Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Copolymers of 4-Benzyloxycarbonylphenyl Methacrylate with Methyl Methacrylate: Synthesis, Characterization, and Reactivity Ratios

C. S. Jone Selvamalar[a]; A. Penlidis[b]; S. Nanjundan[a]
[a] Department of Chemistry, College of Engineering, Anna University, Chennai, India [b] Department of Chemical Engineering, University of Waterloo, Ontario, Canada

To cite this Article Selvamalar, C. S. Jone , Penlidis, A. and Nanjundan, S.(2003) 'Copolymers of 4-Benzyloxycarbonylphenyl Methacrylate with Methyl Methacrylate: Synthesis, Characterization, and Reactivity Ratios', Journal of Macromolecular Science, Part A, 40: 10, 1019 — 1033

To link to this Article: DOI: 10.1081/MA-120024461

URL: http://dx.doi.org/10.1081/MA-120024461

JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. A40, No. 10, pp. 1019–1033, 2003

Copolymers of 4-Benzyloxycarbonylphenyl Methacrylate with Methyl Methacrylate: Synthesis, Characterization, and Reactivity Ratios

C. S. Jone Selvamalar,[1] A. Penlidis,[2] and S. Nanjundan[1],*

[1]Department of Chemistry, College of Engineering, Anna University, Chennai, India
[2]Department of Chemical Engineering, University of Waterloo, Ontario, Canada

ABSTRACT

Copolymers of 4-benzyloxycarbonylphenyl methacrylate (BCPM) with methyl methacrylate (MMA) were synthesized from different feed ratios of the monomers in methyl ethyl ketone (MEK) using benzoyl peroxide (BPO) as a free radical initiator at 70°C ± 1°C. The copolymers were characterized by FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopic techniques. The molecular weights ($\bar{M}_w$ and $\bar{M}_n$) and polydispersity indices of the polymers were determined using a gel permeation chromatograph. The glass transition temperatures (T_g) of the copolymers determined by differential scanning calorimetry revealed that T_g increases with an increase in MMA content in the copolymer. Thermogravimetric analysis of the polymers performed in air showed that the stability of the copolymers increased with an increase in BCPM content. The solubility of the polymers was tested in various polar and non-polar solvents. The monomer reactivity ratios were determined by the application of conventional linearization methods such as Fineman–Ross ($r_1 = 1.4671$; $r_2 = 0.4367$), Kelen–Tüdös ($r_1 = 1.5338$; $r_2 = 0.5333$), extended Kelen–Tüdös ($r_1 = 1.5543$; $r_2 = 0.5160$), as well as by a nonlinear error-in-variables-model (EVM) method using a computer program, RREVM ($r_1 = 1.3944$; $r_2 = 0.4943$).

---

*Correspondence: Dr. S. Nanjundan, Department of Chemistry, College of Engineering, Anna University, Chennai 600 025, India; Fax: +91-044-22200660; E-mail: snanjundan@yahoo.com.

DOI: 10.1081/MA-120024461
1060-1325 (Print); 1520-5738 (Online)
www.dekker.com

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Key Words: 4-Benzyloxycarbonylphenyl methacrylate; Methyl methacrylate; Reactivity ratios; Copolymers; Spectral studies.

INTRODUCTION

Methacrylic copolymers have achieved prime importance in various avenues of industrial application.[1–4] Polymers of substituted benzyl methacrylate are known to exhibit photohardenable properties,[5] that are used in the preparation of organic electrophotographic photoconductor compositions having high sensitivity, a low dark decay rate, low toxicity, and excellent durability.[6,7] They are used as optical data storage materials,[8] UV curable adhesive film,[9] and as an ingredient in erodable ship bottom paints for the control of marine fouling.[10,11] Copolymerization of functional methacrylates with certain monomers provide a simple route for synthesizing biologically active materials.[12,13] Substituted phenyl methacrylate and methyl methacrylate copolymers are used in the production of printing plates and electrical circuits,[14,15] for making glossy polymer film used in optoelectronic material,[16] weather resistant high gloss top coats for automobile finishes, and formulation of base and top coats in leather industries.[17,18]

In the past few decades, ^{1}H-NMR spectroscopic analysis has been established as a powerful tool for the determination of copolymer composition.[19–24] 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 controlled a composition distribution as possible. Knowledge about the monomer reactivity ratios of the comonomers would help in achieving this. Monomer reactivity ratios have traditionally been determined by a number of linearization methods.[25–27] As 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.[28–32] Notable among them is the non-linear error-in-variables-model (EVM) method using a recent computer program (RREVM),[31] which gives accurate results. The present paper reports the synthesis, characterization, and thermal properties of copolymers of 4-benzyloxycarbonylphenyl methacrylate (BCPM) and methyl methacrylate (MMA) and determination of monomer reactivity ratios.

EXPERIMENTAL

Materials

Benzyl-4-hydroxybenzoate (FLUKA) was used without purification. Methyl methacrylate (MERCK) was purified by distillation under reduced pressure. Benzoyl peroxide (BPO) was recrystallized from a chloroform–methanol (1 : 1) mixture. All the solvents were purified by distillation prior to their use.

