

Synthesis and Characterization of Poly(*N*-phenyl methacrylamide-*co*-methyl methacrylate) and Reactivity Ratios Determination

G. Jayasimha Reddy,¹ S. Venkata Naidu,¹ A. V. Rami Reddy²

¹Department of Polymer Science and Technology, Sri Krishnadevaraya University, Anantapur-515 003 (A.P), India
²R. O. Division, CSMCRI, Bhuvanagar-364 002 (Gujarat), India

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ABSTRACT: Free-radical solution copolymerization of *N*-phenyl methacrylamide and methyl methacrylate in various feed ratios was done using a benzoyl peroxide initiator in *N,N*-dimethylformamide at 70°C. The structure of the copolymer was elucidated by infrared and proton nuclear magnetic resonance spectroscopy. The copolymer composition was determined from the corresponding ¹H-NMR spectra of the copolymers. Finemann–Ross and Kelen–Tudos methods were used to determine the reactivity ratios of the monomers. The molecular weight distribution of the copolymers

was determined using gel permeation chromatography. Thermal properties of the copolymers were determined using differential scanning calorimetry and thermogravimetric analysis (TGA). The activation energy for thermal degradation of the copolymers was determined from the TGA data. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2179–2186, 2003

Key words: copolymerization; activation energy; radical polymerization

INTRODUCTION

Polymers derived from acrylic/methacrylic monomers are an important class of functional polymers for their wide range of applications. Acrylic polymers find extensive applications due to the combination of durability, versatility, and the ability to tailor-make molecules for specific end use.^{1–3} Acrylate homopolymers along with their copolymers are used in various fields such as thin films, fibers, filament coatings, lithography, lacquers, adhesives, printing inks, and binders.^{4–7} Acrylic polymers are a class of reactive polymers that finds extensive applications due to the presence of electron-attracting groups in the aromatic ring.^{8–10} The activated acrylate polymers find applications in pharmacological drugs as polymer supports, which are easily degradable, and in the binding of drugs into existing natural and synthetic polymers.^{11–13}

Poly(phenyl methacrylamide) is a distinct class of functional polymers, which finds a variety of applications because of the presence of a phenyl ring, which can undergo many substitution reactions, thus giving a wide scope for synthesizing tailor-made polymers. Imai et al.¹⁴ synthesized polycinnamides with aromatic diiodides using a palladium catalyst. Yoshi-

hiro^{15,16} developed a waterless photosensitive planographic plate using phenyl methacrylamide polymers containing an *o*-quinonediazide/diazo component. Tawfik et al.¹⁷ studied the effect of the substitution of some new *p*-phenyl acrylamide derivatives with organotin monomers. *N*-Substituted *N*-allyl methacrylamide and acrylamides were reported to give polymers containing a cyclic structure in radical polymerization.¹⁸ Sato et al.¹⁹ studied the effect of SnCl₄ on the radical polymerization of *N*-allyl-*N*-phenyl acrylamide. Yoshio and Shigeki²⁰ obtained a patent on the process for the synthesis of an *m*-substituted *N,N*-diphenyl acrylamide polymer and its production. A chlorophenyl acrylamide-based optically active helical polymer through asymmetric synthesis was reported.²¹ Takashi et al.²² prepared a water-soluble electron-beam resist based on phenyl acrylamide precursors.

Copolymerization of butyl vinyl ether with methyl methacrylate (MMA) by combination of radical and radical-promoted cationic mechanisms under photochemical conditions was reported by Braun et al.²³ Functional copolymers²⁴ of MMA and 4-hexyloxy-1-phenyloxy carbonyl-1,4-phenylene ethene were synthesized and tested for their liquid crystalline properties. Photoresist based on the copolymers of 4-(4'-chlorocinnamoyl)phenyl methacrylate with MMA was reported by Balaji et al.²⁵ Hakim et al.²⁶ carried out high-temperature solution polymerization of butyl acrylate with MMA. Thamazharasi et al.²⁷ synthesized the copolymers of 4-chlorophenyl acrylate with MMA

Correspondence to: S. Venkata Naidu (challaninaidu@yahoo.com).

