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Copolymerization of Benzoylphenyl Methacrylate with Methyl Methacrylate: Synthesis, Characterization and Determination of Monomer Reactivity Ratios

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4-Benzoylphenyl methacrylate (BPM) was prepared by reacting 4-hydroxy benzophenone dissolved in methyl ethyl ketone (MEK) with methacryloyl chloride in the presence of triethylamine. The copolymers of BPM with methyl methacrylate (MMA) having different copolymer composition were synthesized in a MEK solution using benzoyl peroxide (BPO) as a free radical initiator at 70 ± 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 ($\bar{M}_w/\bar{M}_n$) of the polymers were determined using gel permeation chromatograph. The glass transition temperatures (T_g) of the copolymers determined by differential scanning calorimeter reveals that T_g increases with increase in BPM content in the copolymer. Thermogravimetric analysis of the polymers performed in air shows that the stability of the copolymer increases with an increase in BPM content. The solubility of the polymers was tested in various polar and non-polar solvents. Copolymer compositions were determined by the ^{1}H-NMR spectroscopy by comparing the integral peak areas of well separated aromatic and aliphatic proton peaks. The monomer reactivity ratios were determined by the application of conventional linearization methods such as Fineman-Ross ($r_1 = 2.201$: $r_2 = 0.814$), Kelen Tüdös ($r_1 = 2.121$: $r_2 = 0.634$), extended Kelen Tüdös ($r_1 = 2.153$: $r_2 = 0.698$), as well as by a non-linear error-in-variable model method (EVM) using a computer program RREVM ($r_1 = 1.638$: $r_2 = 0.543$).

Keywords 4-benzoylphenyl methacrylate, copolymerization, reactivity ratios, methyl methacrylate, ^{1}H-NMR and ^{13}C-NMR spectra, thermal studies

Introduction

The studies on phenyl acrylate and phenyl methacrylate polymers have gained considerable interest in the field of research and synthesis of these polymers is now technologically feasible (1–3). Poly(phenyl methacrylate) polymers have inherent thermal stability, more

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Address correspondence to S. Nanjundan, Department of Chemistry, College of Engineering, Anna University, Chennai 600 025, India. Fax: +91-044-22200660; E-mail: snanjundan@yahoo.com reactivity due to the presence of aromatic ring and their glass transition temperature is higher than their acrylate counterparts, because substitution of the methyl group of the α-H on the main chain restricts the degree of rotation and motion of the polymer backbone. These combinations of excellent properties have enabled them to achieve prime importance in various avenues of industrial applications (4–7). Copolymers of MMA have received significant attention, particularly in the area of major industrial applications. Due to their excellent durability, good transparency and superior performance, they are mainly used in the production of bioimplant materials, (8) bone cements, (9) adhesion in laminates, (10) protective coatings, (11) printing plates and electrical circuits, (12, 13) paint materials, etc. (14) and optical telecommunication materials (15).

The chemical composition of the copolymers mainly depends on the degree of incorporation of the comonomers and also on the relative reactivity between them. Monomer reactivity ratios are very unique important quantitative values to predict the copolymer composition for any starting feed and to understand the kinetic and mechanistic aspects of copolymerization. In the past few decades, ^{1}H-NMR spectroscopic analysis plays a vital role in investigation. Hence, it has been established as a powerful tool for the determination of tacticity, sequence distribution, as well as for the estimation of copolymer composition and exact structure because of its simplicity, rapidity and high sensitivity (16–21). The accurate estimation of copolymer composition and determination of monomer reactivity ratios is extremely significant to synthesize tailor made copolymers with the required physical and chemical properties and in evaluating the specific end application of the copolymers. The main aim in commercial copolymerization is to achieve a product having uniform composition. Knowledge about the monomer reactivity ratios of the comonomers would help in achieving this. Monomer reactivity ratios were determined by a number of linearization methods (22–24). As the monomer reactivity ratios determined by these methods are only approximate, a number of non-linear methods have been proposed to obtain correct values of monomer reactivity ratios (25–29). Notable among them is the non-linear error-in-variables-model (EVM) method using a recent computer program, RREVM, (28) which gives precise and more reliable results.