Synthesis of 4-Benzyloxycarbonylphenyl Methacrylate

Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride using the procedure of Stampel.[33] For the synthesis of BCPM, benzyl-4-hydroxybenzoate (15 g, 0.06 mol) and triethylamine (10.1 mL, 0.07 mol) were dissolved in 250 mL of methyl ethyl ketone (MEK) and placed in a two-necked round bottom flask fitted with a mechanical stirrer and a dropping funnel. The reaction mixture was stirred in an ice bath at 0 to −5°C and methacryloyl chloride (7.0 mL, 0.07 mol) dissolved in 25 mL of MEK was added dropwise through the dropping funnel over a period of 30 min. After the addition, the reaction mixture was stirred for 1 h. Then, the ice bath was removed and the reaction mixture was stirred vigorously 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 twice with 0.1% solution of NaOH and distilled water. The ether solution was dried using anhydrous Na_2SO_4 and ether was removed using the rotary evaporator. The residue obtained was distilled and a liquid boiling at 79°C of 10 mmHg was collected. The yield of BCPM was 71%.

The structure of the monomer was confirmed by elemental analysis, FT-IR, ^{1}H-NMR, and ^{13}C-NMR analysis.

Elemental analysis (%): Carbon; 72.82 (found), 72.96 (calculated); Hydrogen 5.38 (found), 5.44 (calculated).

IR (KBr cm^{1}): 3066 and 3033 (=C—H); 2955 and 2891 (C—H stretching); 1740 and 1719 (C=O); 1637 (CH_2=C<); 1604, 1504 and 1414 (aromatic C=C); 1456 and 1375 (CH_3 bending); 1260 (C—O); 889, 762, and 896 (C—H out of plane bending).

^{1}H-NMR ($CDCl_3$, ppm): 7.03–8.18 (9H) (Ar-H); 6.34 and 5.75 (2H) (CH_2=C); 5.34 (2H) (−OCH_2); 2.03 (3H) (α- methyl).

^{13}C-NMR ($CDCl_3$, ppm): 165.73 and 165.71 (>C=0, ester); 154.41, 136.29, 131.64, 131.63, 129.11, 128.69, and 128.52 (aromatic carbons); 128.31 (=C<); 134.93 (=CH_2); 67.26 (CH_2O); 18.73 (CH_3).

Copolymerization

Predetermined quantities of BCPM, MMA, MEK, and BPO were placed in a standard reaction tube (100 mL) and the mixture was purged with O_2 free N_2 for 20 min. The tube was tightly sealed and immersed in a thermostated water bath maintained at 70°C ± 1°C. In order to follow copolymer composition, conversion levels were restricted to less than 10%. After the required time of 15–35 min, the reaction mixture was poured into excess methanol, the precipitated polymer was filtered off and purified by reprecipitation from chloroform solution using methanol, and finally dried in a vacuum oven at 50°C for 24 h.

Solubility Studies

Solubility of the polymers was tested in various polar and non-polar solvents at room temperature. 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.

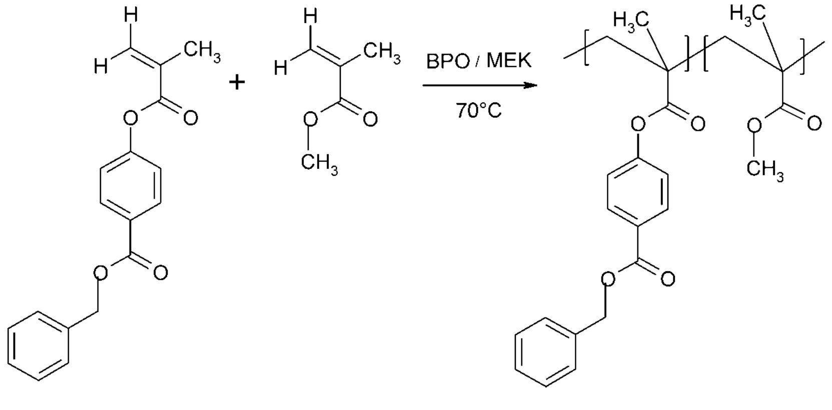
Instrumentation

Elemental analysis was carried out by a Perkin-Elmer C—H analyzer. IR spectra were recorded with a Nicolet 360 FT-IR ESP spectrophotometer as KBR pellets. ^{1}H-NMR spectra of all the monomer and polymer samples were run on a Bruker 270 MHz FT-NMR spectrometer at room temperature using $CDCl_3$ as solvent and TMS as internal standard. The proton decoupled ^{13}C-NMR spectrum was run on the same instrument operating at 22.63 MHz and the chemical shifts were recorded under similar conditions. The molecular weights ($\bar{M}_w$ and $\bar{M}_n$) were determined using a Waters 501 gel permeation chromatograph. Tetrahydrofuran was used as an eluent, and polystyrene standards were employed for calibration. Thermogravimetric analysis was performed with a Mettler TA 3000 Thermal Analyzer in air atmosphere at a heating rate of 15°C/min. The glass transition temperature was determined with NETZSCH Geratebau GmbH Thermal Analyzer at a heating rate of 10°C/min in air. The solubility of the polymers was tested in various polar and non-polar solvents.

RESULTS AND DISCUSSION

Synthesis of Copolymers

Copolymers of BCPM and MMA with different feed compositions were synthesized by free radical solution polymerization in MEK using benzoyl peroxide as initiator. Copolymerization was allowed to proceed to low conversion (less than 10%) in order to obtain polymer samples having homogenous composition as far as possible. The synthesis of copolymer of BCPM with MMA is shown in Sch. 1.



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

Solubility

The copolymers were soluble in chloroform, dimethyl formamide, dimethyl acetamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene, xylene, and insoluble in methanol and ethanol.