for application in leather as a top coat and a base coat. Copolymers of a Schiff base, 3-methoxy-4-methacryloxy benzal phenylimine²⁸ with MMA were synthesized and characterized. Complete kinetic analysis of the copolymerization was studied by examining the conversion, copolymer composition, and molecular weight over the temperature range of 60–140°C for the butyl acrylate/MMA system.²⁹ Copolymers of *p*-biphenyl acrylate with MMA were synthesized and characterized by Rami Reddy et al.³⁰ Mary and Rami Reddy³¹ reported the synthesis and characterization of copolymers of 3-hydroxy-4-acetyl phenyl methacrylate with MMA. Varma et al.³² synthesized the copolymers of MMA and lauryl methacrylate/cetyl methacrylate using benzoyl peroxide as an initiator. Water-soluble and photosensitive copolymers³³ from MMA and sodium-3-vinylphenyl azosulfonate were reported. Copolymerization of MMA with *p*-vinylbenzal polystyrene macromers was carried out by Takaki et al.³⁴ Copolymerization of MMA with ethylene glycol dimethacrylate at 70°C in the presence of chain-transfer reagents and kinetics were studied by Le et al.³⁵ Epple and Schneider³⁶ studied the radical copolymerization of methyl acrylate with a number of monomers containing different electron-donor groups in benzene/tetrahydrofuran (THF) at 60°C. Synthesis, characterization, and thermal degradation studies of styrene/MMA were reported by Rao et al.³⁷ Patel et al.³⁸ synthesized the copolymers of 2-hydroxy-4-acryloxy benzophenone with MMA and the reactivity ratios were determined. Free-radical solution copolymerization of *N*-phenyl methacrylamide and MMA at 70°C using benzoyl peroxide as a free-radical initiator and their characterization using IR, ¹H-NMR, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and monomer reactivity ratios are reported.

EXPERIMENTAL

Materials

Methacrylic acid (Merck, Hyderabad, India), benzoyl chloride (S.D. Fine Chem., Bangalore, India), aniline (Merck), and triethylamine (S.D. Fine Chem.) were purified according to standard procedures.³⁹ Methacryloyl chloride was prepared by Stampel et al.⁴⁰ using methacrylic acid and benzoyl chloride. MMA (Merck) was distilled under a vacuum to remove the inhibitor and impurities. Benzoyl peroxide (Merck) was recrystallized from a chloroform–methanol (1:1) mixture used as an initiator. The solvents were purified by distillation.

Synthesis of *N*-phenyl methacrylamide (PMA)

Aniline (0.1 mol), triethylamine (0.12 mol), and ethyl methyl ketone (100 mL) were taken in a 250-mL

round-bottom flask equipped with a magnetic stirrer, dropping funnel, and thermometer. The reaction mixture was cooled to 0–4°C using an ice and salt mixture. Then, 0.12 mol of methacryloyl chloride in ethyl methyl ketone (50 mL) was added dropwise to the reaction mixture over a period of 1 h while maintaining the temperature of the reaction mixture at 0–5°C. After the addition, the reaction mixture was stirred for 1 h at the same temperature and then at room temperature for 4 h. After removing the formed solid quaternary ammonium salt, the solution was transferred to a separating funnel, washed thoroughly with each of the following: a 5% sodium hydroxide solution, dilute hydrochloric acid, and water, and then dried over anhydrous sodium sulfate. On evaporation of the solvent, solid phenyl methacrylamide was obtained. It was washed with petroleum ether and recrystallized in an ethanol–water mixture. The formation of phenyl methacrylamide was confirmed by IR and proton NMR spectroscopic techniques. Yield: 70%.

The IR spectrum of PMA exhibits bands at 3434, 888, and 756 cm⁻¹ which are due to N–H stretching, N–H wagging, and out-of-plane N–H bendings, respectively. The absorption at 1662 cm⁻¹ is assigned to carbonyl stretching of the amide moiety. The peak at 1324 cm⁻¹ is due to the C–N stretching. The band at 1634 cm⁻¹ indicates the presence of the C=C of vinyl groups.

The ¹H-NMR spectrum of PMA contains resonance signals at 5.71–5.78 ppm and 6.30–6.38 ppm due to vinyl (CH₂=C) protons. The aromatic protons are observed as a multiplet in the range of 7.11–7.61 ppm. The singlet at 2.04 ppm corresponds to the α-methyl group.

