, the terpolymers lost weight in three discrete steps. The TGA curve of terpolymer **5e** is representative and is shown in Figure 9. A small weight loss (about 1–4%) occurs between 100 and 200°C, and is caused by the evaporation of residual solvent and unreacted liquid monomers. GC-MS confirmed that the materials

emitted from the terpolymers in this region are mainly THF, GMA, and HEMA. Quantitative analysis of the total ion current detected by MS indicated that the relative amounts of the residual solvent and volatile monomers to be 41 and 55%, respectively.

The first significant loss of weight normally occurs between 275 and 310°C. GC-MS shows that the gases in this region contain primarily HEMA (**2**) and GMA (**4**) monomers created by depolymerization. The amount of weight lost is directly related to the sum of the concentrations of these

Table III Parameters Calculated from Reaction Rates

Reactive Group	Temperature (°C)	Correlation Coefficient	α	$\ln k$	k	E_{Act} (kJ mol ⁻¹)
Spirobislactone	160	0.9738	14.59	-1.400	0.247	31.0 ± 1.1
	185	0.9954	7.40	-0.461	0.631	
	210	0.9809	5.44	-0.555	0.574	
Epoxy	160	0.9150	25.53	-0.917	0.400	59.1 ± 1.2
	185	0.9360	20.80	-0.601	0.548	
	210	0.9733	20.55	0.737	2.089	

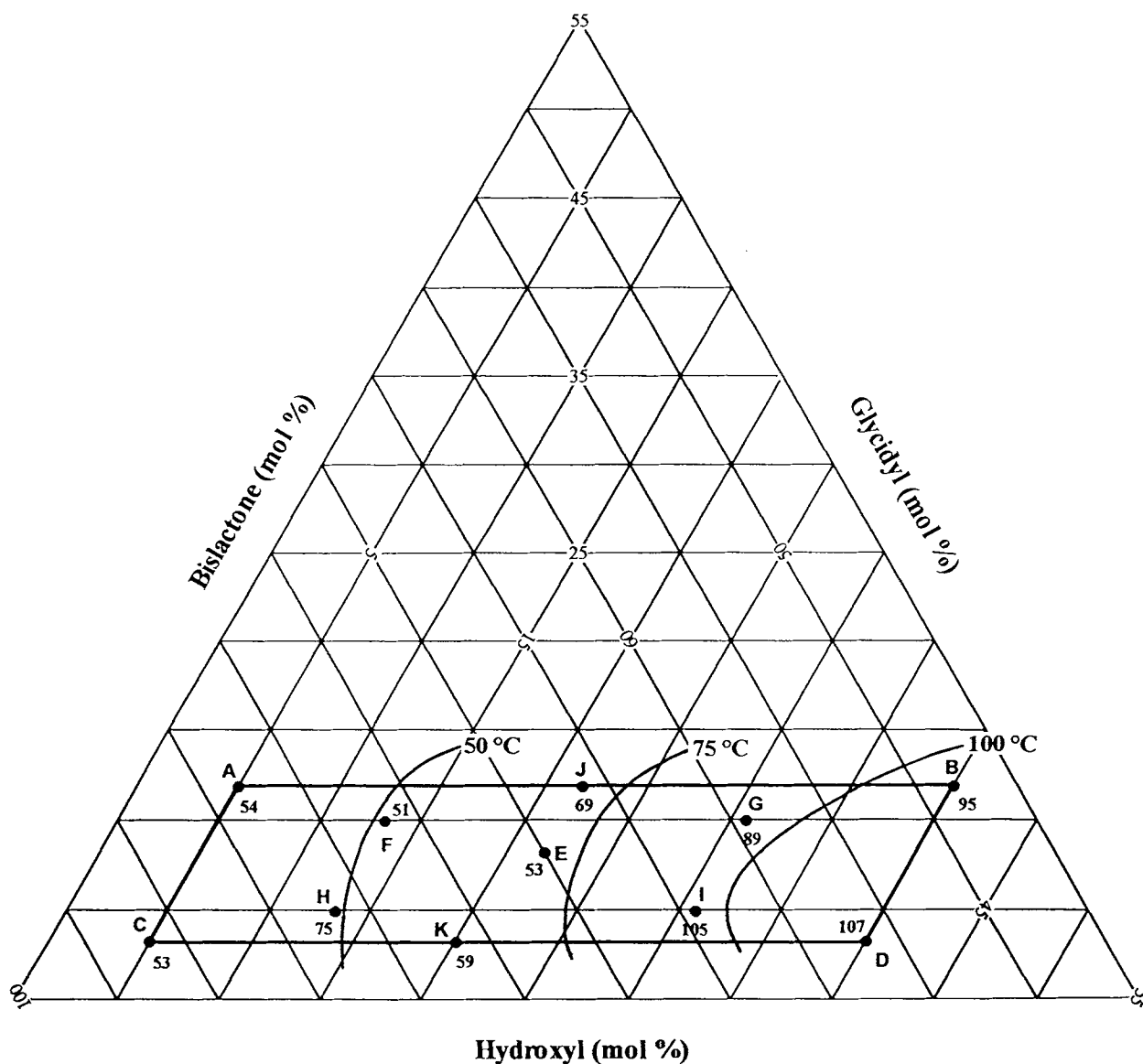


Figure 7 Tricoordinate contour plot relating T_g to terpolymer composition.

