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### Copolymerization of 4-Benzyloxycarbonylphenyl Acrylate with Methyl Methacrylate: Synthesis, Characterization, and Determination of Reactivity Ratios

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## Copolymerization of 4-Benzyloxycarbonylphenyl Acrylate with Methyl Methacrylate: Synthesis, Characterization, and Determination of Reactivity Ratios

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### ABSTRACT

The new acrylic monomer 4-benzyloxycarbonyl phenyl acrylate (BCPA) was synthesized and copolymerized with methyl methacrylate (MMA) in ethyl methyl ketone at  $70 \pm 1^\circ\text{C}$  using benzoyl peroxide as a free radical initiator. The copolymers were characterized by FT-IR,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectroscopic techniques. The compositions of the copolymers were determined by  $^1\text{H-NMR}$  analysis. The reactivity ratios of the monomers were determined using the Fineman–Ross ( $r_1 = 0.6085$  and  $r_2 = 1.7251$ ), Kelen–Tüdös ( $r_1 = 0.6085$  and  $r_2 = 1.7276$ ), Ext. Kelen–Tüdös ( $r_1 = 0.6083$  and  $r_2 = 1.7963$ ) and nonlinear error-in-variables model methods ( $r_1 = 0.6627$  and  $r_2 = 1.7858$ ). The solubilities of the polymers were tested in various polar and non-polar solvents. The elemental analysis was determined by a Perkin–Elmer C–H analyzer. The molecular weights ( $\bar{M}_w$  and  $\bar{M}_n$ ) of the copolymers were determined by gel permeation chromatography. Thermogravimetric analysis of the polymers reveals that the thermal stability of the copolymers decreases with an increase in the mole fraction of MMA in the copolymers. Glass transition temperature of the copolymers was found to increase with an increase in the mole fraction of BCPA in the copolymers.

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**Key Words:** 4-Benzyloxycarbonylphenyl acrylate; Copolymerization; Reactivity ratios; Methyl methacrylate;  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra; Thermal studies.

## INTRODUCTION

Functional polymers are now being synthesized, tested and used not only for their macromolecular properties but also for the properties of the functional groups.<sup>[1]</sup> Acrylic polymers have acquired prime importance in various avenues of applications in leather, textile and building materials. In particular, phenyl acrylate polymers by the incorporation of an active group in the phenyl ring enhance not only the thermal stability of the polymers but also have several potential industrial applications. Copolymers of acrylic monomers with methyl methacrylate have been used as primers for automotive finishes, clean lacquers for polishing metals and enamels for household appliances,<sup>[2]</sup> formulations of base and top coats for leather,<sup>[3,4]</sup> binders in protective coatings because of their durability and transparency,<sup>[5]</sup> drug binding materials,<sup>[6]</sup> optical telecommunication materials and photo resist materials.<sup>[7,8]</sup> The determination of copolymer composition and reactivity ratios of the monomers is important in evaluating the specific applications of the copolymer.<sup>[9]</sup>

$^1\text{H}$ -NMR spectroscopic analysis has been established as a powerful tool for the estimation of copolymer composition.<sup>[10–13]</sup> The accurate estimation of copolymer composition and determination of monomer reactivity ratio is significant for producing tailor-made copolymers. The present article reports the synthesis, characterization and thermal properties of copolymers of 4-benzyloxycarbonylphenyl acrylate with methyl methacrylate. The reactivity ratios of the co-monomers are also reported.

## EXPERIMENTAL

### Materials

Benzyl-4-hydroxy benzoate (FLUKA) was used as such without purification. Methyl methacrylate (E MERK) was purified by distillation under reduced pressure. Benzoyl peroxide (BPO) was recrystallized from chloroform methanol (1:1) mixture. All the solvents were purified by distillation prior to their use.

### Synthesis of 4-Benzyloxycarbonylphenyl Acrylate (BCPA)

Acryloyl chloride was prepared from acrylic acid and benzoyl chloride using the procedure of Stampel *et al.*<sup>[14]</sup> 4-Benzyloxycarbonylphenyl acrylate (BCPA) was synthesized by dissolving benzyl-4-hydroxy benzoate (15 g, 0.06 mol) in ethyl methyl ketone (300 mL) and triethylamine (10.0 mL, 0.07 mol) in a three-necked flask fitted with a mechanical stirrer and a dropping funnel. Acryloyl chloride (5.8 mL, 0.07 mol) dissolved in ethyl methyl ketone (25 mL) and placed in a 100 mL dropping funnel was added dropwise into the flask in such a way that the temperature was maintained around 0–5°C.