Copolymerization of PMA and MMA

Polymerizations were carried out in Pyrex glass tubes containing an inlet and an outlet for the passage of nitrogen. The copolymers were synthesized using PMA and MMA. The copolymerization was carried out in *N,N*-dimethylformamide at 70°C using benzoyl peroxide as an initiator by varying the feed ratio of the monomers. Predetermined quantities of the monomers, initiator, and solvent were mixed in a reaction tube. The reaction mixture was deaerated by passing nitrogen gas for 20 min and sealing the tubes to ensure an inert atmosphere in the polymerization tubes. The sealed tubes were kept in a thermostated water bath at 70 ± 0.1°C. To maintain the copolymer composition in the same ratio throughout the polymerization, the molar conversion of monomer to polymer was restricted to less than 10% by precipitating the polymerization mixture in water for an appropriate time. Pouring the reaction mixture into the nonsolvent stopped the polymerization and the precipitated polymer was filtered. All the copolymers were purified by dissolving

TABLE I
Feed and Copolymer Composition of PMA and MMA Copolymers

Sample	M_1	M_2	m_1	m_2
PMA-MMA ₁	0.848	0.152	0.629	0.371
PMA-MMA ₂	0.592	0.408	0.303	0.697
PMA-MMA ₃	0.482	0.518	0.370	0.630
PMA-MMA ₄	0.383	0.617	0.354	0.646
PMA-MMA ₅	0.293	0.707	0.298	0.702
PMA-MMA ₆	0.210	0.790	0.185	0.815
PMA-MMA ₇	0.065	0.935	0.073	0.927

M_1 and m_1 are the mol fractions of PMA in the feed and copolymer, respectively. M_2 and m_2 are the mol fractions of MMA in the feed and copolymer, respectively.

in *N,N*-dimethylformamide and reprecipitated in water. The same was repeated three times and the mixture was finally dried under a vacuum at room temperature for 3 days.

Characterization methods

IR spectra of the monomers and polymers as KBr pellets or in a chloroform solution were recorded on a Perkin-Elmer 983 G infrared double-beam spectrophotometer. High-resolution ¹H-NMR spectra were obtained with a Bruker 500-MHz FT-NMR spectrometer at room temperature in a CDCl₃/DMSO(d) solution for all the copolymers and PMA. Tetramethylsilane (TMS) was used as the internal reference. The weight and number-average molecular weights of the copolymers were determined by a Waters 501 gel permeation chromatograph equipped with a differential refractometer index (RI 401) detector and ultra-Styrigel columns. THF was used as the mobile phase. Poly(MMA) standards from Millipore were used for calibration. TGA of the copolymers was carried out using a Shimadzu DT 50 thermal analyzer. Thermograms were recorded in a nitrogen atmosphere at a heating rate of 10°C/min. The glass transition temperature of the copolymers and homopolymers were measured using a Shimadzu DT 50 differential scanning calorimeter at a heating rate of 10°C/min in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Characterization of poly(PMA)

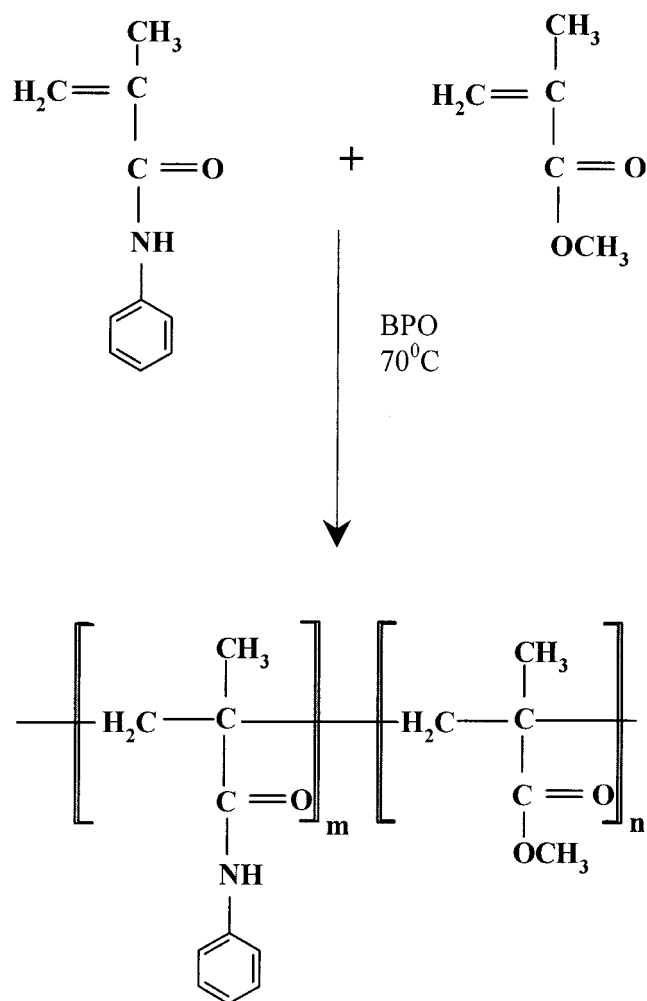
Poly(PMA) was prepared by free-radical solution polymerization using the benzoyl peroxide initiator in *N,N*-dimethylformamide in a thermostat water bath maintained at 70°C. The polymerization was stopped at 15% yield of the polymer by precipitating the polymer in the nonsolvent, water. The polymer was purified by repeatedly precipitating in the nonsolvent and

finally dried under a vacuum at room temperature for 3 days.