two monomers, as can be seen in Figure 10 which is a plot of the sum of the concentrations of these two monomers versus weight loss between 275 and 310°C. Evidently, when the polymer decomposes, only these two monomers are sufficiently volatile to escape. Methacrylates **2** and **4** are liquid at room temperature and boil well below this temperature range, in contrast to the bislactone-substituted ethyl methacrylate monomer **3**.

A second region where weight is lost occurs between 300 and 425°C for each of the terpolymers, and is considerably broader than the first region. The magnitude of weight loss in this region is directly related to the content of monomer **3**, and rep-

resents the decomposition and volatilization of the solid bislactone-substituted ethyl methacrylate monomer created when the uncrosslinked terpolymer depolymerizes between 215 and 275°C. TGA experiments on monomer **3** show that it decomposes and loses weight in this temperature region. Figure 6 shows that the concentration of monomer **3** in a terpolymer and its thermogravimetric weight loss between 300 and 425°C are closely correlated.

Changes in Volume During Polymerization

The change in volume during curing of the terpolymers was investigated by TMA. It was hoped that

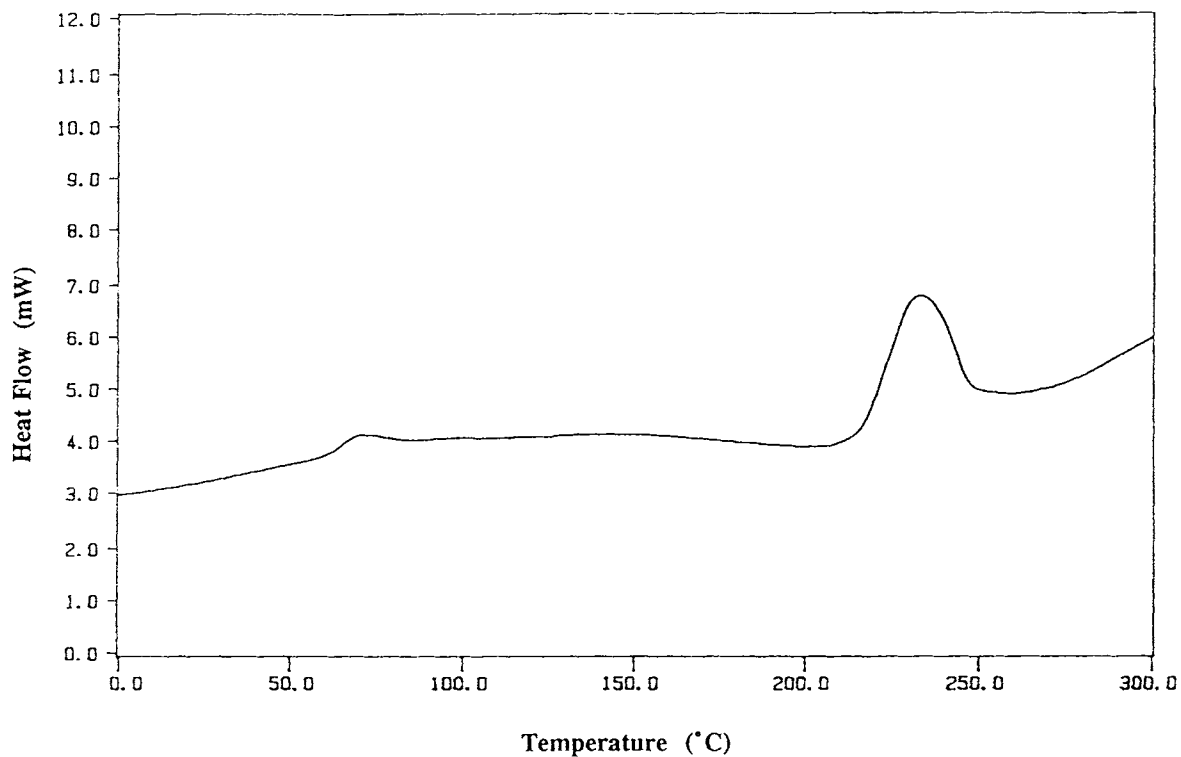


Figure 8 Initial DSC heating trace for terpolymer 5e.