The present article describes the synthesis, characterization, and thermal properties of copolymers of 4-benzoylphenyl methacrylate with methyl methacrylate. The monomer reactivity ratios of the comonomers are also reported.

Experimental

Materials

4-Hydroxy benzophenone (Lancaster) was used as such without purification. Methyl methacrylate (EMERK) was purified by distillation under reduced pressure. Benzoyl peroxide (BPO) (Fluka) was recrystallized from a chloroform methanol (1 : 1) 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 86–89°C was collected and used. Methacrylic acid (CDH) and benzoyl chloride (SRL) were used as such. All the solvents were purified by distillation prior to their use.

Synthesis of 4-Benzoylphenyl Methacrylate (BPM)

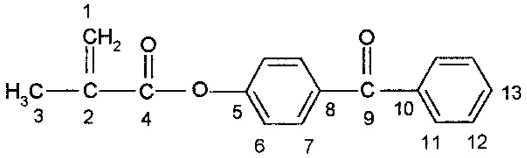
Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride using the procedure of Stampel et al. (30). For the synthesis of 4-benzoylphenyl methacrylate (BPM), 4-hydroxy benzophenone (15 g, 0.07 mol) and triethylamine (11.6 mL, 0.08 mol) were dissolved in methyl ethyl ketone (MEK) (300 mL) in a three-necked flask fitted with a mechanical stirrer and a dropping funnel and placed in an ice bath. Methacryloyl chloride (8 mL, 0.08 mol) dissolved in MEK (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 0–10°C. The reaction was allowed to proceed for 1 h at 0–10°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 then evaporated to get crude 4-benzoylphenyl methacrylate. The product was recrystalized from ethanol to get white crystals. The yield of the monomer was 85% and the melting point was 66.67°C.

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

Elemental analysis (%): C = 76.59 (found), 76.68 (Calcd), H = 5.22 (found), 5.30 (Calcd).

IR (cm^{-1}, KBr): 3106 and 3048 (=C–H), 2984 and 2926 (C–H), 1734 (>C=O ester), 1652 (>C=O ketone), 1635 (>C=C<, olefinic), 1596, 1499 and 1408 (>C=C<, aromatic), 1379$_{(s)}$ and 1445$_{(as)}$ (CH_3 bending), 1280 and 1161 (C–O stretching), 805, 734 and 698 (C–H out of plane bending), 498 (C=C out of plane bending).

^{1}H-NMR (ppm, $CDCl_3$): 7.24 (d, 2H), 7.52 (q, 2H), 7.66 (q, 1H), 7.97 (d, 2H) and 8.02 (d, 2H) (aromatic), 5.80 (d, 1H) and 6.39 (d, 1H) (CH_2=), 2.11 (s, 3H) (α-methyl).



^{13}C-NMR (ppm, $CDCl_3$), 195.40 (C_9), 165.14 (C_4), 154.05 (C_5), 137.33 (C_{10}), 135.37 (C_1), 134.96 (C_8), 132.29 (C_{13}), 131.49 (C_{11}), 129.61 (C_7), 128.61 (C_{12}), 127.75 (C_2), 121.41 (C_6), 18.14 (C_3).

Copolymerization

Predetermined quantities of BPM, MMA, MEK and BPO were placed in a standard reaction tube (100 ml) and the mixture was flushed with O_2 free N_2 for 20 min. The tube was tightly sealed and immersed in a water bath at 70 ± 1°C. In order to follow copolymer equation, conversion levels were restricted to less than 10%. After the required time ranging from 10 min to 1.30 h, 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. About 5–10 mg of the polymer was added to about 2 ml of the solvent 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 recorded on a Bruker 270 MHz FT-NMR spectrometer at room temperature using $CDCl_3$ and TMS as a solvent and internal standard, respectively. The proton decoupled ^{13}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 weight average molecular weight ($\bar{M}_w$) and number average molecular weight ($\bar{M}_n$) was determined using a Waters 501 gel permeation chromatograph equipped with styragel columns and differential refractive index detector. Tetrahydrofuran was used as an eluent and polystyrene standards were used for calibration.

Thermogravimetric analysis was performed with a Mettler TA 3000 thermal analyzer in air at a heating rate of 15° C/min. The glass transition temperature was determined with a NETZSCH-Geratebau Gmbh DSC 204 thermal analyzer at a heating rate of 10°C/min in air.