### Copolymerization of 4-Benzyloxycarbonylphenyl Acrylate

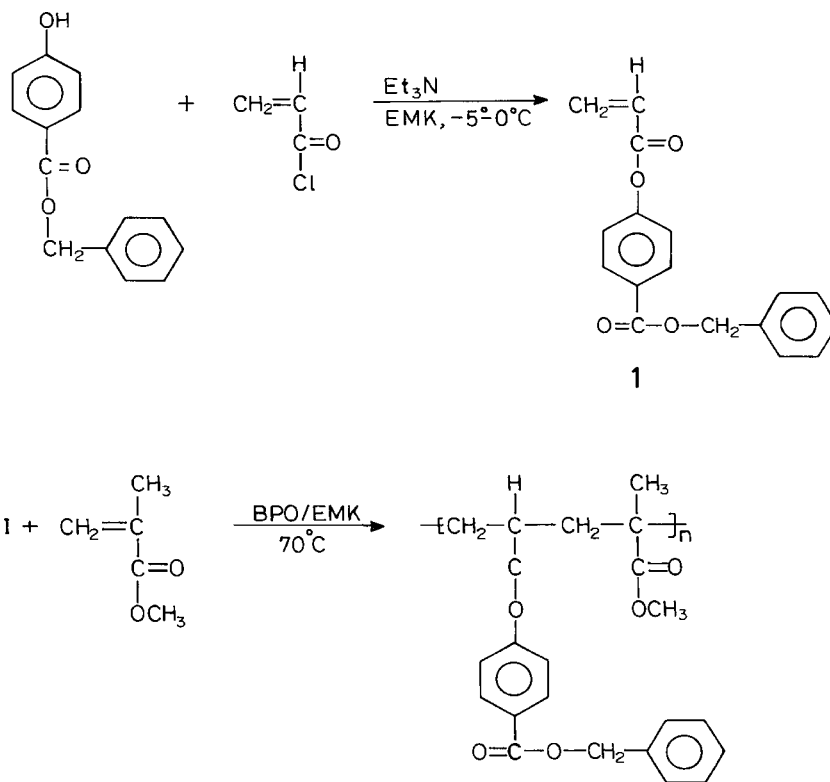
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The reaction was allowed to proceed for 1 h at 0°C with constant stirring. Then the ice bath was removed and the reaction mixture was stirred at room temperature for a further period of 1 h. The precipitated triethylammonium chloride was filtered off and the solvent in the filtrate was removed using a rotary evaporator. The residue obtained was dissolved in ether and washed with 0.1% NaOH and distilled water. The ether solution was evaporated and the residue obtained was recrystallized from ethanol to get white flakes of pure 4-benzyloxycarbonylphenyl acrylate (M.P.60°C). The yield was 65%. Sch. 1 shows the reaction for the synthesis of BCPA.

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

### Copolymerization

Copolymers of BCPA and methyl methacrylate having different compositions were synthesized in ethyl methyl ketone solution using BPO as a free radical initiator. Predetermined quantities of BCPA, MMA, BPO (0.25% w/v) and ethyl methyl ketone were mixed in a polymerization tube, and the reaction was carried out under N<sub>2</sub>



Scheme 1. Synthesis of poly(BCPA-co-MMA).



Elemental analysis:	Carbon 72.34 (found), 72.41 (Calcd.) Hydrogen 4.96 (found), 4.98 (Calcd.)
IR (KBr, $\text{cm}^{-1}$ ):	3066 and 3033 ( $=\text{C}-\text{H}$ ), 2984 and 2951 ( $\text{C}-\text{H}$ ), 1719 and 1686 ( $>\text{C}=\text{O}$ ), 1634 (olefinic $\text{C}=\text{C}$ ), 1604, 1586, 1503, 1445 and 1406 (aromatic $\text{C}=\text{C}$ ), 1173 and 1207 ( $\text{C}-\text{O}$ ), 755 and 700 ( $\text{C}-\text{H}$ out of plane bending), 503 ( $\text{C}=\text{C}$ out of plane bending)
$^1\text{H}$ -NMR ( $\text{CDCl}_3$ , ppm):	8.26 (d, 2H), 7.56–7.27 (m, 5H) and 7.23 (d, 2H) (aromatic); 6.89–6.83 (q, 1H) and 6.70–6.61 (q, 1H) ( $\text{CH}_2=$ ); 6.39–6.28 (q, 1H) ( $=\text{CH}-$ ); 5.4 (s, 2H) ( $\text{OCH}_2$ )
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , ppm):	166.20 ( $\text{COOCH}_2$ ), 164.42 ( $=\text{CH}-\text{COO}$ ), 154.75, 136.26, 133.76, 131.75, 129.04, 128.98, 127.92 and 122.03 (aromatic), 132.43 ( $=\text{CH}-$ ), 115.67 ( $\text{CH}_2=$ ), 67.32 ( $\text{OCH}_2$ )

atmosphere at  $70 \pm 1^\circ\text{C}$ . After a desired time ( $< 10\%$  conversion), the copolymer was precipitated by pouring the contents into excess methanol. The precipitated polymer was filtered, washed with methanol, and purified by repeated precipitation from the solution of polymer in EMK by methanol. The polymer was finally dried in vacuum at  $45^\circ\text{C}$ .

