

# Homopolymer and Copolymers of 4-Benzyloxycarbonylphenyl Acrylate with Glycidyl Methacrylate: Synthesis, Characterization, Reactivity Ratios, and Application as Adhesive for Leather

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**ABSTRACT:** 4-Benzyloxycarbonylphenyl acrylate (BCPA) was prepared by reacting benzyl-4-hydroxy benzoate dissolved in methyl ethyl ketone with acryloyl chloride in the presence of triethylamine. The homopolymer and copolymers of BCPA with glycidyl methacrylate (GMA) having different compositions were synthesized in methyl ethyl ketone using benzoyl peroxide as a free-radical initiator at  $70 \pm 1^\circ\text{C}$ . All the polymers were characterized by FTIR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectroscopic techniques. The solubility of the polymers was tested in various polar and nonpolar solvents. The molecular weights ( $\overline{M}_w$  and  $\overline{M}_n$ ) and polydispersity indices of the polymers were determined using gel permeation chromatography. The glass-transition temperatures of the copolymers increased with increasing GMA content in the copolymer. Thermogravimetric analysis of the polymers performed in air showed that the thermal stability

of the copolymer increased with increasing BCPA content. Copolymer compositions were determined using  $^1\text{H-NMR}$  analysis. The monomer reactivity ratios were determined by the application of conventional linearization methods such as Fineman–Ross ( $r_1 = 0.5237$ ;  $r_2 = 1.9646$ ), Kelen–Tüdös ( $r_1 = 0.4996$ ;  $r_2 = 1.8741$ ), and extended Kelen–Tüdös ( $r_1 = 0.4652$ ;  $r_2 = 1.9046$ ) as well as a nonlinear error-in-variables model (EVM) method, using the computer program RREVM ( $r_1 = 0.4644$ ;  $r_2 = 1.8324$ ). The peel strength of the leather adhesives prepared from the copolymers was also determined. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3604–3612, 2004

**Key words:** 4-benzyloxycarbonylphenyl acrylate; glycidyl methacrylate; thermal properties; NMR; adhesives

## INTRODUCTION

Polymers with reactive functional groups are synthesized because of their specific end applications.<sup>1</sup> Because of the reactive nature of the epoxy group, copolymers containing GMA have led to an interesting class of new materials.<sup>2,3</sup> Polymers based on GMA find important applications in biology for binding of drugs and biomolecules,<sup>4</sup> and in electronics as negative electron beam resists.<sup>5</sup> Epoxy group-containing compounds are also used as excellent thermosetting adhesives, which are heat resistant and decrease the flow cracking in the manufacture of semiconductor packaging,<sup>6,7</sup> and overhead projector (OHP) sheets.<sup>8</sup> Substituted benzyl acrylate polymers are known to exhibit photohardenable properties<sup>9</sup> that are mainly used in the preparation of organic electrophotographic photoconductor composition<sup>10</sup> having high sensitivity, a low dark-decay rate, low toxicity, and excellent durability. They are used in optical data

storage materials,<sup>11</sup> as ingredient in paints,<sup>12</sup> UV-curable adhesive coatings,<sup>13</sup> and mate coatings that prevent corrosion.<sup>14</sup> Finally, substituted phenyl acrylate and GMA copolymers have high thermal stability and are used in the formulation of leather-to-leather and leather-to-rubber bonding adhesives.<sup>15,16</sup>

In the past few decades,  $^1\text{H-NMR}$  spectroscopic analysis has been established as a powerful tool for the determination of copolymer composition.<sup>17–23</sup> The accurate determination of copolymer composition and estimation of monomer reactivity ratios are significant for tailor-made copolymers with desirable physical and chemical properties and in evaluating the specific end application of copolymers. The main aim in commercial copolymerization is to achieve as specific a composition distribution as possible. Knowledge about the monomer reactivity ratios would help in achieving this. Monomer reactivity ratios were determined by a number of linearization methods.<sup>24–26</sup> Because the monomer reactivity ratios determined by these methods are not accurate, a number of nonlinear methods have been proposed to obtain correct values of monomer reactivity ratios.<sup>27–31</sup> Notable among them is the nonlinear error-in-variables model (EVM) method using a recent computer program, RREVM,<sup>30</sup>

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which gives reliable results. The present article reports the synthesis, characterization, and adhesive properties of copolymers of 4-benzyloxycarbonylphenyl acrylate (BCPA) and glycidyl methacrylate (GMA) and the determination of monomer reactivity ratios.

## EXPERIMENTAL

### Materials

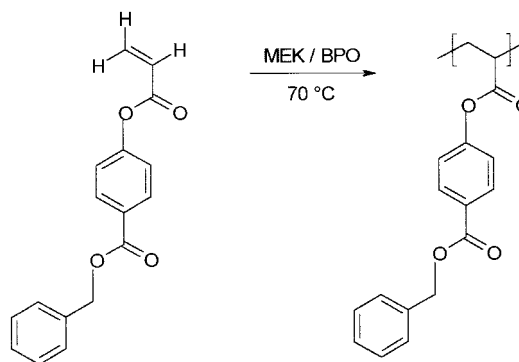
Benzyl-4-hydroxy benzoate (Fluka, Buchs, Switzerland) was used as received without purification. Glycidyl methacrylate (GMA; E. Merck, Darmstadt, Germany) was purified by distillation under reduced pressure. Benzoyl peroxide (BPO; Fluka) was purified by recrystallization in a 1:1 mixture of chloroform and methanol mixture. Triethylamine (Fluka) was allowed to stand over sodium hydroxide for 12 h and distilled in the presence of 2% (w/v) naphthyl isocyanate. The fraction boiling between 86 and 89°C was collected and used. Acrylic acid (CDH) and benzoyl chloride (SRL) were used as such. All the solvents were purified by distillation before use.