Results and Discussion

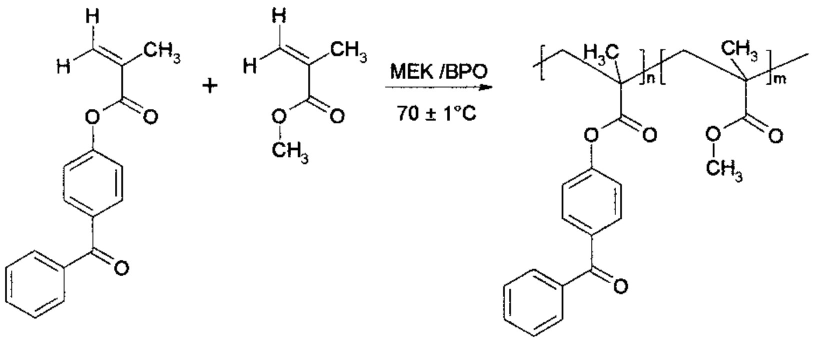
Synthesis of Copolymers

Copolymers of BPM 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 utilize the copolymer equation. The synthesis of copolymer of BPM with MMA is shown in Scheme 1.

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.



Scheme 1. Synthesis of poly(BPM-*co*-MMA).

IR Spectrum

The IR spectrum of the copolymer, poly(BPM-*co*-MMA) (0.6363:0.3637) is shown in Figure 1. It shows peaks at 3059 cm^{-1} corresponding to the aromatic C–H stretching. The asymmetrical and symmetrical stretching due to the methyl and methylene groups are observed at 2993, 2948, and 2849 cm^{-1}. The peak at 1751 cm^{-1} is attributed to the ester carbonyl stretching of both BPM and MMA units. The keto carbonyl stretching of BPM unit occurs at 1660 cm^{-1}. The aromatic >C=C< stretching is observed at 1598, 1501, and 1410 cm^{-1}. The bending vibration of methyl group is seen at 1447 cm^{-1}. The C–O stretching due to the ester group in BPM and MMA units give rise to signals at 1203, 1164 and 1113 cm^{-1}. The C–H out of plane bending vibrations of the aromatic nuclei is observed at 738 and 701 cm^{-1}. The >C=C< out of plane bending vibration of aromatic nuclei is seen at 503 cm^{-1}.

^{1}H-NMR Spectrum

^{1}H-NMR spectrum of the copolymer, poly(BPM-*co*-MMA) (0.6363:0.3637) is shown in Figure 2. The aromatic protons show resonance signals at 8.22–7.05 ppm. The resonance signal at 3.72 ppm is due to the methoxy protons of MMA unit. Due to the existence of tacticity, the resonance signals corresponding to the methylene group of the backbone are observed between 1.84–2.81 ppm. The α-methyl protons of BPM and MMA units show resonance signals at 1.85–0.74 ppm.

^{13}C-NMR Spectrum

The proton decoupled ^{13}C-NMR spectrum of poly(BPM-*co*-MMA) (0.6363:0.3637) is shown in Figure 3. The resonance signal at 195.21 ppm (C_9) is due to the keto carbonyl carbon of BPM unit. The signals at 176.77 (C_4) and 174.40 ppm (C_{17}) are due to the