### Spectral Measurements

Elemental analysis was carried out with a Perkin–Elmer C–H analyzer. IR spectra were recorded with a Nicolet 360, FT-IR, ESP spectrophotometer as KBr pellets.  $^1\text{H}$ -NMR spectra of the monomer and all the polymer samples were run on a Bruker 270 MHz FT-NMR spectrometer at room temperature using  $\text{CDCl}_3$  as the solvent and TMS as an internal standard. The proton decoupled  $^{13}\text{C}$ -NMR spectra were run on the same instrument operating at 22.63 MHz and the chemical shifts were recorded under similar conditions. The molecular weights were determined using Waters 501 gel permeation chromatograph. Tetrahydrofuran was used as an eluent and polystyrene standards were employed for calibration. Thermogravimetric analysis was performed with Mettler TA 3000 thermal analyzer in air atmosphere at a heating rate of  $15^\circ\text{C}/\text{min}$ . The glass transition temperature was determined with a Perkin–Elmer d7 differential scanning calorimeter at a heating rate of  $10^\circ\text{C}/\text{min}$  in  $\text{N}_2$  atmosphere.

## RESULTS AND DISCUSSION

Copolymers of BCPA and MMA having different compositions were prepared in ethyl methyl ketone solvent by free radical solution polymerization. The reaction time was selected from 20 to 50 min to give low conversion ( $< 10\%$ ) in order to obey to copolymer equation and to obtain polymer samples having homogeneous composition as far as possible. The monomer units in the copolymer are shown in Sch. 1. The copolymer composition data of the monomers in the feed and copolymers are presented in Table 1.

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### Characterization

#### Solubility

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

#### FT-IR Spectrum

The FT-IR spectrum of the copolymer, poly(BCPA-*co*-MMA) (0.3799: 0.6201) is shown in Fig. 1. It shows peaks at 3059 and 3022  $\text{cm}^{-1}$  corresponding to the aromatic C—H stretching. The asymmetrical and symmetrical stretching due to the methyl and methylene groups is observed at 2993, 2951 and 2892  $\text{cm}^{-1}$ . The shoulder at 1760 and peak at 1724  $\text{cm}^{-1}$  are attributed to the ester carbonyl stretching of BCPA and MMA units. The aromatic C=C stretching is observed at 1603, 1502 and 1413  $\text{cm}^{-1}$ . The asymmetrical and symmetrical bending vibrations of methyl group are seen at 1452 and 1381  $\text{cm}^{-1}$  respectively. The C—O stretching due to the ester groups in BCPA and MMA units give rise to signals at 1160, 1274 and 1381  $\text{cm}^{-1}$ . The C—H out of plane bending vibrations of the aromatic nuclei are observed at 758 and 696  $\text{cm}^{-1}$ . The C=C out of plane bending vibration of aromatic nuclei is seen at 502  $\text{cm}^{-1}$ .

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

$^1\text{H-NMR}$  spectrum of the copolymer, poly(BCPA-*co*-MMA) (0.3799: 0.6201) is shown in Fig. 2. The chemical shift assignments for the copolymers were based on

**Table 1.** Composition data for free radical copolymerization of BCPA (1) with MMA (2) in EMK solution at 70°C.

Copolymer	Feed		Intensities of protons			Copolymer composition ( $m_1$ ) <sup>a</sup>
	composition ( $M_1$ ) <sup>a</sup>	Conversion (%)	$I_{\text{Ar}}$	$I_{\text{AlI}}$	C	
1	0.1506	9.85	9.174	87.623	0.1047	0.0899
2	0.3445	8.63	25.507	85.968	0.2967	0.2399
3	0.5009	8.90	31.089	62.365	0.4985	0.3799
4	0.6311	7.86	40.489	57.091	0.7092	0.5098
5	0.8092	8.23	41.584	37.838	1.0990	0.7149
6	0.9013	9.40	45.055	32.526	1.8852	0.8423

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

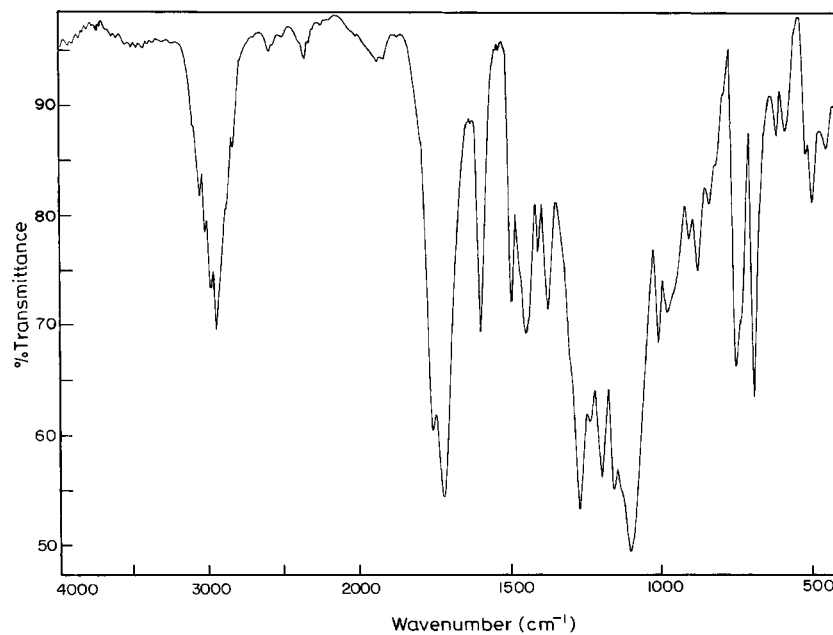


Figure 1. IR Spectrum of poly(BCPA-co-MMA) (0.3799:0.6201).