### Synthesis of BCPA

Acryloyl chloride was prepared from acrylic acid and benzoyl chloride using the procedure of Stampel.<sup>32</sup> Benzyl-4-hydroxybenzoate (15 g, 0.06 mol) and triethylamine (10.0 mL, 0.07 mol) were dissolved in a 300 mL of methyl ethyl ketone (MEK) and placed in a two-neck round-bottom flask fitted with a mechanical stirrer. A dropping funnel was fitted to the other neck. The reaction mixture was stirred in an ice bath of 0–5°C. Acryloyl chloride (5.8 mL, 0.07 mol) dissolved in 25 mL of MEK was added dropwise to the well-cooled reaction mixture through a dropping funnel over a period of 30 min. After the addition the reaction mixture was stirred well at room temperature for a further period of 1 h. Then the precipitated triethylammonium chloride was filtered off and the solvent in the filtrate was removed using a rotary evaporator. The residue obtained was dissolved in ether and washed twice with 0.1% solution of NaOH and then with distilled water. The ether solution was then evaporated to obtain crude 4-benzyloxycarbonyl phenyl acrylate. The product was recrystallized from ethanol to obtain white flakes. The yield of the monomer was 79% and the melting point was 60–61°C.

The structure of the monomer was confirmed by elemental analysis, FTIR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectra.

Elemental analysis (%): C = 72.34 (found), 72.41 (calcd); H = 4.96 (found), 4.99 (calcd). IR (cm<sup>-1</sup>, KBr): 3066 and 3033 (=C—H); 2980 and 2984 (C—H); 1740 and 1799 (>C=O, ester), 1634 (olefinic C=C); 1604, 1586, 1503, 1445, 1406 (aromatic C=C); 1173, 1207



Scheme 1 Synthesis of poly(BCPA).

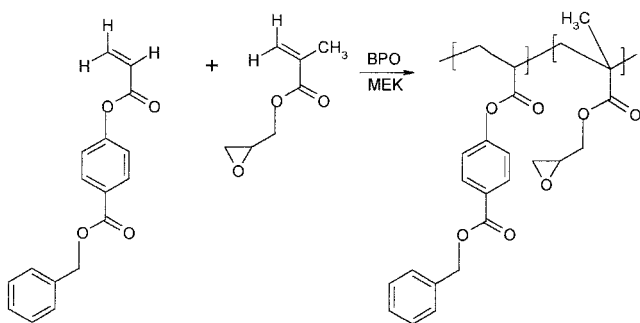
(C—O); 755 and 700 (C—H out-of-plane bending); 503 (C=C out-of-plane bending). <sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>): 8.26 (d, 2H); 7.56–7.23 (m, 5H), and 7.23 (d, 2H) (aromatic); 6.89–6.83 (q, 1H) (CH<sub>2</sub>=); 6.39–6.28 (q, 1H) (=CH-); 5.40 (s, 2H) (OCH<sub>2</sub>). <sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>): 166.20 (COOCH<sub>2</sub>); 164.42 (=CH—COO); 154.75, 136.26, 133.76, 131.75, 129.04, 128.98, 127.92, and 122.03 (aromatic); 132.43 (=CH-); 115.67 (CH<sub>2</sub>=); 67.32 (OCH<sub>2</sub>).

### Homopolymerization of BCPA

A 1-g sample of the monomer (BCPA) and BPO (0.5% wt of catalyst) as the free-radical initiator dissolved in 10 mL of MEK were charged to a polymerization tube purged by purified N<sub>2</sub> gas for 15 min. Then the solution was thermostated at 70 ± 1°C and after 10 h the polymer was precipitated in excess methanol. The polymer was purified by repeated reprecipitation by methanol from a solution of polymer in MEK. This step was repeated twice and the product was dried at ambient temperature. The yield of the polymer was 65%. Scheme 1 shows the reaction for the synthesis of poly(BCPA).

### Synthesis of copolymers of poly(BCPA-co-GMA)

Copolymerization reactions were carried out in MEK solution at 70°C using BPO as a free-radical initiator. Predetermined quantities of BCPA, GMA, and BPO (0.5 wt % of catalyst) were dissolved in MEK in a standard reaction tube (100 mL) and purged with pure N<sub>2</sub> gas for 20 min. The tube was tightly sealed and kept in a thermostated water bath maintained at 70 ± 1°C. After the desired time, ranging from 15 min to 2 h, the copolymerization was stopped at low conversion (<10% wt). These copolymers were precipitated by pouring into excess methanol, filtered, purified by reprecipitation from a solution of the polymer in MEK by methanol and dried at 40°C for 24 h. Scheme 2



Scheme 2 Synthesis of poly(BCPA-co-GMA).

shows the reaction for the synthesis of poly(BCPA-co-GMA).