Characterization of Polymers

The IR spectrum of the copolymer, poly(BCPM-co-MMA) (0.6236 : 0.3764) is shown in Fig. 1. The peaks at 3074 and 3044 cm^{-1} correspond to the C—H stretching of aromatic system. The symmetrical and asymmetrical C—H stretching due to the methyl and methylene groups are observed at 2992, 2949, and 2850 cm^{-1}. The shoulder at 1749 and the peak at 1721 cm^{-1} are attributed to the ester carbonyl stretching of both BCPM and MMA units. The ring stretching vibrations of the aromatic system are observed at 1604, 1504, and 1413 cm^{-1}. The symmetrical and asymmetrical bending vibrations of the methyl groups are seen at 1379 and 1453 cm^{-1}. The C—O stretchings of the ester group of BCPM and MMA units are observed at 1201, 1161, and 1092 cm^{-1}. The C—H out-of-plane bending vibrations of the aromatic

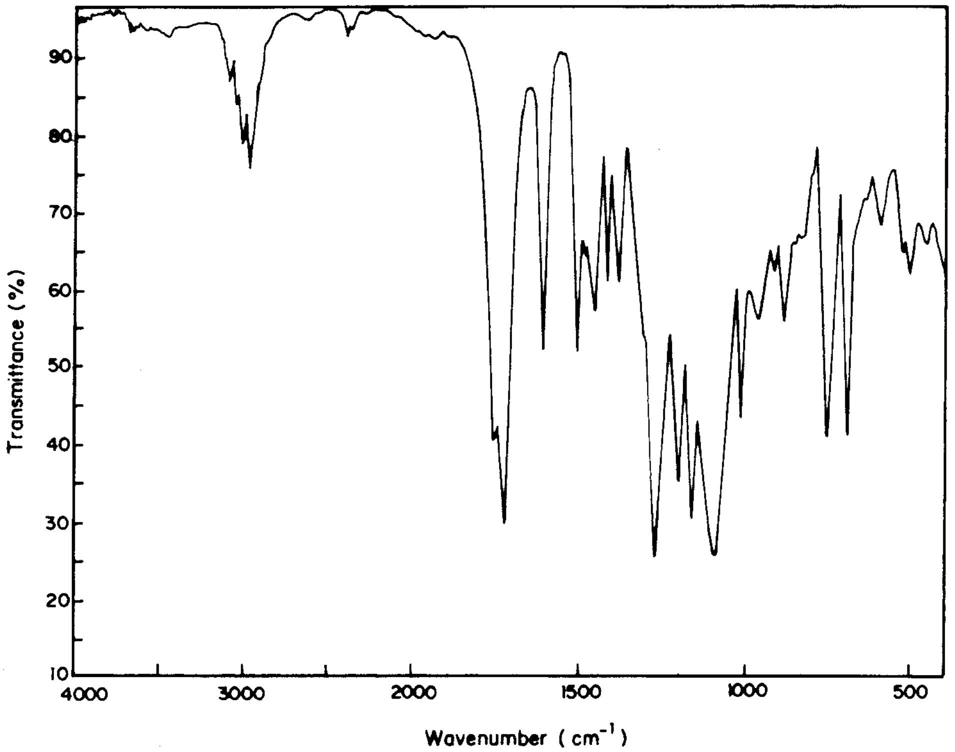


Figure 1. IR spectrum of poly(BCPM-co-MMA) (0.6236 : 0.3764).

nuclei are observed at 757 and 694 cm^{-1}. The C=C out-of-plane bending vibrations occur at 503 cm^{-1}.

The ^{1}H-NMR spectrum of the copolymer poly(BCPM-co-MMA) (0.6236 : 0.3764) is shown in Fig. 2. The aromatic protons show signals between 7.95 and 6.84 ppm. The signals at 5.24 ppm are due to the methylenoxy protons in BCPM units. The methoxy protons of the MMA unit show a signal at 3.48 ppm. Due to the existence of tacticity, the resonance signals corresponding to the backbone methylene protons are observed at 2.66–1.54 ppm. The α-methyl protons of both monomer units show signals at 1.54–0.58 ppm.

The proton decoupled ^{13}C-NMR spectrum of poly(BCPM-co-MMA) (0.6236 : 0.3764) is shown in Fig. 3. The resonance signals at 174.62 and 174.64 are due to the methacrylate ester cabonyl carbons of BCPM and MMA units and the signal at 165.16 ppm is due to the benzoate ester carbonyl carbon of BCPM unit. The aromatic carbon attached to the oxygen atom shows a resonance signal at 149.64 ppm. The other aromatic carbon signals are observed at 135.87, 131.29, 128.58, 128.26, 128.11, and 121.04 ppm. The methyleneoxy carbon of BCPM unit shows a signal at 66.79. The methoxy carbon signal of MMA unit is observed at 54.67 ppm. The signals due to the backbone methylene and tertiary carbon atoms are observed at 52.45, 52.17, 45.76, and 45.45 ppm, respectively. The α-methyl group of both monomer units shows a signal at 18.56 and 18.72 ppm.