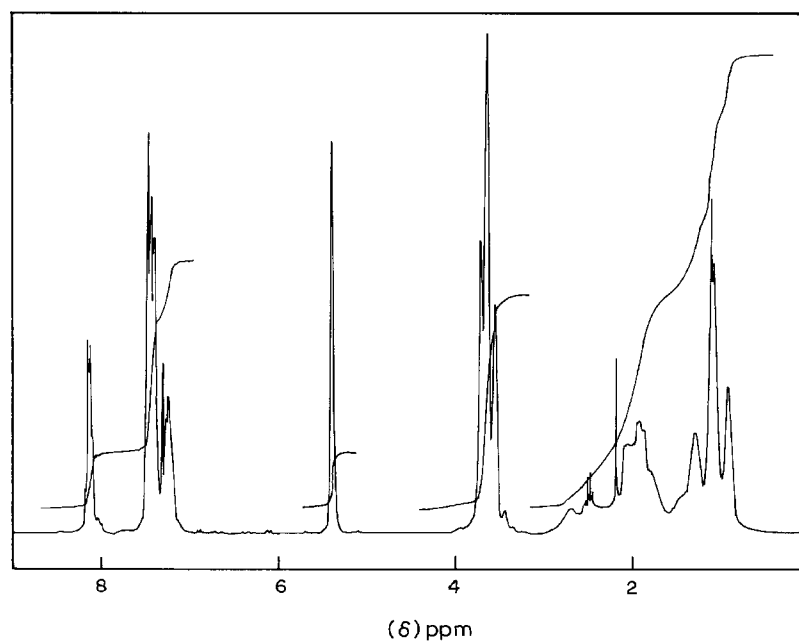


Figure 2. <sup>1</sup>H-NMR Spectrum of poly(BCPA-co-MMA) (0.3799:0.6201).

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the chemical shifts observed for the respective homopolymers. The aromatic protons show resonance signals at 8.23 to 6.96 ppm. The peak at 5.36 ppm is due to the methylenoxy protons in BCPA units. The resonance signals at 3.86–3.58 ppm are due to the methoxy protons of MMA unit. The methyne protons of the backbone show signal between 2.88 and 2.35 ppm. Due to the existence of tacticity, the resonance signals corresponding to the methylene group of the backbone are observed between 2.26–1.62 ppm. The  $\alpha$ -methyl protons of the MMA unit show signal at 1.62–0.73 ppm.

 **$^{13}\text{C}$ -NMR Spectrum**

The proton decoupled  $^{13}\text{C}$ -NMR spectrum of poly(BCPA-*co*-MMA) (0.3799: 0.6201) is shown in Fig. 3. The resonance signal at 168.88 ppm ( $\text{C}_3$  and  $\text{C}_{17}$ ) and 165.96 ppm ( $\text{C}_8$ ) are due to the carbonyl carbon attached to the polymer backbone and the aromatic ring, respectively. The resonance signals at 154.65 ppm ( $\text{C}_4$ ) and 136.30 ppm ( $\text{C}_{10}$ ) are due to the aromatic carbons attached to the oxygen atom and methylene group respectively. The other aromatic carbon signals are observed at 131.70 ppm ( $\text{C}_{13}$ ), 129.01 ppm ( $\text{C}_{11}$  and  $\text{C}_{12}$ ), 128.70 ppm ( $\text{C}_6$  and  $\text{C}_7$ ) and 121.90 ppm ( $\text{C}_5$ ). The signal at 67.22 ppm is due to the methylenoxy group of the BCPA unit. The methoxy carbon signal of MMA unit is observed at 62.62 ppm. The signal due to the backbone tertiary carbon, methyne and methylene carbon atoms are observed at 44.96 ppm ( $\text{C}_{15}$ ), 55.29 ppm ( $\text{C}_2$ ), 54.85 and