### Measurements

Elemental analysis was performed with a Perkin-Elmer C-H analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT). Infrared spectra were recorded with a Nicolet 360 FTIR spectrophotometer (Nicolet Analytical Instruments, Madison, WI) using KBr pellets.  $^1\text{H-NMR}$  spectra for all monomer and polymer samples were run on a Bruker 270 MHz FT-NMR spectrometer (Bruker Instruments, Billerica, MA) at room temperature using  $\text{CDCl}_3$  as a solvent and TMS as an internal standard, respectively. The proton-decoupled  $^{13}\text{C-NMR}$  spectrum was run on the same instrument operating at 22.63 MHz at room temperature and the chemical shifts were recorded under similar conditions. The molecular weights ( $\overline{M}_w$  and  $\overline{M}_n$ ) were determined using a Waters 501 gel permeation chromatograph (Waters Chromatography Division/Millipore, Milford, MA). Tetrahydrofuran was used as the eluent and polystyrene standards were used for calibration. Thermogravimetric analysis was performed with a Mettler TA 3000 thermal analyzer (Mettler, Greifensee, Switzerland) in air atmosphere at a heating rate of  $15^\circ\text{C}/\text{min}$ . The glass-transition temperature was determined with a Netzsch-Gerätebau GmbH (Bavaria, Germany) thermal analyzer at a heating rate of  $10^\circ\text{C}/\text{min}$  in nitrogen atmosphere. The peel strength of adhesives prepared from the copolymers was estimated using Satra AM I and II.

### Estimation of peel strength of adhesives

Two poly(BCPA-co-GMA) samples having different compositions (0.2862 : 0.7138 and 0.4486 : 0.5514) were chosen to study the adhesive properties on leather. The copolymers were individually crosslinked using 40% diethanolamine (based on the weight of GMA in chloroform) and the paste obtained was used as the adhesive. Cow side leathers of length 15 cm and breadth 2.5 cm were used for determining the peel

strength of adhesives prepared. After the grains of the leather were removed with the help of emery paper, 0.75 g of the adhesive was applied uniformly over an area of  $7.5 \times 2.5$  cm at one end of the buffed surface of each strip. The adhesive film was allowed to dry and when it was still tacky, the coated surfaces of the two leather strips were carefully aligned face to face such that no air bubble was trapped inside and the free ends of the leather strips lay in the same direction. The effect of two different curing temperatures (50 and  $90^\circ\text{C}$ ) on the peel strength of leather to leather adhesive was determined.

### Solubility studies

Solubility of the polymers was tested in various polar and nonpolar solvents. About 5–10 mg of the polymer was added to about 2 mL of different solvents in a test tube and kept overnight with the tube tightly closed. The solubility of the polymers was noted after 24 h.

## RESULTS AND DISCUSSION

Poly(BCPA) was obtained by free-radical solution polymerization of the monomer BCPA at  $70 \pm 1^\circ\text{C}$  in MEK solvent using BPO as the initiator. The copolymerization of BCPA with GMA in MEK was studied over a wide composition interval with mole fractions of BCPA ranging from 0.15 to 0.9 in the feed.

### Solubility

The homopolymers and the copolymers were soluble in chloroform, acetone, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene, and xylene, but insoluble in *n*-hexane and hydroxyl group-containing solvents such as methanol and ethanol.

### Characterization of homopolymer

#### Infrared spectrum

The IR spectrum of poly(BCPA) shows peaks at 3066 and  $3033\text{ cm}^{-1}$  attributed to the C—H stretching of the aromatic ring. The peaks at 2950 and  $2881\text{ cm}^{-1}$  were attributed to the asymmetrical and symmetrical C—H stretching of the methylene and methyl groups. When compared to the monomer, the ester carbonyl stretching was shifted to higher frequency and was observed at  $1758\text{ cm}^{-1}$ , attributed to the loss of conjugation after polymerization. The other carbonyl stretching attributed to the second ester group was observed at  $1718\text{ cm}^{-1}$ . The ring-stretching vibrations of the two aromatic nuclei were observed at 1603, 1504, 1455, and  $1412\text{ cm}^{-1}$ . The peaks at 1273 and  $1161\text{ cm}^{-1}$  were attributed to C—O stretching. The C—H out-of-plane

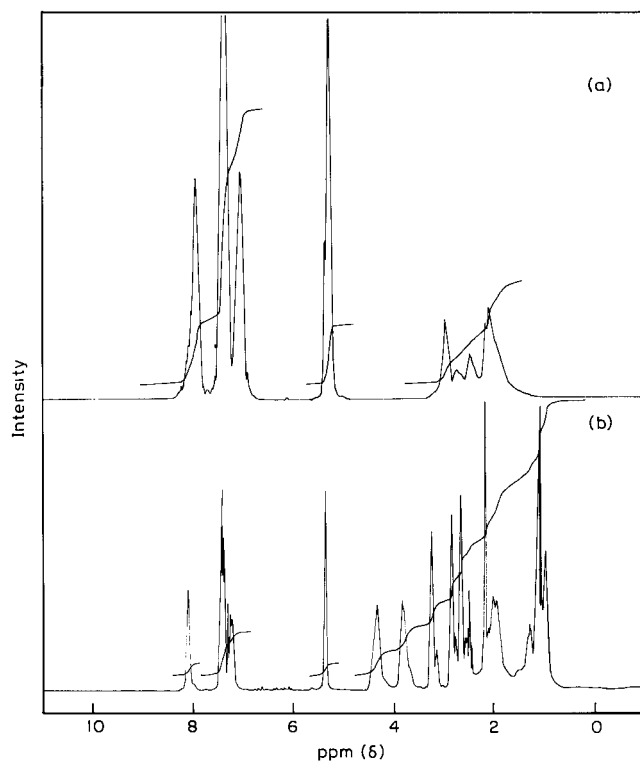


Figure 1  $^1\text{H-NMR}$  spectrum of (a) poly(BCPA); (b) poly(BCPA-co-GMA) (0.3530 : 0.6470).

bending vibration of aromatic nuclei was observed at 755 and 694  $\text{cm}^{-1}$ . The  $\text{C}=\text{C}$  out-of-plane bending of the aromatic nuclei were seen at 590 and 501  $\text{cm}^{-1}$ .