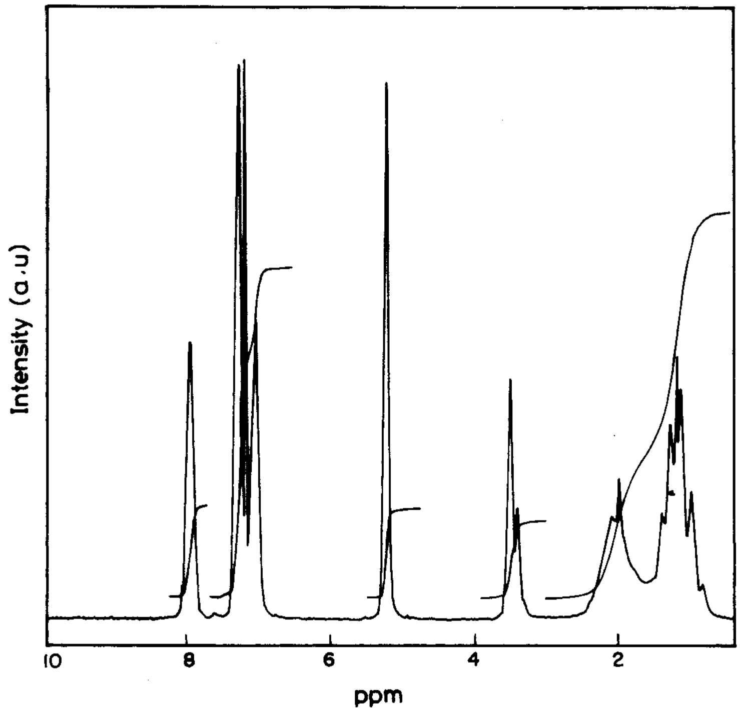


Figure 2. ^{1}H-NMR spectrum of poly(BCPM-co-MMA) (0.6236 : 0.3764).

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

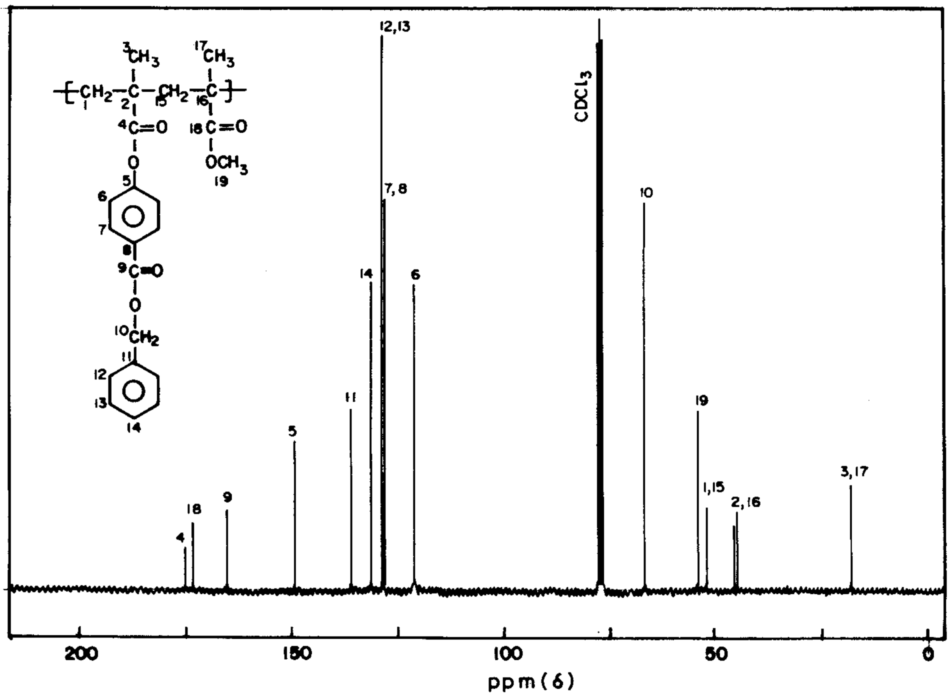


Figure 3. ^{13}C-NMR spectrum of poly(BCPM-co-MMA) (0.6236 : 0.3764).

Molecular Weights

The number and weight-average molecular weights of poly(BCPM), poly(MMA) and six samples of copolymers determined by gel permeation chromatography are presented in Table 1. The polydispersity indices of poly(BCPM) and poly(MMA) are 2.01 and 1.84, respectively. The theoretical value of $\bar{M}_w/\bar{M}_n$ for polymers produced via radical combination and disproportionation are 1.5 and 2.0, respectively.[34] The value of $\bar{M}_w/\bar{M}_n$ for

Table 1. Molecular weight data for homo- and copolymers of BCPM and MMA.

Polymers	m_1[a]	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
Poly(BCPM)	1.0000	5.34	2.66	2.01
Poly(BCPM-co-MMA)	0.2524	3.48	1.89	1.84
	0.4696	3.63	1.94	1.87
	0.6236	3.20	1.93	1.85
	0.7350	3.46	1.81	1.90
	0.8731	3.53	1.85	1.91
	0.9471	3.45	1.78	1.94
Poly(MMA)	0.0000	2.43	1.32	1.84

[a]Mole fraction of BCPM in the copolymer.

poly(BCPM) suggests that the chain termination takes place mainly by disproportionation. The polydispersity index values of the copolymers suggest that chain termination takes place predominantly by disproportionation.

Glass Transition Temperature

The glass transition temperature (T_g) of the copolymers was determined by differential scanning calorimetry and the data are presented in Table 2. The T_g of poly(BCPM) is 83°C and that of poly(MMA) is 105°C. The results clearly indicate that the T_g value of copolymers depends on the composition of copolymer and the value decreases with an increase in BCPM units in the copolymer.

Thermogravimetric Analysis

The TGA data for the homopolymers and copolymers of BCPM and MMA are given in Table 2. TGA curves of poly(BCPM), poly(MMA), and poly(BCPM-co-MMA) (0.6236 : 0.3764) are shown in Fig. 4. The thermograms clearly indicate that poly(BCPM), poly(BCPM-co-MMA), poly(MMA) undergo a single stage decomposition. The initial decomposition temperatures of poly(BCPM), poly(BCPM-co-MMA), and poly(MMA) are 266°C, 257°C, and 244°C. TGA results indicate that the thermal stability of the copolymer increases with an increase in BCPM content in the copolymer.