The IR spectrum of poly(PMA) exhibits bands at 3392, 987, and 750 cm⁻¹, which are due to N—H stretching, N—H wagging, and out-of-plane N—H, bending, respectively. The absorptions at 1452 and 1403 cm⁻¹ are due to the C—H and terminal CH₂ scissorings, respectively. The peak at 1324 cm⁻¹ is due to the C—N stretching of amide.

The ¹H-NMR spectrum of the poly(PMA) homopolymer shows a peak at 9.0 ppm corresponding to the N—H proton. The aromatic protons are observed as a multiplet in the range of 7.0–7.6 ppm. The singlet at 2.6 corresponds to the two protons of the CH₂ group present in the PMA. The peak at 0.8–1.2 ppm shows the presence of CH₃ protons.

The number-average and weight-average molecular weights and molecular weight distribution (MWD) of PMA, determined by GPC, were 34,340, 69,700, and 2.030, respectively. The glass transition temperature of poly(PMA) from the DSC thermogram was 147°C.



Scheme 1 Copolymerization of PMA and MMA.

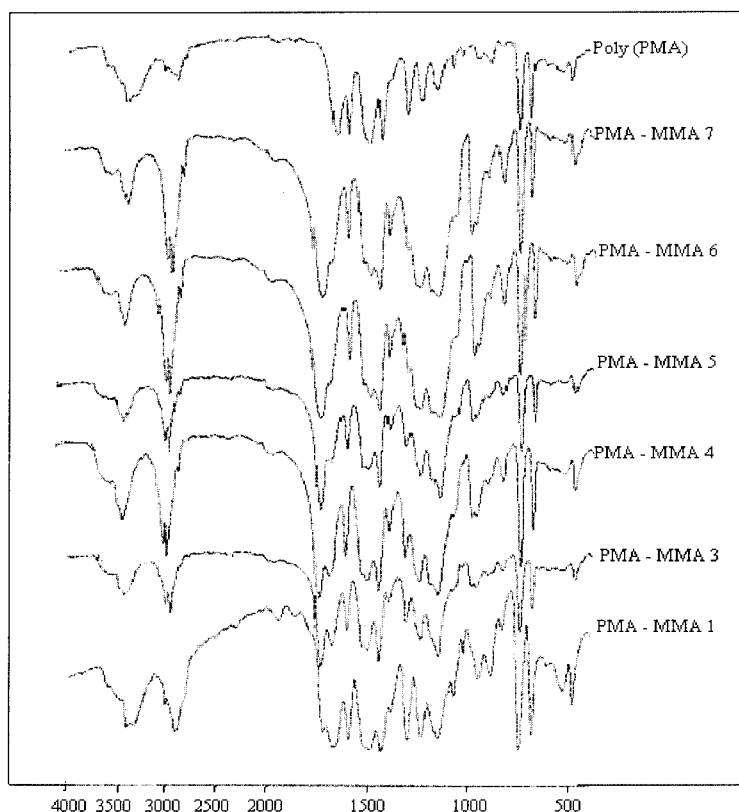


Figure 1 IR spectra of PMA-MMA copolymers.

Copolymerization of PMA and MMA

Copolymerization of PMA and MMA in *N,N*-dimethylformamide was carried out by varying the mol fraction of PMA from 0.864 to 0.073 in the feeds using benzoyl peroxide as an initiator at 70°C under a nitrogen atmosphere. The reaction time was restricted by trials to give conversions less than 10 wt %, to satisfy the differential copolymerization equation. The feed

ratio of the monomers PMA and MMA are presented in Table I. The PMA and MMA copolymer structure is shown in Scheme 1.