#### $^1\text{H-NMR}$ spectrum

The  $^1\text{H-NMR}$  spectrum of poly(BCPA) is shown in Figure 1(a). The two aromatic protons present in the phenylene ring at the *ortho* position to the group  $-\text{COOCH}_2\text{Ph}$  are shifted upfield and appear at 7.95 ppm, whereas the other aromatic protons are observed at 6.87–7.54 ppm. The resonance signals at 5.31 ppm are attributed to the methylenoxy group. The methyne protons give a broad signal between 2.35 and 3.25 ppm. The broad signal between 1.67 and 2.35 ppm is attributed to the backbone methylene protons.

#### $^{13}\text{C-NMR}$ spectrum

The proton-decoupled  $^{13}\text{C-NMR}$  spectrum of poly(BCPA) is shown in Figure 2. The resonance signals at 171.61 ppm ( $\text{C}_3$ ) and 165.60 ppm ( $\text{C}_8$ ) are attributed to the ester carbonyl carbon attached directly to the backbone of the polymer chain and the aromatic ring, respectively. The aromatic carbon attached to the oxygen atom gave a signal at 154.07 ppm ( $\text{C}_4$ ). The other

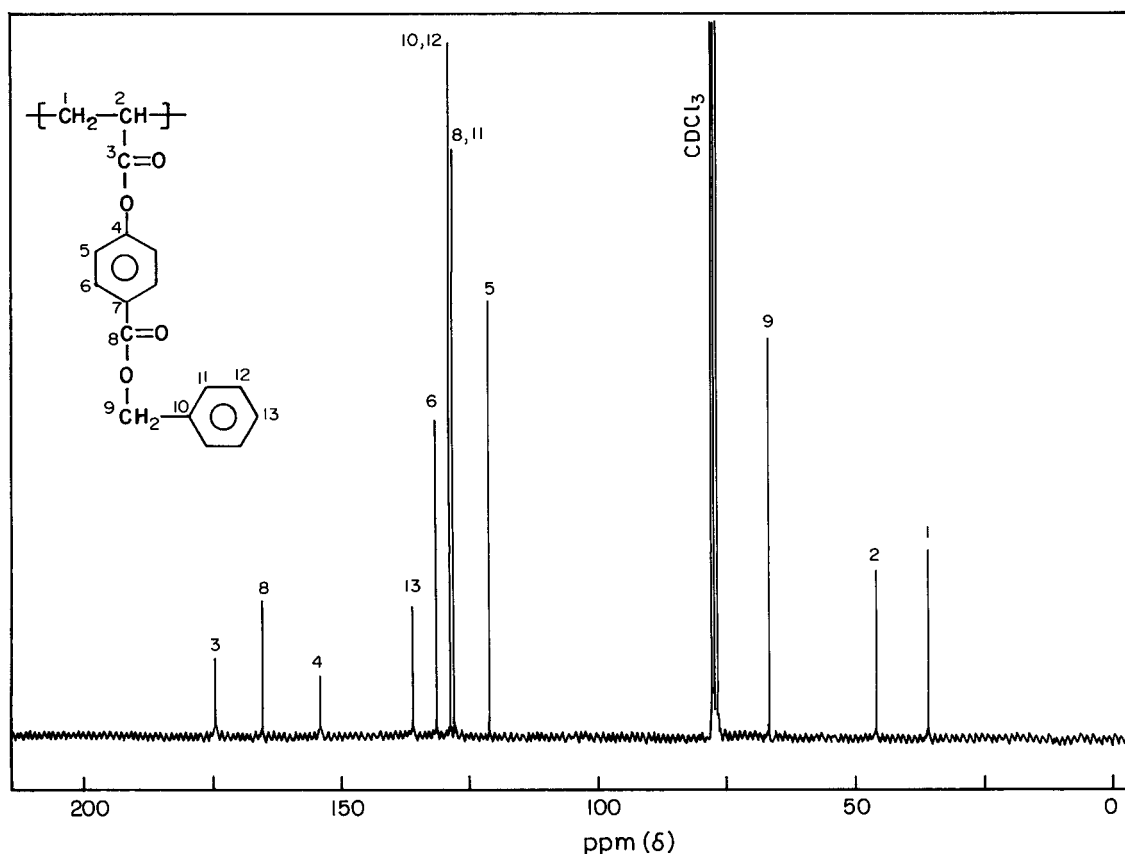


Figure 2  $^{13}\text{C-NMR}$  spectrum of poly(BCPA).