Copolymer Composition

Copolymer compositions were determined by ^{1}H-NMR analysis. The assignment of the resonance peaks in the ^{1}H-NMR spectrum allows for evaluation of each kind of monomeric content incorporated into the copolymer chain.

The following method is used to determine the composition of the copolymers. Let m_1 be the mole fraction of BCPM and $(1 - m_1)$ that of MMA. 4-Benzyloxycarbonylphenyl

Table 2. DSC and TGA data for BCPM-MMA copolymer system.

			Temperature at weight loss (°C)					
Polymers	m_1	IDT[a]	10%	30%	50%	70%	90%	T_g(°C)
Poly(MMA)	0.0000	244	270	284	300	334	380	105
Poly(BCPM-co-MMA)	0.4696	251	288	306	324	353	393	88
	0.6236	257	305	328	348	372	406	86
	0.7350	264	322	350	372	391	419	85
Poly(BCPM)	1.0000	270	339	372	395	409	432	83

[a] Initial decomposition temperature.

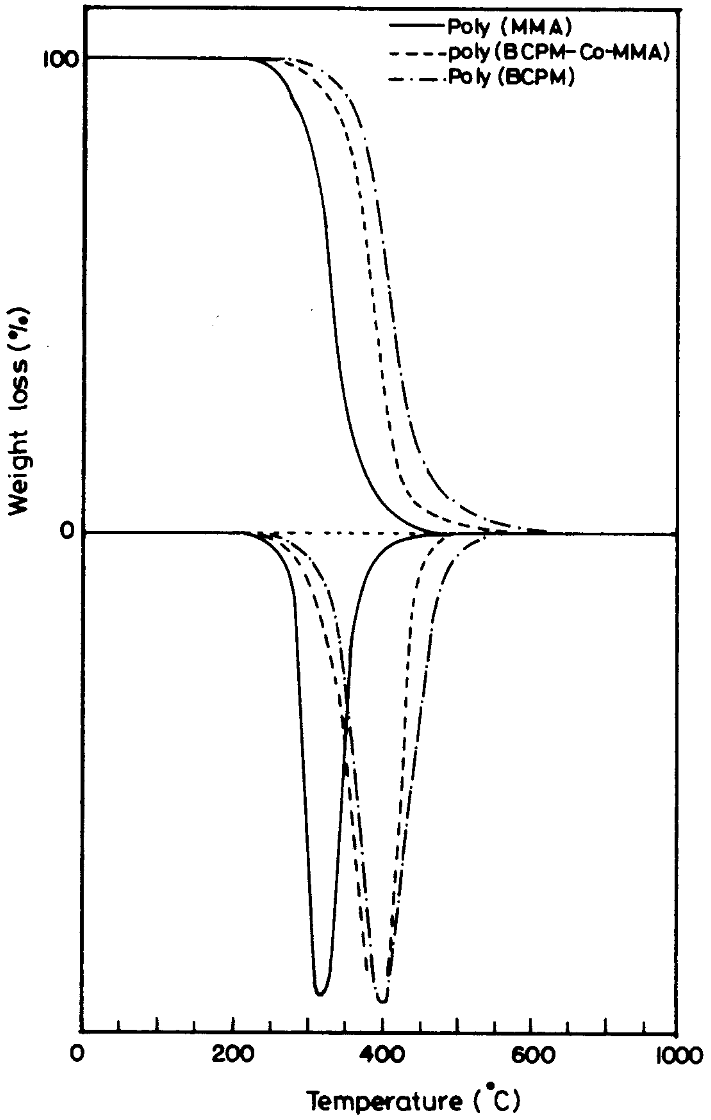


Figure 4. TGA curves for poly(MMA), poly(BCPM-co-MMA), and poly(BCPM).

methacrylate contains nine aromatic protons and seven aliphatic protons, whereas MMA contains eight aliphatic protons.

$$C = \frac{\text{Integrated peak area of aromatic protons } (I_{\text{Ar}})}{\text{Integrated peak area of aliphatic protons } (I_{\text{Ali}})} = \frac{9m_1}{7m_1 + 8(1 - m_1)} \qquad (1)$$

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

which on simplification gives:

$$m_1 = \frac{8C}{9 + C} \tag{2}$$

From Eq. (2), the mole fraction of BCPM in all the copolymers was calculated by measuring the integrated peak areas of the aromatic proton signals and aliphatic proton signals from the spectra of all copolymer samples. Table 3 shows the values of C, and the mole fractions of the monomers in the feed as well as in the copolymers.

The kinetic behavior of the copolymerization was determined by plotting the mole fractions of BCPM in the feed (M_1) vs. that in the copolymer (m_1) (Fig. 5). The copolymer composition curve indicates that the composition with respect to BCPM in the copolymer is always higher than that in the feed.

From the monomer feed ratios and the resultant copolymer compositions, the monomer reactivity ratios of BCPM and MMA were evaluated by the application of methods of Fineman–Ross, Kelen–Tüdös and extended Kelen–Tüdös. The analysis for F-R, K-T and Ext. K-T for the copolymers is presented in Tables 4 and 5. The K-T and Ext. K-T plots are shown in Fig. 6. The monomer reactivity ratios determined by conventional linearization methods are only approximate and usually employed as good starting values for non-linear parameter estimation schemes.

To determine more reliable values of monomer reactivity ratios, EVM method is used utilizing the computer program, RREVM. The r_1 and r_2 values from all methods are presented below.