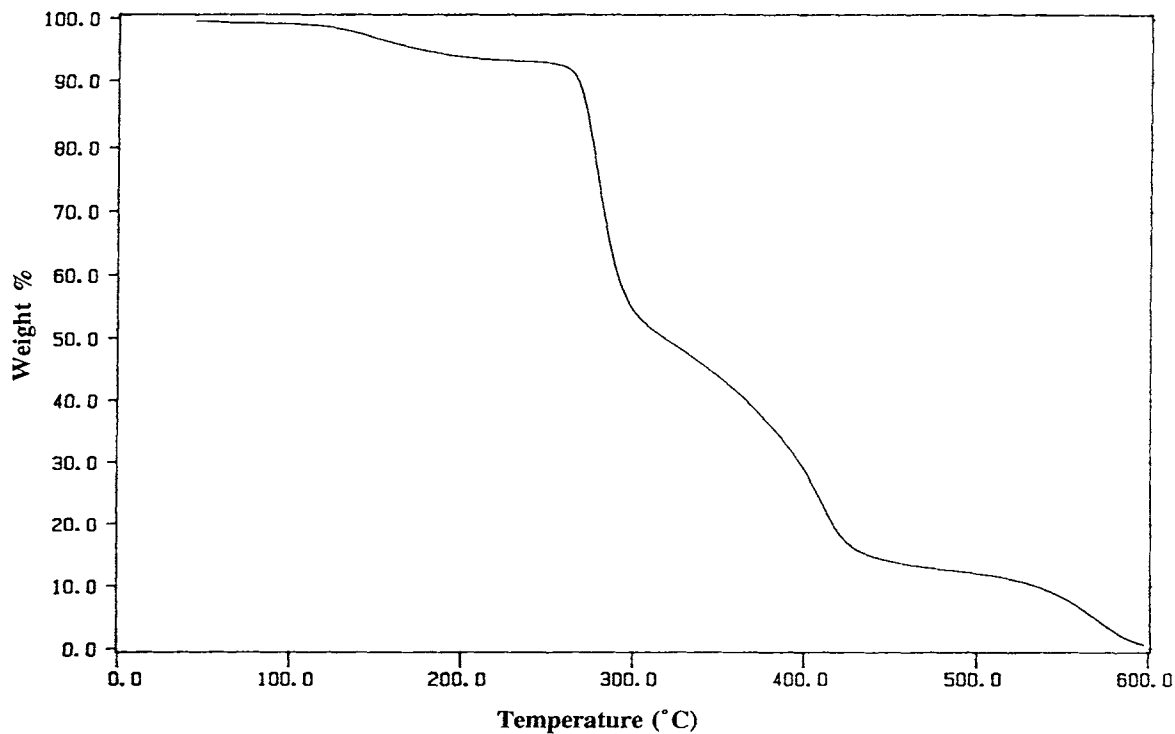


Figure 9 TGA weight loss curve for terpolymer 5e.

this technique would demonstrate the thermal expansion behavior of the materials in the glassy and rubbery states during heating to the cure temperature, curing, and cooling the product to room temperature. Initial TMA curing experiments of solvent-cast samples at a heating rate of $5^{\circ}\text{C min}^{-1}$ showed anomalous expansion between 120 and 150°C . Foaming of the samples caused by evaporation of trapped solvent and residual volatile monomers caused an increase in sample height ranging from 25 to 75%.

To alleviate this problem, samples of terpolymer **5 f** were molded under compression at 140°C with short (3–5 min) residence times between the heated plates. During an initial thermal excursion from room temperature to 175°C at $5^{\circ}\text{C min}^{-1}$, the sample ($T_g = 51^{\circ}\text{C}$) showed a dramatic expansion between 75 and 140°C . Although the sample was kept at 175°C for 45 h, expansion was complete in 15 min. FTIR analysis demonstrates that bislactone groups do not react appreciably below 175°C . Consequently, this expansion is attributed to relaxation of the stress introduced into the sample during

compression molding. The sample was cooled to room temperature and then heated to 200°C . Heating and cooling curves show roughly parallel expansion and contraction contours; volume change was found to be +1.0% on heating and -1.3% on cooling. Clearly thermal effects dominate volume change during cross-linking, and double ring opening of the spirobislactone groups has little or no effect on volume.