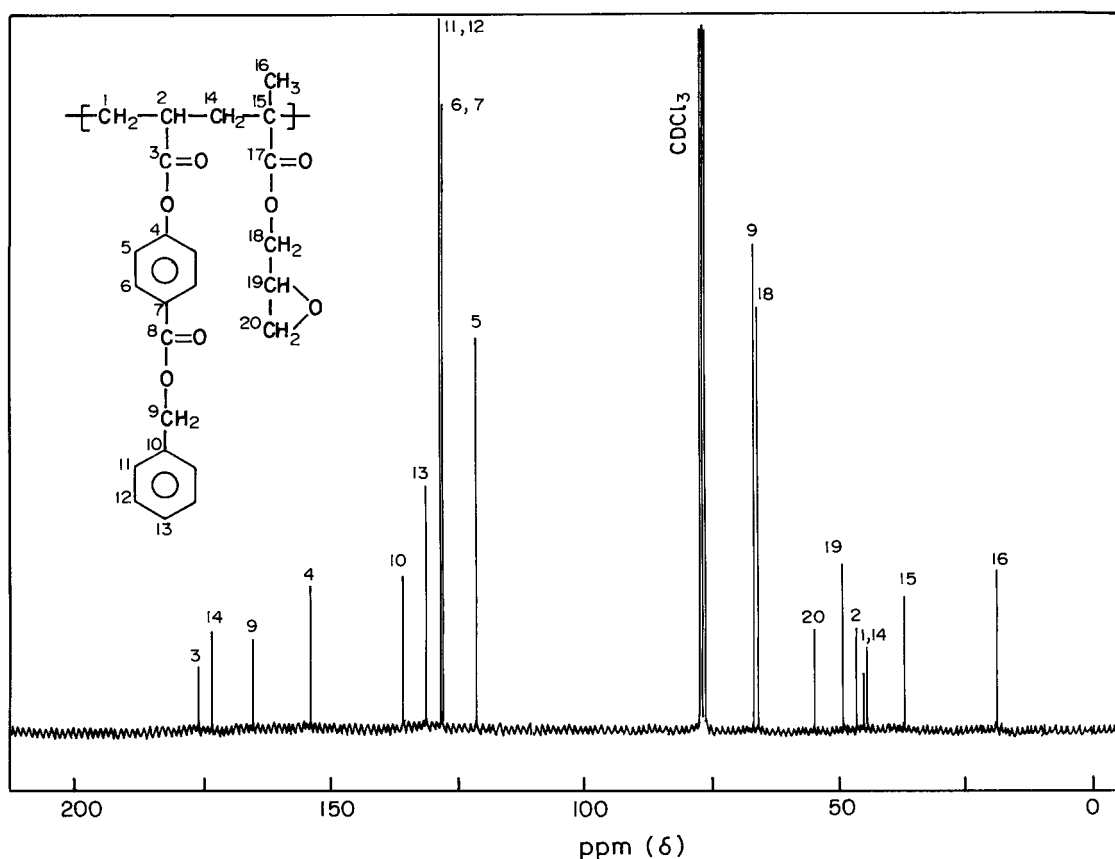


Figure 3  $^{13}\text{C}$ -NMR spectrum of poly(BCPA-co-GMA) (0.3530 : 0.6470).

aromatic carbons show signals at 136.28 ( $\text{C}_{13}$ ), 131.72 ( $\text{C}_6$ ), 128.97 ( $\text{C}_{10}$  and  $\text{C}_{12}$ ), 128.50 ( $\text{C}_7$  and  $\text{C}_{11}$ ), and 121.80 ppm ( $\text{C}_5$ ). The signal at 67.19 ppm ( $\text{C}_9$ ) is attributed to the methyleneoxy group. The backbone methylene carbon is observed at 42.15–42.31 ppm ( $\text{C}_1$ ), whereas the methyne carbon is observed at 35.56–34.97 ppm ( $\text{C}_2$ ).

### Characterization of the copolymer

#### Infrared spectrum

The IR spectrum of the copolymer, poly(BCPA-co-GMA) (0.3530 : 0.6470) showed a peak at  $3064\text{ cm}^{-1}$  corresponding to the C—H stretching of the aromatic ring. The symmetrical and asymmetrical stretchings attributed to the methyl and methylene groups were observed at 2989, 2948, and  $2850\text{ cm}^{-1}$ . The peaks at 1756 and  $1722\text{ cm}^{-1}$  were attributed to the ester carbonyl stretching of both BCPA and GMA units. The aromatic C=C stretchings were observed at 1603, 1501, and  $1452\text{ cm}^{-1}$ . The symmetrical and asymmetrical bending vibrations of the methyl groups were seen at 1381 and  $1450\text{ cm}^{-1}$ . The symmetrical and asymmetrical stretchings of the epoxy group were observed at 1274 and  $907\text{ cm}^{-1}$ . The C—O stretching

was observed at 1202 and  $1161\text{ cm}^{-1}$ . The C—H out-of-plane bending vibrations of the aromatic nuclei were observed at 847, 758, and  $697\text{ cm}^{-1}$ . The C=C out-of-plane bending vibrations occurred at 503 and  $451\text{ cm}^{-1}$ .

#### $^1\text{H}$ -NMR spectrum

The  $^1\text{H}$ -NMR spectrum of the copolymer poly(BCPA-co-GMA) (0.3530 : 0.6470) is shown in Figure 1(b). The chemical shift assignments for the copolymers were based on the chemical shifts observed for the respective homopolymers. The aromatic protons show a signal between 7.01 and 8.21 ppm. The methyleneoxy protons of BCPA unit show a signal at 5.34 ppm. The spectrum shows two signals at 4.32 and 3.79 ppm, which are attributed to  $-\text{COOCH}_2-$  groups of GMA units. The peak at 3.27 ppm is attributed to the methyne proton of the epoxy group. The methylene protons of the epoxy group show signals at 2.81 and 2.62 ppm. The backbone methyne and methylene groups show signals at 2.37–2.57 and 1.57–2.37 ppm, respectively. The  $\alpha$ -methyl proton of the GMA unit shows signals between 0.55 and 1.57 ppm.