Fineman–Ross: $r_1 = 1.4671$; $r_2 = 0.4367$;
Kelen–Tüdös: $r_1 = 1.5338$; $r_2 = 0.5333$;
Ext. Kelen–Tüdös: $r_1 = 1.5543$; $r_2 = 0.5160$;
RREVM: $r_1 = 1.3944$; $r_2 = 0.4943$; $r_1 r_2 = 0.6893$

The 95% joint confidence region for the determined r_1 and r_2 values using RREVM is shown in Fig. 7. A value of r_1 (1.3944) larger than 1 and that of r_2 (0.4943) less than 1

Table 3. Composition data for copolymerization of BCPM with MMA in MEK solution at 70°C.

			Integrated peak area of protons			
Copolymer	M_1[a]	Conversion %	I_{Ar}	I_{Ali}	C	m_1[a]
1	0.1519	7.16	22.650	77.321	0.2933	0.2524
2	0.3529	7.78	35.951	64.049	0.5613	0.4696
3	0.5051	8.50	43.212	56.788	0.7609	0.6236
4	0.6501	8.01	47.662	52.338	0.9106	0.7350
5	0.7936	9.75	51.025	47.071	1.0840	0.8731
6	0.9235	8.45	50.064	42.137	1.1881	0.9471

[a] M_1 and m_1 are the mole fractions of BCPM in the feed and in the copolymers, respectively.

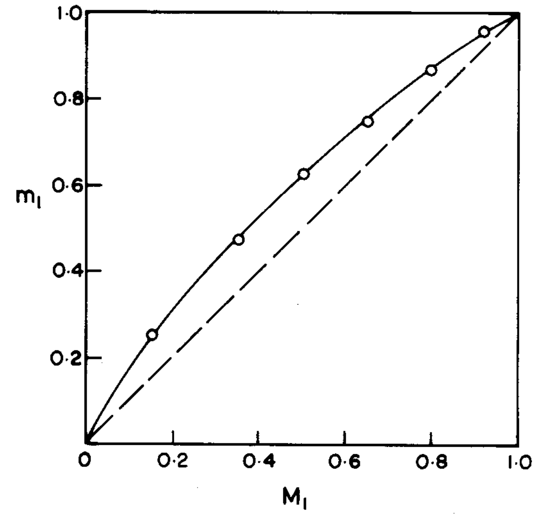


Figure 5. Copolymer composition diagram of poly(BCPM-co-MMA) system.

suggests the presence of a higher amount of BCPM units in the copolymer than in the feed. However, the product of r_1 and r_2 is less than 1 (0.6893), which indicates that the copolymer shows a slightly alternating tendency and therefore, there would be longer sequence of BCPM units in the copolymer chain.

CONCLUSION

Poly(BCPM) and the copolymers of BCPM with MMA were synthesized in solution by free radical polymerization. Characterization of poly(BCPM-co-MMA) were performed with FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopic techniques. The copolymers were soluble in chloroform, dimethyl formamide, dimethyl acetamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene, xylene, and insoluble in *n*-hexane, methanol, and ethanol. Thermogravimetric analysis indicates that the thermal stability of the

Table 4. F-R and K-T parameters for the copolymerization of BCPM with MMA.

$F = M_1/M_2$	$F = m_1/m_2$	$H = F^2/f$	$G = F(f-1)/f$	$\eta = G/(\alpha + H)$[a]	$\xi = H/(\alpha + H)$[a]
0.1791	0.3376	0.0950	−0.3514	−0.3606	0.9750
0.5453	0.8853	0.3358	−0.0706	−0.0581	0.2763
1.0206	1.6567	0.6287	0.4045	0.2682	0.4169
1.8579	2.7735	1.2445	1.1880	0.5593	0.5859
3.8449	6.8802	2.1486	3.2860	1.0852	0.7096
12.0718	17.9035	8.1396	11.3975	1.2637	0.9025

[a] $\alpha = 0.8793$.

Table 5. Extended K-T parameters from BCPM vs. MMA copolymer system.

S. no. (copolymer)	1	2	3	4	5	6
ζ_2	0.0547	0.0561	0.0578	0.0565	0.0564	0.0574
ζ_1	0.1031	0.0910	0.0938	0.0843	0.1009	0.0851
Z	1.9343	1.6525	1.6543	1.5142	1.8321	1.5045
F	0.1745	0.5357	1.0014	1.8316	3.7533	11.8999
H	0.0902	0.3241	0.6053	1.2096	2.0497	7.9095
G	−0.3424	−0.0694	0.3969	1.1712	3.2095	11.2352
η	−0.2236	−0.0393	0.1939	0.4418	0.9194	1.2015
ξ	0.0589	0.1836	0.2958	0.4563	0.5871	0.8458

Note: $\alpha = (F_{\min} \times F_{\max})^{1/2} = 1.4410$; $\mu = 0.3378$.

copolymer increases with an increase of BCPM units in the copolymer. The values of polydispersity indices of poly(BCPM) and poly(BCPM-co-MMA) suggest a tendency for chain termination by disproportionation. The copolymer composition was determined by ^{1}H-NMR analysis of the copolymers. The monomer reactivity ratios were determined by conventional linearization methods such as F-R, K-T, Ext.K-T and compared with