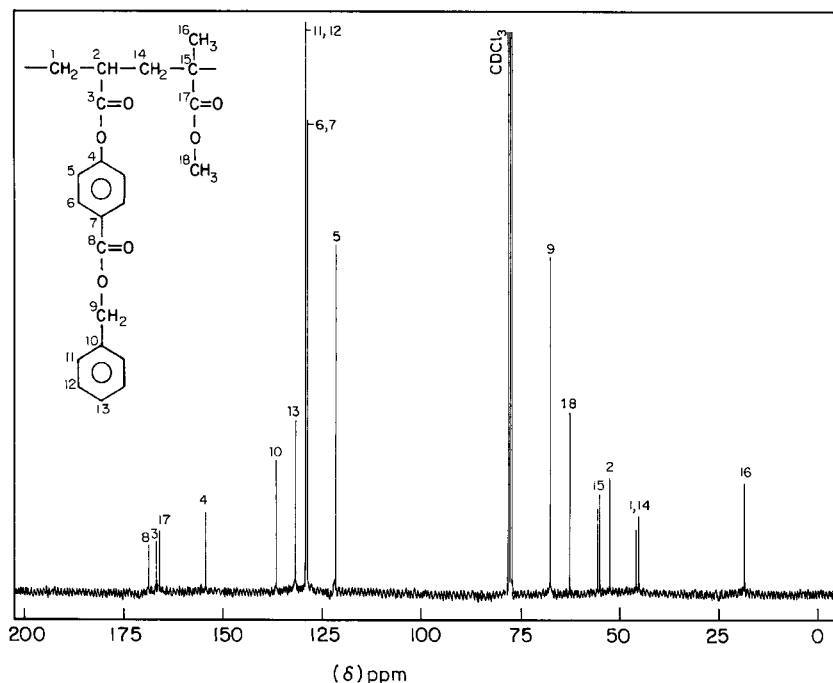


Figure 3.  $^{13}\text{C}$ -NMR Spectrum of poly(BCPA-*co*-MMA) (0.3799: 0.6201).



**Table 2.** Molecular weight data for homo and copolymers of BCPA and MMA.

Polymer	$m_1^a$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
Poly(BCPA)	0.0000	3.21	1.90	1.69
Poly(BCPA-co-MMA)	0.0899	3.83	2.06	1.86
	0.2399	3.78	2.09	1.81
	0.3799	3.63	2.04	1.78
	0.5098	3.59	2.09	1.72
	0.7149	3.61	2.07	1.74
	0.8423	3.31	1.97	1.68
Poly(MMA)	0.0000	2.43	1.32	1.84

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

52.40 ppm ( $C_1$  and  $C_{14}$ ) respectively. The  $\alpha$ -methyl group of the MMA unit shows resonance signal at 18.36 ppm ( $C_{16}$ ).

### Molecular Weights

The number and weight average molecular weights ( $\bar{M}_w$  and  $\bar{M}_n$ ) and polydispersity index of homopolymers, as well as copolymers determined by gel permeation chromatography are given in Table 2. The polydispersity indices of poly(BCPA) and poly(MMA) are 1.69 and 1.84, respectively. The theoretical value of ( $\bar{M}_w/\bar{M}_n$ ) for polymers produced through radical combination and disproportionation were 1.5 and 2.0, respectively.<sup>[15]</sup> In the homopolymerization of MMA, the chain termination by disproportionation predominates coupling.<sup>[16]</sup> The value of  $\bar{M}_w$  and  $\bar{M}_n$  for poly(BCPA) suggests that the chain termination by dimerisation predominates disproportionation. The polydispersity indices of the copolymers suggest that the chain termination by disproportionation was predominant when the mole fraction of MMA in the feed was very high and radical combination was predominant when the mole fraction of BCPA was high in the feed.

### Thermal Analysis

#### Glass Transition Temperature

The glass transition temperature ( $T_g$ ) of the copolymers were determined by differential scanning calorimetry and the  $T_g$  data are presented in Table 3. The  $T_g$  value of poly(BCPA) is 16.25°C, and that of poly(MMA) is 105°C. All the prepared copolymers show a single  $T_g$ , showing the absence of formation of a mixture of homopolymers or the formation of a block copolymer.  $T_g$  value of the copolymers is found to depend on the composition of comonomers and the value increases with increase in MMA content in the copolymer.

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**Table 3.** TGA and DSC data for BCPA–MMA copolymer system.

Polymers	$m_1$	IDT <sup>a</sup> (°C)	Temperature (°C) at wt loss(%)					$T_g^b$ (°C)
			10%	30%	50%	70%	90%	
Poly(MMA)	0.0000	244	270	284	300	334	380	105.00
Poly(BCPA- <i>co</i> -MMA)	0.0899	248	285	301	315	348	391	47.95
	0.2399	251	299	317	329	363	401	29.40
	0.3799	258	328	346	358	490	401	23.55
	0.5098	262	311	350	361	393	429	20.70
	0.7149	266	333	354	364	396	439	18.15
	0.8423	274	337	356	370	402	455	17.15
Poly(BCPA)	1.0000	290	345	360	382	413	459	16.25

<sup>a</sup> IDT—Initial decomposition temperature.<sup>b</sup>  $T_g$ —Glass transition temperature.**Thermogravimetric Analysis**

The TGA data for the homopolymers and copolymers of BCPA and MMA are given in Table 3. TGA traces of poly(BCPA), poly(MMA) and poly(BCPA-*co*-MMA) (0.3799:0.6201) are shown in Fig. 4. The thermograms clearly indicate that all the polymers undergo single stage decomposition. The initial decomposition temperature of poly(MMA), poly(BCPA-*co*-MMA) and poly(BCPA) are 244°, 254° and 290°C, respectively. TGA results indicate that the thermal stability of the copolymer increases with increase in BCPA content in the copolymer.

**Copolymer Compositions**

The copolymer composition was determined by <sup>1</sup>H-NMR spectral analysis of the copolymer. The assignment of the resonance peaks in the <sup>1</sup>H-NMR spectrum allows the accurate evaluation of the content of each kind of monomer incorporated into the copolymer chain.