TABLE I  
Molecular Weight Data for Homo- and Copolymers of BCPA and GMA

Polymer	$m_1^a$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
Poly(BCPA)	1.0000	3.21	1.90	1.69
	0.0920	4.12	2.18	1.89
Poly(BCPA-co-GMA)	0.1899	3.94	2.11	1.87
	0.3530	4.23	2.34	1.81
	0.4751	3.81	2.07	1.84
	0.6799	3.94	2.25	1.75
	0.8311	3.84	2.21	1.74
Poly(GMA)	0.0000	4.02	2.04	1.97

<sup>a</sup>  $m_1$  is the mole fraction of BCPA in the copolymer.

### <sup>13</sup>C-NMR spectrum

The proton-decoupled <sup>13</sup>C-NMR spectrum of poly(BCPA-co-GMA) (0.3530 : 0.6470) is shown in Figure 3. The resonance signals at 176.86 ppm (C<sub>3</sub>), 174.10 ppm (C<sub>14</sub>), and 165.45 (C<sub>9</sub>) are attributed to the ester carbonyl carbons. The aromatic carbons attached to the oxygen atom show resonance signals at 154.65 ppm (C<sub>4</sub>). The other aromatic carbon signals are observed at 135.84 (C<sub>10</sub>), 131.23 (C<sub>13</sub>), 128.55 (C<sub>11</sub> and C<sub>12</sub>), 128.24 and 128.11 (C<sub>6</sub> and C<sub>7</sub>), and 121.52 ppm (C<sub>5</sub>). The resonance signals at 66.74 ppm (C<sub>9</sub>) are attributed to the methyleneoxy group of the BCPA unit. The methyleneoxy group flanked between the carbonyl group and the epoxy group in the GMA unit shows signals at 65.85 ppm (C<sub>18</sub>). The methyne and methylene carbons of the epoxy group show signals at 53.97 ppm (C<sub>19</sub>) and 48.81 ppm (C<sub>20</sub>), respectively. The signal assigned to the backbone methylene carbon atoms is observed at 44.47–44.66 ppm (C<sub>1</sub> and C<sub>14</sub>) and that assigned to the methyne carbon is observed at 46.42 ppm (C<sub>2</sub>). The  $\alpha$ -methyl groups of both monomer units show resonance signal at 18.38 ppm.

### Molecular weights

The number- and weight-average molecular weights of poly(BCPA), poly(GMA), and six copolymer samples determined by GPC are presented in Table I. The

polydispersity indices of poly(BCPA) and poly(GMA) are 1.69 and 1.97, respectively. The theoretical values of polydispersity indices for polymers produced by radical combination and disproportionation are 1.5 and 2.0 respectively.<sup>33</sup> In the homopolymerization of GMA the growing chains seem to undergo termination mainly by disproportionation. The values of  $\bar{M}_w/\bar{M}_n$  in copolymerization are also known to depend on chain termination in the same way as in homopolymerization. In the case of copolymers the tendency for chain termination by disproportionation increases with the increase of GMA content in the copolymer.

### Glass-transition temperature

The glass-transition temperature ( $T_g$ ) of the copolymers was determined using differential scanning calorimetry and the data are presented in Table II. All the copolymers show a single  $T_g$ , showing the absence of formation of a mixture of homopolymers or a block copolymer. The  $T_g$  of poly(BCPA) is 16°C and that of poly(GMA) is 74°C.<sup>34</sup> The  $T_g$  of the copolymers increases with the increase in GMA content.

### Thermogravimetric analysis

The results of the thermogravimetric analysis of poly(BCPA), poly(GMA), and poly(BCPA-co-GMA) (0.3530 :

TABLE II  
TGA and DSC Data for BCPA-GMA Copolymer System

Polymer	$m_1$	$m_2$	IDT <sup>a</sup>	Temperature at weight loss					$T_g$ (°C)
				10%	30%	50%	70%	90%	
Poly(GMA)	0.0000	1.000	188	260	292	308	322	372	74
Poly(BCPA)	0.0920	0.9080	208	268	305	325	343	390	46.40
	0.1899	0.8108	228	277	318	342	364	408	34.77
	0.3530	0.6470	250	285	332	360	386	427	25.98
	0.4751	0.5249	259	300	339	266	393	435	22.54
	0.6799	0.3201	268	315	346	271	400	443	19.11
Poly(BCPA)	0.8311	0.1688	270	330	353	277	407	451	17.52
	1.0000	0.0000	290	345	360	382	413	459	16.25

<sup>a</sup> IDT is initial decomposition temperature.

TABLE III  
Composition Data for Free-Radical Copolymerization of BCPA with GMA in MEK Solution at 70°C

Copolymer	$M_1^a$	Conversion (%)	Integrated peak areas of protons		C	$m_1^a$	$m_2^b$
			$I_{Ar}$	$I_{Ali}$			
1	0.1572	9.35	7.917	91.215	0.0868	0.0920	0.9080
2	0.3101	9.50	15.894	0.1889	0.1889	0.1899	0.8101
3	0.5112	8.18	27.395	0.3854	0.3859	0.3530	0.6470
4	0.6488	9.37	35.937	0.5609	0.5609	0.4751	0.5249
5	0.8059	8.62	47.040	0.9272	0.9272	0.6799	0.3201
6	0.9037	8.90	57.931	1.2800	1.2800	0.8311	0.1688

<sup>a</sup>  $m_1$  and  $M_1$  are the mole fraction of BCPA in the feed and copolymer, respectively.