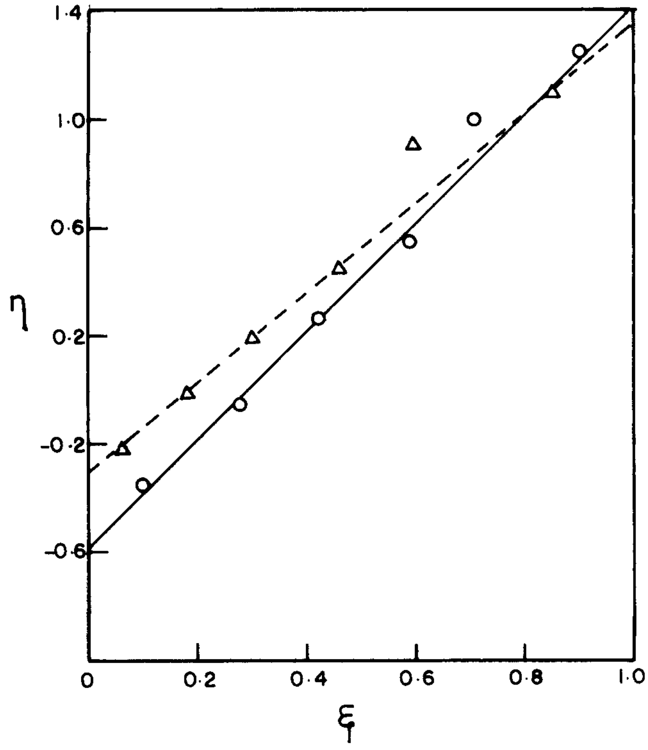


Figure 6. K-T (○) and Ext. K-T (△) plots for poly(BCPM-co-MMA) system.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

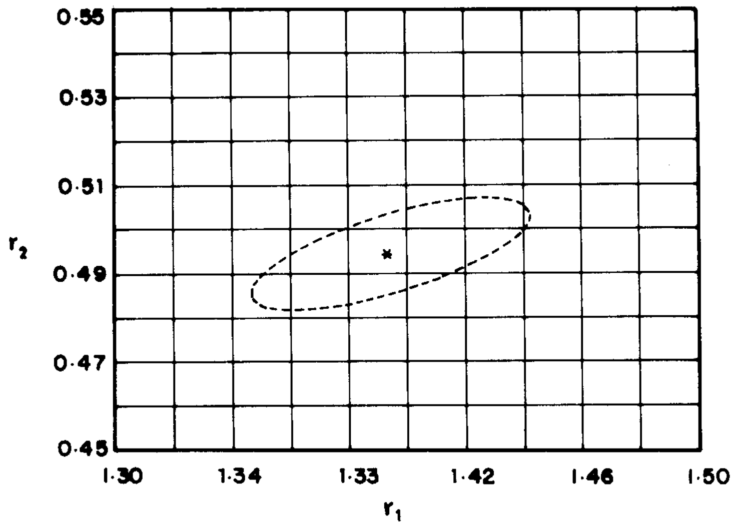


Figure 7. Ninety-five percent joint confidence region of r_1 and r_2 values by RREVM for BCPM-MMA copolymer system.

those obtained by non-linear EVM using a computer program, RREVM. The r_1 values of these methods are greater than 1 and this indicates that BCPM is more reactive than MMA. The product of $r_1 \cdot r_2(0.6892)$ is less than 1 and this indicates a slightly alternating tendency with longer sequences of BCPM units in the copolymer chain.

REFERENCES

1. Vogl, O.; Albertsson, A.C.; Janovic, Z. Functional polymers. XXXVII. New developments in specialty polymers and polymeric stabilizers. Polymer **1985**, *26* (9), 1288–1296.
2. Panye, A.F. *Organic Coating Technology*; Wiley & Sons: New York, 1964; Vol. 1, 27.
3. Ichimura, K.; Nishio, Y. Photocrosslinkable polymers having p-phenylene diacrylate group side chain. Argon laser photo resists. J. Polym. Sci., Part A, Polym. Chem. **1987**, *25*, 1579–1590.
4. Vijayaraghavan, P.G.; Reddy, B.S.R. Copolymerization of 4-methyl and 4-methoxyphenyl acrylates with glycidyl methacrylate: synthesis, characterization, reactivity ratios and application as adhesives for leather Industry. J. Appl. Polym. Sci. **1996**, *61*, 936–943.
5. Andreas, H.; Gunner, S.; Reinhold, L. German Offen De 3,604,581(1987); Chem. Abstr. **1998**, *108*, 65993v.
6. Masami, S.; Masataka, M.; Masanori, S.; Yuko, N. Eur. Pat. Appl. Ep. 67,954 (1982); Chem. Abstr. **1983**, *99*, 184989c.
7. Toshiba Corp., Jpn. Kokai Tokkyo Koho Jp 58,219,556(1983); Chem. Abstr. **1984**, *101*, 46282a.
8. Eiichi, A.; Yu, Norihiro, M.; Kazuo, A. Influence of spacer structure on the molecular dynamics of side-chain liquid-crystalline polyacrylates as studied by dielectric relaxation spectroscopy. J. Chem. Soc. Faraday Trans. **1998**, *14*, 1995–2003.