Hence, in the present investigation, the copolymer compositions were determined by measuring the ratios of integrated peak intensities of aromatic protons to that of total aliphatic protons in the copolymer. The following formula was derived, to determine the composition of the copolymers. If  $m_1$  is the mole fraction of BCPA and  $(1 - m_1)$  be that of MMA, then:

$$C = \frac{\text{Intensities of aromatic protons } (I_{Ar})}{\text{Intensities of total aliphatic protons } (I_{Ali})}$$

$$C = \frac{9 m_1}{5 m_1 + 8 (1 - m_1)} \quad (1)$$

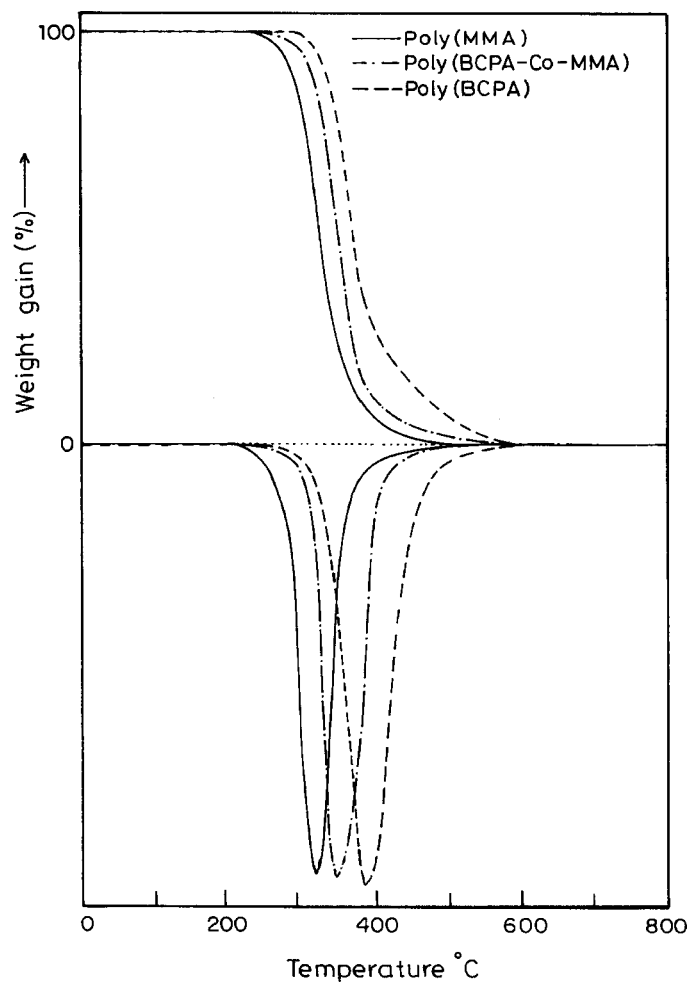


Figure 4. TGA curves for poly(MMA), poly(BCPA-co-MMA) and poly(BCPA).

which, on further simplification gives;

$$m_1 = \frac{8C}{9 + 3C} \quad (2)$$

Based on Eq. (2), the mole fraction of BCPA in all the copolymers was calculated by measuring the signal intensities of aromatic protons and aliphatic protons from the spectra of all the copolymers. Table 1 gives the values of  $C$  and the corresponding mole fraction in the copolymers. The kinetic behavior was determined by plotting the mole fraction of BCPA in the feed against that in the copolymer (Fig. 5).

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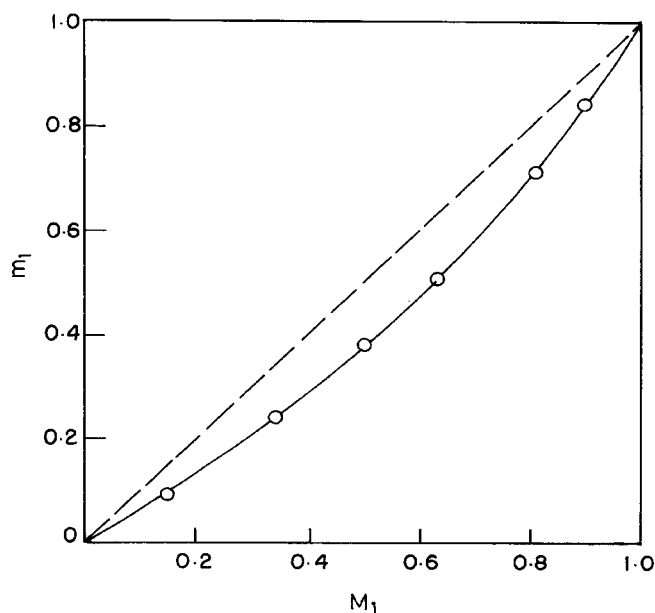


Figure 5. Copolymer composition diagram of poly(BCPA-co-MMA) system.

## Reactivity Ratios

The type of copolymer formed will be understood from the values of reactivity ratio of the comonomers. By the application of Fineman–Ross,<sup>[17]</sup> Kelen–Tüdös,<sup>[18]</sup> extended Kelen–Tüdös<sup>[19]</sup> and non-linear error-in-variables model<sup>[20]</sup> methods, the reactivity ratios of BCPA and MMA were evaluated from the monomer feed ratios and the resultant copolymer compositions. The significant parameters of F–R, K–T and ext. K–T equation are presented in Tables 4 and 5. The reactivity ratios for BCPA ( $r_1$ ) and MMA ( $r_2$ ) from the F–R plot (Fig. 6), K–T plot and ext. K–T plot (Fig. 7) are given in Table 6.