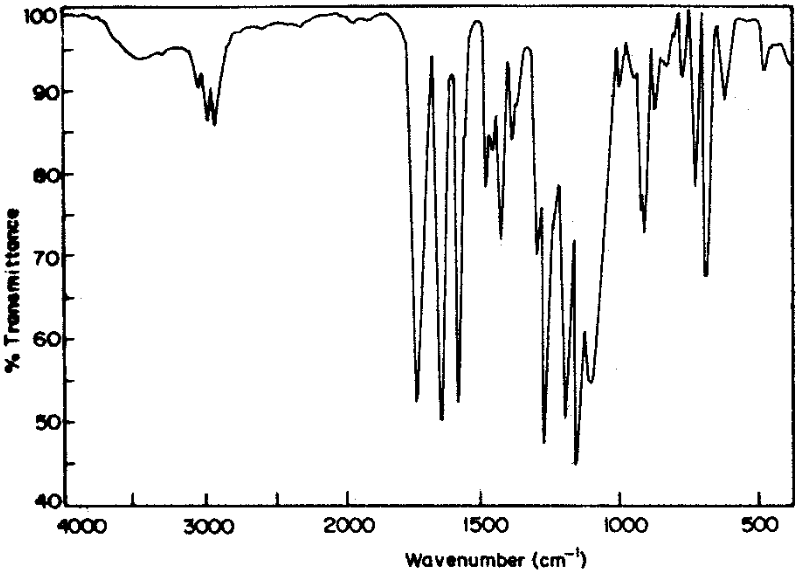


Figure 1. IR spectrum of poly(BPM-*co*-MMA) (0.6363:0.3637).

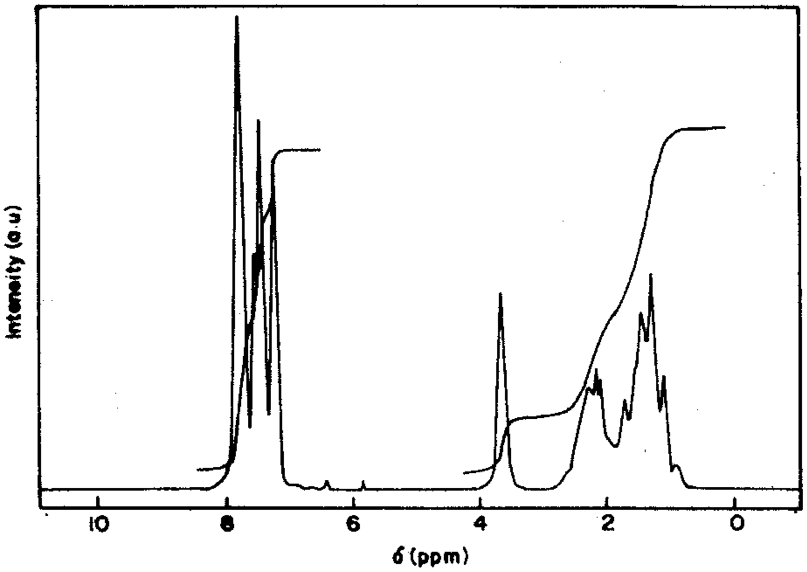


Figure 2. ^{1}H-NMR spectrum of poly(BPM-*co*-MMA) (0.6363:0.3637).

ester carbonyl carbon groups of BPM and MMA units, respectively. The resonance signal at 153.63 ppm (C_5) and 137.39 (C_{10}), 135.26 ppm (C_8) are due to aromatic carbon attached to the oxygen and keto groups, respectively. The other aromatic carbon signals are observed at 132.57 (C_{13}), 129.86 (C_{11}), 128.33 (C_7 & C_{12}) and 121.15, 120.93 ppm (C_6). The methoxy carbon signal of MMA unit is observed at 54.57 ppm (C_{18}).

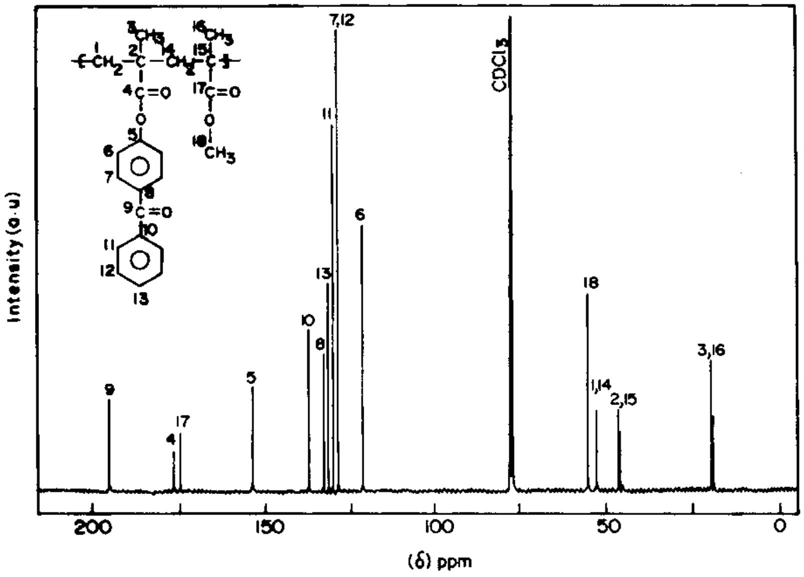


Figure 3. ^{13}C-NMR spectrum of poly(BPM-*co*-MMA) (0.6363:0.3637).