9. Mayumi, N.; Yoichi, N.; Mitushubishi Rayon Co. Ltd. Jpn., Jpn. Kokai Tokkyo Koho JP 2001,354,932 (Cl.C09J133/14), 25 Dec. 2001, Jp. Appl. 2000/108,565, 2000.
10. Gitlitz, M.H.; Rusell, D.B.; Leiner, H.H. US Patent 4,532,269 (1985); Chem. Abstr. **1985**, *103*, 125141y.
11. Rusell, D.B.; Gitlitz, M.H.; Leiner, H.H.; Khuddus, M.A.; Berger A. PCT Int. Appl. WO 8402, 915 (1984); Chem. Abstr. **1985**, *102*, 63730h.
12. Pandeya, S.C.; Rather, N.; Singh, A. Synthesis and characterization of biologically active barium containing polymer films. J. Polym. Mat. **1999**, *16* (3), 253–258.
13. Batz, H.G.; Franzman, G.F.; Ringsdorf, H. Pharmologically active polymers 3: model reactions for synthesis of pharamologically active polymers by way of monomeric and polmeric reactive esters. Macromol. Chem. **1973**, *27*, 172–176.
14. George, D.C.; Edward, I.; Ewald, L. Eur. Pat. Appl. 1985 EP 155,231; Chem. Abstr. **1986**, *104*, 177740h.
15. Hans, S.; Albert, E.; Peter, J.K.; Reinhold, L. German Offen De 1985, 3,331,691; Chem. Abstr. **1985**, *103*, 11348h.
16. Johnka, M.; Mullera, L.; Neyera, A.; Hofstrat, A. Copolymer of halogenated acrylates and methacrylates for the optical telecommunication, optical properties, thermal analysis and determination of unsaturation by quantitative F-T Raman and F-T spectroscopy. Eur. Polym. J. **2000**, *36* (6), 1251–1264.
17. Ito, M.; Ichimura, K. Jpn. Kokai Tokkyo Koho Jp **1984**, *61*, 145, 260.
18. Kamalakkannan, V.; Siddarathan, S.; Olivannan, M.S.; Rajadurai, S. Modified chlorinated rubber finishes as top coats for football leathers. Leather Science **1983**, *30*, 205–208.
19. Ivin, K.J.; Pitchumani, S.; Rami Reddy, A.V.; Rajadurai, S. Reactivity ratios of ethylacrylate-n-butyl methacrylate copolymer system by ^{1}H-NMR analysis. J. Polym. Sci. Polym. Chem. **1982**, *29*, 277–282.
20. Tacx, J.C.J.F.; Vander Velden, G.P.M.; German, A.L. Investigation of the intramolecular structure of styrene-ethyl methacrylate copolymers by nuclear magnetic resonance: 2. comparison of the microstructure of solution and emulsion copolymers obtained at high conversion. Polymer **1988**, *29* (9), 1675–1682.
21. Brar, A.S.; Khausik, D. Microstructure and compositional sequence determination of acrylonitrile and acrylic acid copolymers by NMR spectroscopy. Eur. Polym. J. **1988**, *34* (11), 1585–1597.
22. Narashimaswamy, T.; Sumathi, S.C.; Reddy, B.S.R. 2,4,6-tribromophenyl acrylate-co-GMA polymer: synthesis, charecterisation and reactivity ratios. J. Polym. Sci. Part A; Polym. Chem. **1992**, *30*, 2165–2172.
23. Balaji, R.; Nanjundan, S. Copolymerization of 3-methoxy-4-acrloyloxy benzal phenyl amine with methyl methacrylate. Eur. Polym. J. **1999**, *35* (7), 1133–1138.
24. Vijayanand, P.S.; Radhakrishnan, S.; Arun Prasath, R.; Nanjundan, S. Synthesis and charecterization of hompolymer of 3,5-Dimethylphenyl methacrylate and its copolymer with glycidyl methacrylate. Eur. Polym. J. **2002**, *38*, 1319–1326.
25. Fineman, M.; Ross, S.D. Linear method for determining monomer reactivity ratios in copolymerization. J. Polym. Sci. **1950**, *5*, 259–262.
26. Kelen, T.; Tudos, F. Analysis of the linear methods for determining monomer reactivity ratios 1. A new improved linear graphical method. J. Macromol. Sci. Chem. **1975**, *A9*, 1–27.

27. Kelen, T.; Tudos, F.; Turesanyi, B.; Kennedy, J.P. Analysis of the linear method for determining copolymerization reactivity ratios IV. A comprehensive and critical reexamination of carbocationic copolymerization data. J. Polym. Sci. Poly. Chem. **1977**, *15*, 3041–3071.
28. Tidewell, P.M.; Mortimer, G.A. An improved method of calculating copolymerization reactivity ratios. J. Polym. Sci., Part A **1965**, *3*, 369–387.
29. Barson, C.; Fenn, D.R. A method for determining the reactivity ratios when copolymerizations are influenced by penultimate effects of both monomers. Eur. Polym. J. **1989**, *25*, 719–720.
30. Bharel, R.; Choudhary, V.; Varma, I.K. Preparation, characterization and thermal behavior of MMA—*N*-arylmaleimide copolymers. J. Appl. Polym. Sci. **1994**, *54*, 2165–2170.
31. Dube, M.; Amin Sanayei, R.; Penlidis, A.; O'Driscoll, Reilly, P.M. A microcomputer program for estimation of copolymerization reactivity ratios. J. Polym. Sci., Part A. Poly. Chem. **1991**, *29*, 703–708.
32. Aota, H.; Sanai, Y.; Matsumoto, A.; Kamachi, M. Electron spin resonance spectroscopic pursuit of network formation in free-radical crosslinking polymerizations. I. Microscopic environmental evaluation around copper(II) tetraphenyl-porphyrin spin probe incorporated into or excluded from polymer network in methyl methacrylate-ethylene dimethacrylate copolymerization. Polym. J. **1996**, *28* (10), 867–873.
33. Stampel, G.M.; Gross, R.P.; Malieha, R.D. The preparation of acryloyl chloride. J. Am. Chem. Soc. **1950**, *72*, 2299–2301.
34. Teramachi, S.; Hasegara, A.; Atasuka, M.; Yamashita, A.; Takemoto, N. Molecular weight distribution and correlation between chemical composition and molecular weight in high conversion copolymer of copolymer of styrene-methylacrylate. Macromolecules **1978**, *11* (6), 1206–1210.

Received March 2003
Revised April 2003

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016