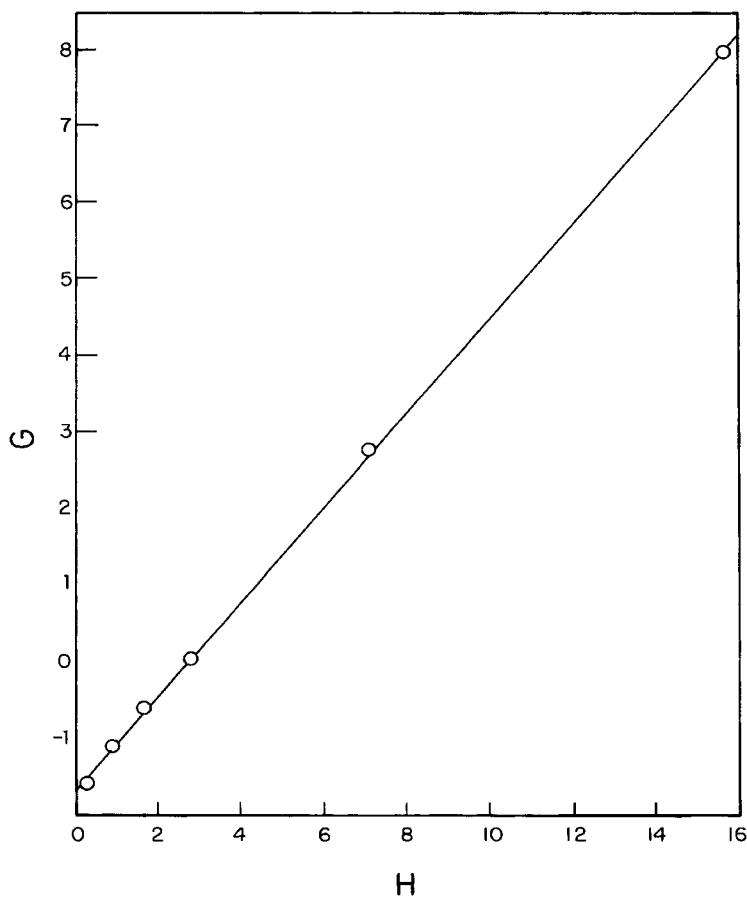
Table 4. F–R and K–T parameters for the copolymerization of BCPA with MMA.

Copolymer	$F = M_1/M_2$	$f = m_1/m_2$	$H = F_2/f$	$G = F(f - 1)/f$	$\eta = G/(\alpha + H)^\alpha$	$\xi = H/(a + H)^a$
1	0.1773	0.0987	0.3184	-1.6190	-0.6354	0.1249
2	0.5255	0.3156	0.8750	-1.1395	-0.3670	0.2818
3	1.0036	0.6126	1.6441	-0.6346	-0.1638	0.4244
4	1.7107	1.0399	2.8142	0.0656	0.0130	0.5579
5	4.2410	2.5075	7.1729	2.5496	0.2711	0.7628
6	9.1317	5.3411	15.6125	7.4219	0.4159	0.8750

<sup>a</sup>  $\alpha = (H_{\max} \times H_{\min})^{1/2} = 2.2296$ .

**Table 5.** Extended K–T parameters for BCPA–MMA copolymer system.

Parameters	Copolymer system					
	1	2	3	4	5	6
$\xi_2$	0.1148	0.1125	0.1242	0.0555	0.1318	0.1563
$\xi_1$	0.0639	0.0676	0.0758	0.0337	0.0779	0.0914
Z	0.5415	0.5865	0.5944	0.6006	0.5738	0.5640
F	0.1823	0.5381	1.0306	1.7314	4.3699	9.4700
H	0.3366	0.9175	1.7339	2.8828	7.6159	16.1916
G	-1.6645	-1.1669	-0.6517	0.0664	2.6272	7.6970
$\eta$	-1.0080	-0.5229	-0.2138	0.0158	0.2942	0.4397
$\xi$	0.2039	0.4111	0.5689	0.6869	0.8529	0.9249