CONCLUSIONS

Acrylic terpolymers containing various concentrations of glycidyl, hydroxyl, and spirobislactone pendant groups were prepared by radical chain polymerization and characterized. High molecular weight terpolymers with weight average molecular weights (relative to polystyrene) ranging from 156,000 to 725,000 g mol^{-1} were formed. The T_g s, molecular weights, thermal stabilities, and cross-linking kinetics of the polymers exhibited a wide range of values, depending on the relative proportions of the

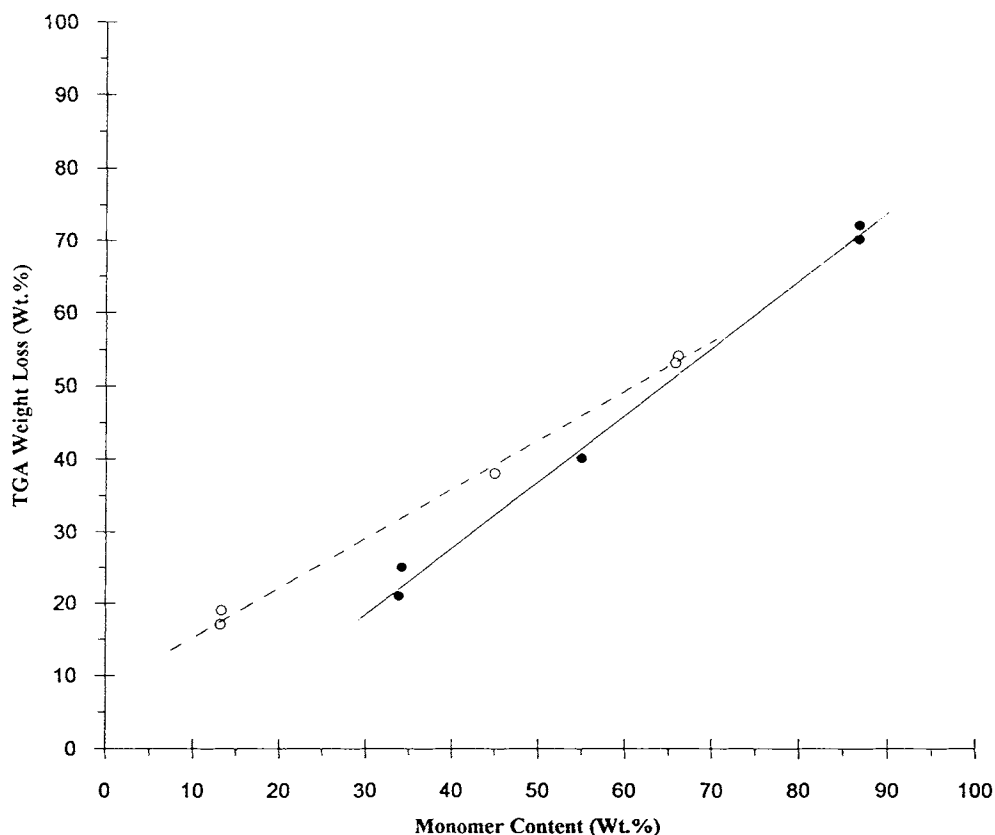


Figure 10 Plot of the sum of the weight of monomers **2** and **4** (●) and the weight of the bislactone methacrylate monomer **3** (○) against the loss in weight of linear polymer **5e** between 275 and 310°C .

monomers used to make the polymers. T_g s, determined by DSC, fell in the range from 51–107°C. The T_g was influenced primarily by composition and much less by molecular weight; terpolymers with higher levels of the bislactone comonomers and lower levels of the glycidyl comonomers exhibited higher T_g s.

The terpolymers exhibited an endotherm in their DSC thermogram between 215 and 275°C caused by depolymerization of the methacrylic backbone chains. This was supported by TGA and GC-MS results indicating that, at temperatures just above the DSC endotherms, each terpolymer lost an amount of weight proportional to its content of volatile comonomers in the terpolymer.

Kinetics of cross-linking measured by FTIR spectroscopy showed that, in terpolymers with low bislactone content (5–13 mol %), the bislactone ring opening reaction occurred very rapidly. This reaction did not go to completion in terpolymers with a bislactone content exceeding 25 mol %. This suggests that approximately 15–25 mol % of the bislactone group is its optimum concentration for cross-linking in the terpolymers.

An Arrhenius analysis of the curing kinetics was made for the terpolymer (**5e**) composed of 70 mol % of GMA, 22 mol % of spirobislactone-substituted HEMA monomer, and 8 mol % of HEMA monomer. The activation energies for the bislactone and epoxy ring opening reactions between 160 and 210°C were found to be 31.0 ± 1.1 and 59.1 ± 1.2 kJ mol⁻¹, respectively.

The reaction of spirobislactone groups during the curing of epoxy groups within a preformed polymer matrix can be controlled, but is not a useful means to regulate the volume change of a gelled network. The impact of thermal effects on volume change during cross-linking overwhelms any contribution from the mechanism of the reaction. The thermal stability of the poly(ethyl methacrylate) backbone chains will limit the use of these materials in demanding applications above 275°C.

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