The backbone methylene carbons show signals at 52.35, 52.09 ppm (C_1 & C_{12}) and tertiary carbons at 45.85, 45.41 ppm (C_2 and C_{15}). The α-methyl group of both the monomeric units show resonance signal at 18.81 ppm (C_3 and C_{16}).

Molecular Weights

The weight average molecular weight ($\bar{M}_w$), number average molecular weight ($\bar{M}_n$) and polydispersity indices ($\bar{M}_w/\bar{M}_n$) of homopolymers, as well as copolymers determined by gel permeation chromatography are given in Table 1. The polydispersity indices of poly(BPM) and poly(MMA) are 1.79 and 1.84, respectively. The theoretical value of for polymers produced through radical combination and disproportionation were 1.5 and 2.0 respectively (31). In the homopolymerization of both MMA and BPM, the chain termination by disproportionation predominates coupling. The polydispersity indices of the copolymers range between 1.80 and 1.85, which suggests that in copolymerization also the chain termination by disproportionation was predominant than coupling.

Glass Transition Temperature

The glass transition temperature (T_g) of the copolymers was determined by differential scanning calorimetry and the T_g data are presented in Table 2. The T_g value of poly(BPM) is 118°C, (32) 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 BPM content in the copolymer as shown in Figure 4.

The TGA data for the homopolymers and copolymers of BPM and MMA are given in Table 2. TGA traces of poly(BPM), poly(MMA) and poly(BPM-*co*-MMA) (0.6363: 0.3637) are shown in Figure 5. The thermograms clearly indicate that poly(MMA) undergoes decomposition in a single stage whereas poly(BPM) and poly(BPM-*co*-MMA) undergo decomposition in two stages. The initial decomposition temperature of poly(MMA), poly(BPM-*co*-MMA), poly(BPM) are 244, 245 and 246°C, respectively. TGA results indicate that the thermal stability of the copolymer increases with increase in BPM content in the copolymer.

Table 1

Molecular weight data for homo and copolymers of BPM 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(BPM)	1.0000	3.78	2.11	1.79
Poly(BPM-*co*-MMA)	0.2433	4.06	2.18	1.85
	0.4657	3.87	2.14	1.81
	0.6363	3.94	2.16	1.82
	0.7732	3.76	2.09	1.80
	0.9007	3.90	2.14	1.82
	0.9516	3.81	2.07	1.84
Poly(MMA)	0.0000	2.43	1.32	1.84

[a] m_1 is the mole fraction of BPM in the copolymer.

Table 2
TGA and DSC data for BPM-MMA copolymer system

Polymers	m_1	IDT[a] (°C)	Temperature (°C) at weight loss (%) 10%	30%	50%	70%	90%	T_g[b] (°C)
Poly(MMA)	0.0000	244	269	291	312	334	365	105
Poly(BPM-*co*-MMA)	0.4657	245	276	303	320	355	393	114
	0.6363	245	283	320	348	377	419	116
	0.7732	246	291	330	361	397	440	117
Poly(BPM)	1.0000	246	298	339	373	415	459	118

[a] IDT—Initial decomposition temperature.
[b] T_g—Glass transition temperature.
Thermogravimetric analysis.