<sup>b</sup>  $m_2$  is the mole fraction of GMA in the copolymer.

0.6470) are presented in Table II. The thermograms clearly indicate that poly(BCPA), poly(GMA), and poly(BCPA-co-GMA) all undergo a single-stage decomposition. The initial decomposition temperatures of poly(BCPA), poly(BCPA-co-GMA), and poly(GMA) are 290, 259, and 188°C, respectively, and 80% weight loss was observed at 382, 360, and 308°C. TGA results indicate that the thermal stability of the copolymer increases with an increase in the BCPA content in the copolymer.

### Copolymer composition

The copolymer composition was determined by <sup>1</sup>H-NMR spectroscopy. The assignment of the resonance peaks in the <sup>1</sup>H-NMR spectrum allowed evaluation of the content of each kind of monomeric unit incorporated into the copolymer chains. Thus, the mole fraction of BCPA in the copolymer chain was calculated by measuring the integrated peak areas of aromatic protons of BCPA and aliphatic protons of BCPA and GMA units.

Let  $m_1$  be the mole fraction of BCPA and  $(1 - m_1)$  that of GMA. BCPA contains 9 aromatic protons and 5 aliphatic protons, whereas GMA contains 10 aliphatic protons.

$$C = \frac{I_{Ar}}{I_{Ali}}$$

$$C = \frac{9m_1}{5m_1 + 10(1 - m_1)} \quad (1)$$

where  $I_{Ar}$  and  $I_{Ali}$  represent the integrated peak areas of aromatic protons and aliphatic protons, respectively. On simplification this gives

$$m_1 = \frac{10C}{9 + 5C} \quad (2)$$

By using eq. (2), the mole fraction of BCPA in the copolymer was determined by measuring the inte-

grated peak areas of aromatic proton signals and aliphatic proton signals. The values of C and the corresponding mole fractions of BCPA in the copolymer are given in Table III. The plot of mole fractions of BCPA in the feed versus that in the copolymer is shown in Figure 4. The composition curve indicates that the composition of BCPA in the copolymer is always lower than that in the feed.

### Monomer reactivity ratios

From the monomer feed ratios and the copolymer compositions, the monomer reactivity ratios of BCPA and GMA were determined by the application of the Fineman-Ross (F-R), Kelen-Tüdös (K-T), and extended Kelen-Tüdös (Ext. K-T) methods. The F-R and K-T parameters for the copolymers are presented in Table IV and those for the Ext. K-T are shown in Table V. The monomer reactivity ratios determined by conventional linearization methods are only approximate and are usually used as good starting values for non-linear parameter estimation schemes. Hence to deter-

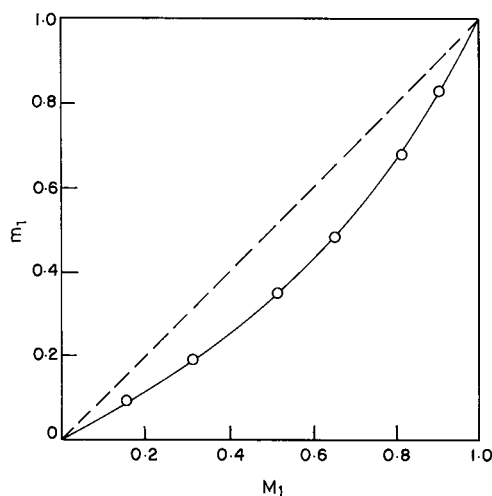


Figure 4 Copolymer composition diagram of poly(BCPA-co-GMA) system.

TABLE IV  
F-R and K-T Parameters for the Copolymerization of BCPA with GMA<sup>a</sup>

Copolymer	$F = M_1/M_2$	$f = m_1/m_2$	$H = F_2/f$	$G = F(f - 1)/f$	$\eta = G/(\alpha + H)^b$	$\xi = H/(\alpha + H)^b$
1	0.1865	0.1013	0.3433	-1.6545	-0.5864	0.1216
2	0.4494	0.2344	0.8616	-1.4678	-0.4395	0.2580
3	1.0458	0.5455	2.0049	-0.8713	-0.1943	0.4472
4	1.8473	0.9051	3.7703	0.1936	-0.0309	0.6034
5	4.2105	2.1240	8.3466	2.2281	0.2058	0.7710
6	9.3842	4.9235	17.8863	7.4781	0.3672	0.8783

<sup>a</sup> F-R, Fineman-Ross; K-T, Kelen-Tüdös.

<sup>b</sup>  $\alpha = 2.4779$ .

mine more reliable values of monomer reactivity ratios a nonlinear error-in-variables model (EVM) method using the computer program RREVM was used. The  $r_1$  and  $r_2$  values from all methods are presented as follows.

Method	$r_1$	$r_2$	$r_1 r_2$
Fineman-Ross	0.5237	1.9646	
Kelen-Tüdös	0.4996	1.8741	
Ext. Kelen-Tüdös	0.4652	1.9046	
RREVM	0.4644	1.8324	0.8609

The 95% joint confidence region for the determined  $r_1$  and  $r_2$  values using RREVM is shown in Figure 5.