**Figure 6.** F–R plot for poly(BCPA-co-MMA) system.

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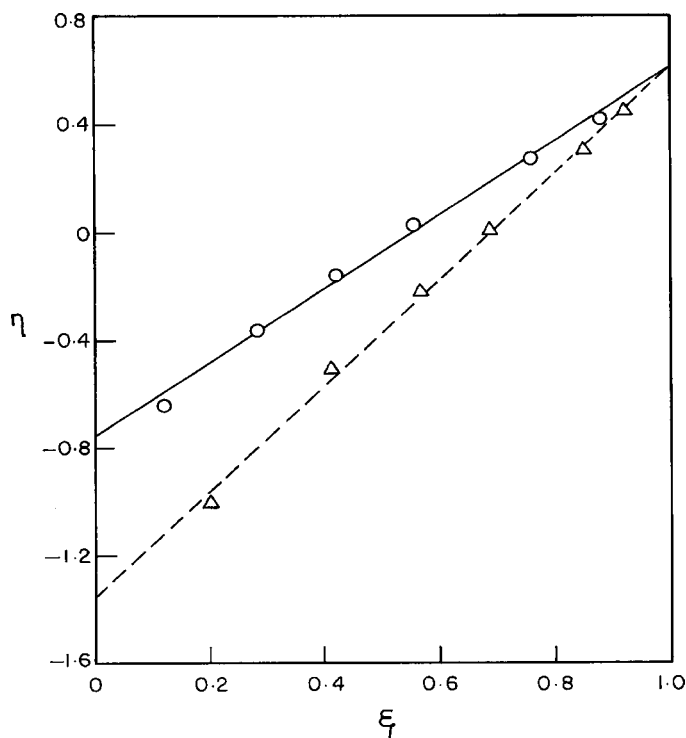


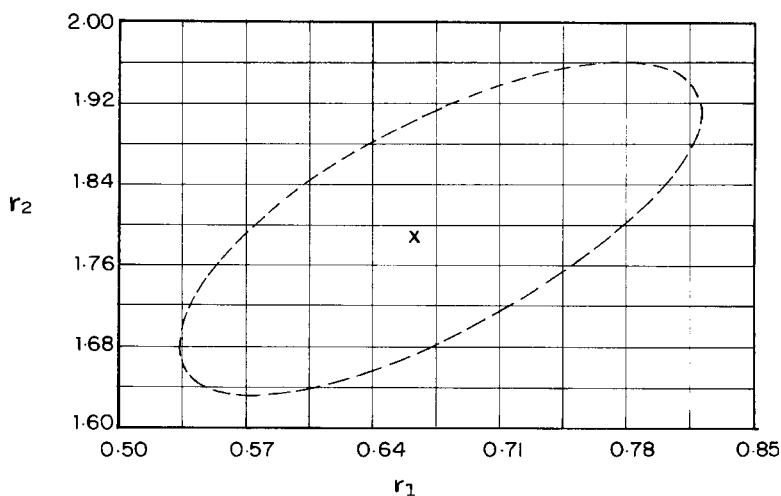
Figure 7. K-T (O) and Ext. K-T ( $\Delta$ ) plot for poly(BCPA-co-MMA) system.

The monomer reactivity ratios determined by conventional linearization methods are not accurate and several non-linear methods have been attempted to determine their value.<sup>[21]</sup> The reactivity ratios determined by the error-in-variables model method using the RREVM Computer Program are  $r_1 = 0.6627$ ;  $r_2 = 1.7858$ . The 95% joint confidence region for the determined  $r_1$  and  $r_2$  values using RREVM is shown in Fig. 8. The value of  $r_1$  is less than 1 and that of  $r_2$  is greater than 1, which indicates the presence of higher amount of MMA units in the copolymer than that in the feed. However, the product of  $r_1$  and  $r_2$  is greater than 1, which indicates the system leads to

Table 6. Copolymerization parameter, for the free radical copolymerization of BCPA with MMA.

Methods	$r_1^a$	$r_2^a$	$r_1 r_2$
Fineman-Ross	0.6085	1.7251	1.0498
Kelen-Tüdös	0.6085	1.7256	1.0500
Ext. Kelen-Tüdös	0.6083	1.7963	1.0927
RREVM	0.6627	1.7858	1.1834

<sup>a</sup>  $r_1$  and  $r_2$  are the reactivity ratios for BCPA and MMA, respectively.



**Figure 8.** 95% Joint confidence region of  $r_1$  and  $r_2$  values by RREVM for BCPA-MMA copolymer system.

random distribution of the monomeric units with longer sequence of MMA units in the copolymer chain.

### CONCLUSION

The new acrylic monomer, BCPA was synthesized. Copolymers of BCPA and MMA having different composition were synthesized in solution by free radical polymerization. The structure of the monomer and the copolymers was confirmed by the FT-IR,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectroscopic techniques. The copolymers were soluble in chloroform, acetone, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene, xylene and insoluble in n-hexane and hydroxyl group containing solvents such as methanol and ethanol. Thermogravimetric analysis indicated that the thermal stability of the copolymers increases with increase in BCPA units in the copolymer. The  $T_g$  of the copolymers is found to increase with increase in MMA units in the copolymer. The polydispersity index values of poly(BCPA), poly(BCPA-co-MMA) and poly(MMA) obtained from GPC suggests a strong tendency for chain termination by disproportionation at very high mole fraction of MMA and recombination at high mole fraction of BCPA in the feed. The copolymer composition was calculated by  $^1\text{H-NMR}$  spectroscopic technique. The reactivity ratios of the comonomers were determined by F-R, K-T and Ext. K-T methods as well as by a non-linear error-in-variables model method. The value of  $r_1$  is less than 1 and that of  $r_2$  is greater than 1 indicating that MMA is more reactive than BCPA. The value of the product  $r_1r_2$  is greater than 1, which indicates the random distribution of the monomeric units with longer sequence of MMA units in the copolymer chain.



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