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 BPM and m_2 $(1 - m_1)$ be that of MMA. BPM contains 9 aromatic protons and 5 aliphatic protons, whereas MMA contains 8 aliphatic protons.

$$C = \frac{\text{Integrated peak area of aromatic protons } (I_{Ar})}{\text{Integrated peak area of aliphatic protons } (I_{Ali})}$$

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

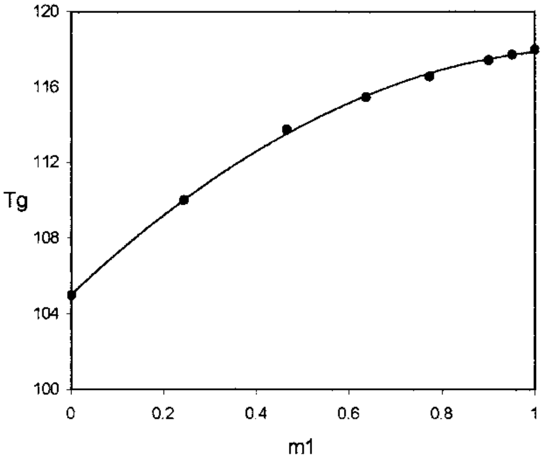


Figure 4. Variation of T_g with composition of poly(BPM-*co*-MMA).

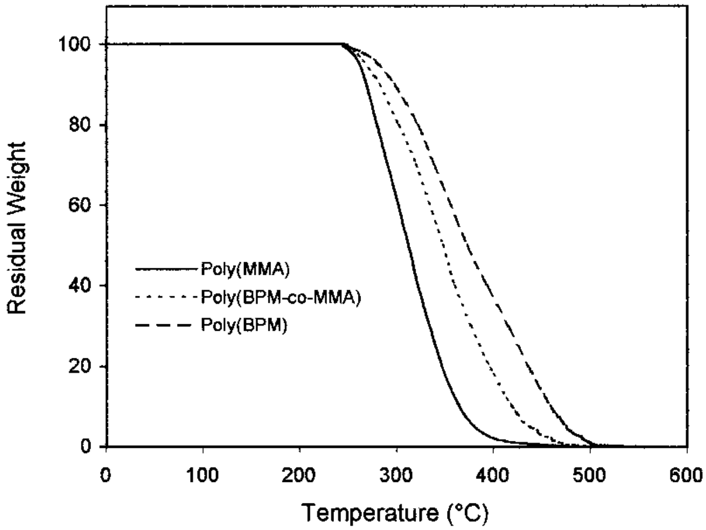


Figure 5. TGA curves for poly(MMA), poly(BPM-*co*-MMA) (0.6363:0.3637) and poly(BPM).

On simplification it gives,

$$m_1 = \frac{8C}{9 + 3C} \tag{2}$$

From Equation (2), the mole fraction of BPM 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 BPM in the feed (M_1) vs. that in the copolymer (m_1). Figure 6 shows the

Table 3

Composition data for the copolymerization of BPM with MMA

			Intensities of protons				
Copolymer	M_1[a]	Conversion (%)	I_{Ar}	I_{Ali}	C	m_1[b]	m_2[b]
1	0.1490	9.65	23.149	76.851	0.3012	0.2433	0.7567
2	0.3463	8.48	44.209	69.630	0.6349	0.4657	0.5343
3	0.5121	8.90	48.464	51.536	0.9403	0.6363	0.3637
4	0.6578	8.62	54.420	44.417	1.2252	0.7732	0.2268
5	0.8152	7.80	59.510	38.892	1.5301	0.9007	0.0993
6	0.9021	8.58	61.235	36.784	1.6647	0.9516	0.0484

[a] M_1 is the mole fraction of BPM in the feed.

[b] m_1 and m_2 are the mole fraction of BPM and MMA in the copolymer, respectively.

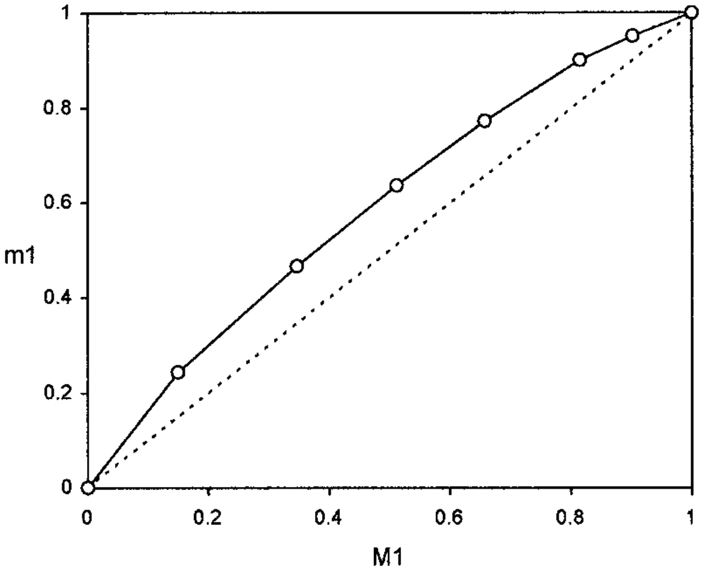


Figure 6. Copolymer composition diagram of poly(BPM-*co*-MMA) system.

copolymer composition curve, which indicates that the BPM content in the copolymer is always higher than that in the feed.