The value of  $r_1$  is  $<1$  and that of  $r_2$  is  $>1$ , which indicates the presence of a higher amount of GMA units in the copolymer than that in the feed. However, the product  $r_1 r_2$  is  $<1$ , which indicates that the system leads to random distribution of monomer units with a longer sequence of GMA units in the copolymer chain.

#### Application of the copolymers as leather adhesives

Two different compositions of poly(BCPA-co-GMA) samples (0.2862 : 0.7138 and 0.4486 : 0.5514) were chosen for studying the adhesive properties on leather. These copolymer samples were individually crosslinked with 40% diethanolamine (based on the weight of GMA) in chloroform. The peel strength for the adhesives prepared

from the copolymers containing 71 and 55% GMA was 0.83 and 0.67 N/mm at 50°C, respectively. The corresponding values for these adhesives at 90°C were 1.47 and 1.10 N/mm, respectively. The peel strength was enhanced with the increase in epoxy group content in the copolymers. All these compositions showed good adhesive character even at room temperature. When the copolymer solution of chloroform was treated with ethanolamine, the amino group of the latter readily reacted with the epoxy group of the copolymer to give a pasty product having more free volume and lower  $T_g$  value. The paste still contained some unreacted epoxy groups that, when applied over leather, would react with the functional groups in its surface to form a chemical bonding. Adhesive properties of poly(glycidyl methacrylate-co-2-(N-phthalimido)ethyl methacrylate), poly(glycidyl methacrylate-co-3,5-dimethylphenyl acrylate), and poly(glycidyl methacrylate-co-4-chlorophenyl acrylate) were previously reported.<sup>35-37</sup> Because the composition of glycidyl methacrylate in the copolymers prepared at high conversion in these cases and in the present study are different, it is not possible to make a true comparative study of the adhesive properties of these systems.

#### CONCLUSIONS

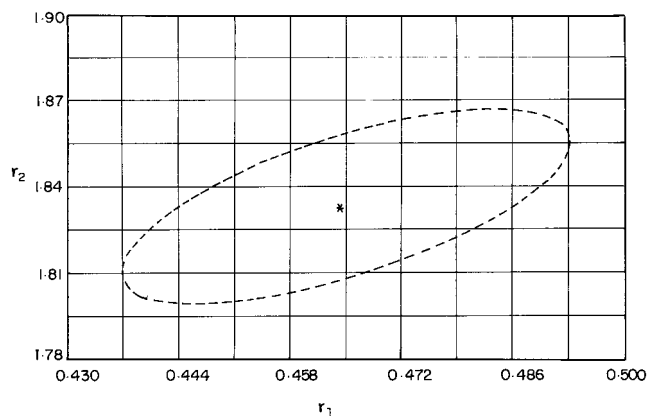
Poly(BCPA) and the copolymers of BCPA with GMA were synthesized by free-radical solution polymeriza-

TABLE V  
Extended K-T Parameters for BCPA-GMA Copolymer System<sup>a</sup>

Parameter	Copolymer system					
	1	2	3	4	5	6
$\zeta_2$	0.1052	0.1266	0.1190	0.1563	0.1546	0.1612
$\zeta_1$	0.0571	0.0660	0.0620	0.0765	0.0779	0.0845
$Z$	0.5289	0.5044	0.5051	0.4682	0.4829	0.5022
$\bar{F}$	0.1915	0.4647	1.0799	1.9331	4.3984	9.8038
$H$	0.3621	0.9213	2.1381	4.1288	9.1083	19.5218
$G$	-1.6991	-1.5178	-0.8998	-0.2026	2.3276	7.8126
$\eta$	-0.9808	-0.6623	-0.2564	-0.0368	0.2221	0.3739
$\xi$	0.2090	0.4020	0.6094	0.7508	0.8692	0.9344

<sup>a</sup>  $\alpha = (\bar{F}_{\max} \times \bar{F}_{\min})^{1/2} = 1.3701$ ;  $\mu = 0.5035$ .





**Figure 5** Joint confidence (95%) region of  $r_1$  and  $r_2$  values by RREVM for BCPA-GMA copolymer system.

tion. They were characterized by FTIR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectroscopic techniques. The homopolymer and copolymers were soluble in chloroform, acetone, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene, and xylene, and insoluble in *n*-hexane and hydroxyl group-containing solvents such as methanol and ethanol. The values of polydispersity indices of poly(BCPA-*co*-GMA) and poly(GMA) suggested a tendency for chain termination by disproportionation. The glass-transition temperature of the copolymer increased with increase of GMA content. Thermogravimetric analysis indicated that the thermal stability of the copolymers increased with the increase of BCPA units in the copolymer. Copolymer compositions were determined by  $^1\text{H-NMR}$  analysis of the polymers. The reactivity ratios were determined by F-R, K-T, and Ext. K-T methods as well as by a nonlinear error-in-variables model (EVM) method using a computer program, RREVM.

The  $r_1$  values from all these methods were  $<1$  and  $r_2$  values were  $>1$ , which indicates that the composition of GMA in the copolymer was greater than that in the feed. The product  $r_1r_2 < 1$  suggests random distribution with a longer sequence of GMA units in the copolymer chain. The adhesives prepared from poly(BCPA-*co*-GMA) with diethanolamine as crosslinking agent and applied on leather had good peel strength at 50 and 90°C. These copolymers showed good adhesive character even at room temperature.

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