Monomer Reactivity Ratios

From the monomer feed ratios and the resultant copolymer compositions, the monomer reactivity ratios of BPM and MMA were evaluated using 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 4 and that of Ext. K-T in Table 5. The F-R plot is shown in Figure 7. The K-T and Ext. K-T plots are shown in Figure 8. The monomer reactivity ratios determined by conventional linearization methods are only approximate and are usually employed as good starting values for non-linear parameter estimation schemes.

To determine more reliable values of monomer reactivity ratios, a non-linear error-in-variables-model (EVM) method is used utilizing the computer program, RREVM. The r_1 and r_2 values from all methods are presented below:

Fineman-Ross:	$r_1 = 2.201$,	$r_2 = 0.814$	
Kelen-Tüdös:	$r_1 = 2.121$,	$r_2 = 0.634$	
Ext. Kelen-Tüdös:	$r_1 = 2.153$,	$r_2 = 0.698$	
RREVM:	$r_1 = 1.638$,	$r_2 = 0.543$,	$r_1r_2 = 0.889$

The 95% joint confidence region for the determined r_1 and r_2 values using RREVM is shown in Figure 9. The value of r_1 (1.638) is larger than 1 and that of r_2 (0.543) less than 1 suggests the presence of higher amount of BPM units in the copolymer than

Table 4

F-R and K-T parameters for the copolymerization of BPM with MMA

Copolymer no.	$F = M_1/M_2$	$f = m_1/m_2$	F-R parameters		K-T parameters	
			$G = F(f-1)/f$	$H = F^2/f$	$\eta = G/(\alpha + H)^a$	$\xi = H/(\alpha + H)^a$
1	0.1750	0.3215	−0.3693	0.0952	−0.5014	0.1292
2	0.5297	0.8716	−0.0780	0.3219	−0.0809	0.3342
3	1.0496	1.7495	0.4496	0.6297	0.3537	0.4954
4	1.9222	3.4091	1.3583	1.0838	0.7874	0.6282
5	4.4112	9.0704	3.9248	2.1452	1.4085	0.7698
6	9.2145	19.6611	8.7458	4.3185	1.7633	0.8707

[a] $\alpha = (H_{min} \times H_{max})^{1/2} = 0.6412$.

Table 5
Extended K-T parameters for the BPM-MMA copolymer system

Parameter	1	2	3	4	5	6
ζ_2	0.0762	0.0615	0.0597	0.0523	0.0395	0.0410
ζ_1	0.1400	0.1012	0.0995	0.0928	0.0812	0.0877
Z	1.9029	1.6795	1.7026	1.8131	2.1013	2.1870
$\bar{F}$	1.1690	0.5189	1.0275	1.8803	4.3166	8.9900
H	0.0888	0.3089	0.6035	1.0370	2.0542	4.1106
G	−0.3566	−0.0764	0.4402	1.3287	3.8407	8.5327
η	−0.2699	−0.0495	0.2397	0.6406	1.1685	1.5970
ξ	0.0672	0.2003	0.3287	0.4822	0.6250	0.7693

$\alpha = (\bar{F}_{min} \times \bar{F}_{max})^{1/2} = 1.2326$, $\mu = 0.3759$.

that in the feed. However, the product of r_1 and r_2 is less than 1 (0.889), which indicates the formation a random copolymer with longer sequence of BPM units in the copolymer chain.

Conclusions

Poly(BPM) and the copolymers of BPM with MMA were synthesized in solution by free radical polymerization. Characterization of poly(BPM-*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 and hydroxyl-group containing solvents such as methanol and ethanol. Thermogravimetric analysis indicates that the

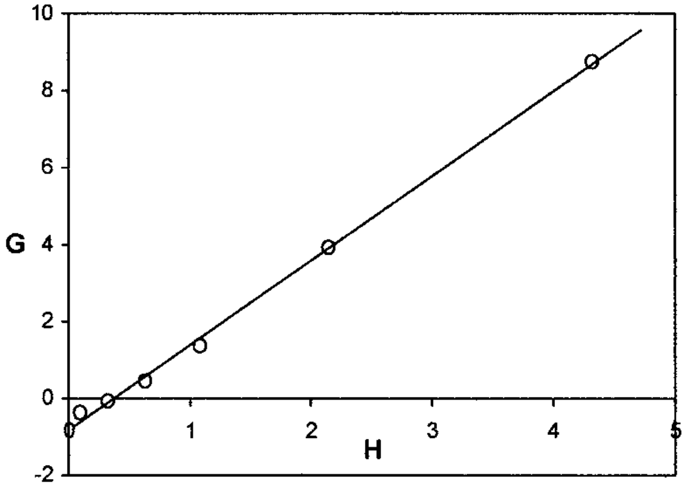


Figure 7. F-R plot for poly(BPM-*co*-MMA) system.

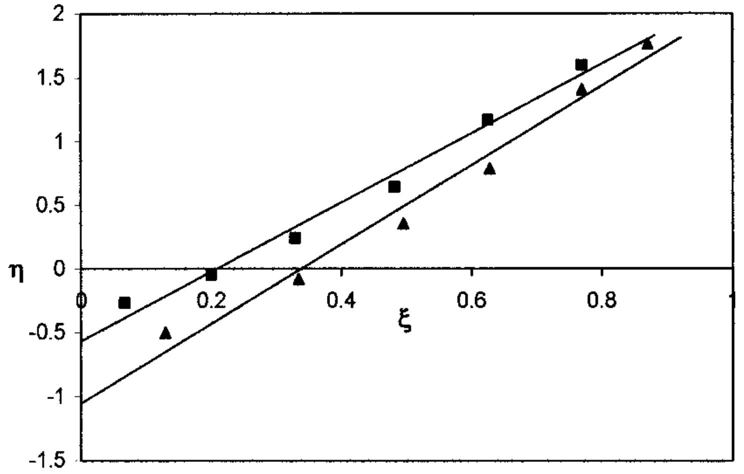


Figure 8. K-T (▲) and Ext. K-T (■) plot for poly(BPM-*co*-MMA) system.

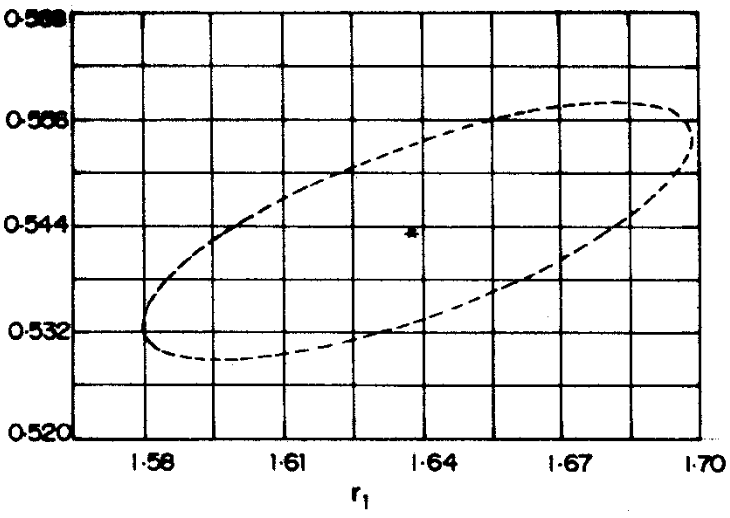


Figure 9. 95% Joint confidence region of r_1 and r_2 values by RREVM for BPM-MMA copolymer system.

thermal stability of the copolymers increase with increase in BPM content. The polydispersity indices of the polymers suggest greater tendency for chain termination by disproportionation than coupling. 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 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 BPM is more reactive than MMA. The product of $r_1 \cdot r_2$ indicates that the system forms a random copolymer with longer sequences of BPM units in the copolymer chain.

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