Copolymer characterization

The copolymers containing different amounts of PMA and MMA were soluble in chloroform, dimethyl sul-

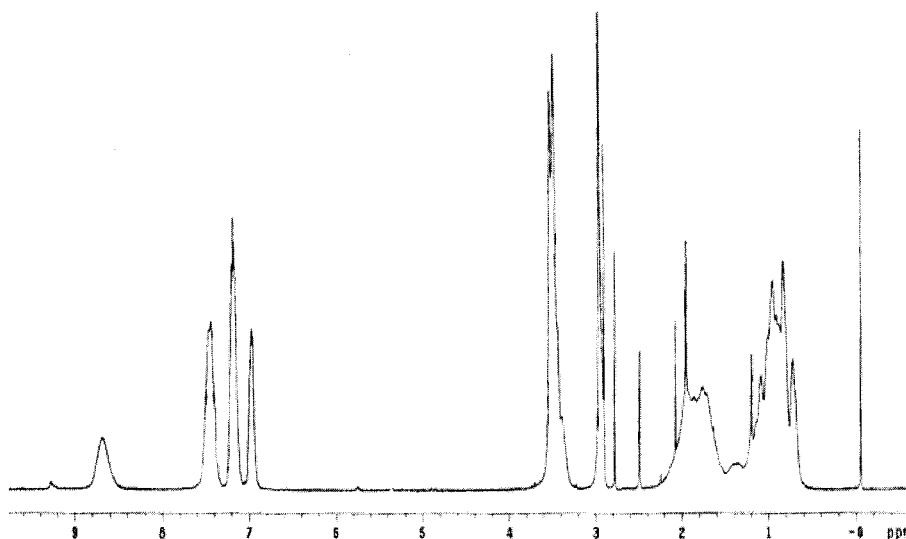


Figure 2 $^1\text{H-NMR}$ spectrum of copolymer PMA-MMA₃.

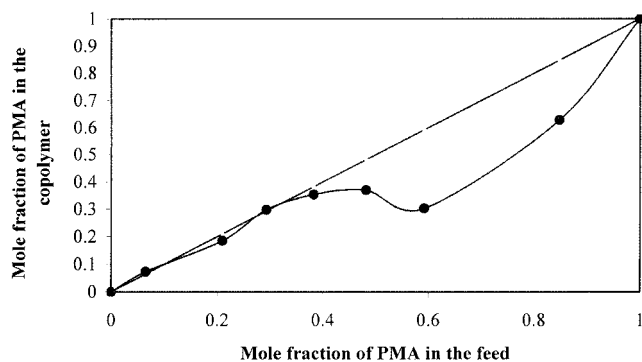


Figure 3 Variation of PMA mol fraction in the feed with copolymer.

foxide, dimethylformamide, THF, and butane-2-one and insoluble in hexane, heptane, petroleum ether, and water. Samples 1–3 were soluble in methanol, whereas 4–7 were insoluble in methanol.

The IR spectra (Fig. 1) of the PMA–MMA copolymers exhibit bands at 3575, 986, and 751 cm^{-1} , which are due to N–H stretching, N–H wagging, and out-of-plane N–H bending, respectively. The absorption at 2963 cm^{-1} indicates CH_3 stretching. The absorption at 1598 cm^{-1} is assigned to carbonyl stretching of the amide moiety. The absorptions at 1478 and 1438 cm^{-1} are due to C–H scissoring and terminal CH_2 scissoring, respectively. The peak at 1386 cm^{-1} is due to the C–N stretching of amide. The absorption at 1726 cm^{-1} corresponds to the ester carbonyl group of MMA.

$^1\text{H-NMR}$ spectra of PMA–MMA copolymers

Proton nuclear magnetic resonance spectroscopy helps in the elucidation of the structure of the copolymer. The spectra of PMA–MMA copolymers with different compositions are presented in Figure 2. The aromatic protons are observed as a multiplet in the range of 7.0–7.6 ppm. The two singlets at 1.9 and 2.4 ppm correspond to the two protons of CH_2 groups present in the PMA and MMA, respectively. The resonance signal at 3.5 ppm corresponds to the methoxy

TABLE III
Reactivity Ratios of PMA and MMA

Method	r_1	r_2	$1/r_1$	$1/r_2$	$r_1 r_2$
F–R method	0.164	0.788	6.098	1.269	0.129
K–T method	0.180	0.798	5.556	1.253	0.144
Average	0.172	0.793	5.814	1.261	0.136

protons. The peaks in between 0.7 and 1.0 ppm show the presence of $\alpha\text{-CH}_3$ protons of PMA and MMA.

Copolymer composition

The average composition of the copolymers of PMA and MMA at different feed ratios was determined using $^1\text{H-NMR}$ spectroscopy. The assignment of resonance peaks allows accurate determination of the content of the each kind of monomeric unit incorporated into the copolymer chain. Thus, the mol fraction of the PMA in the copolymer chain is determined from the integrated intensities of the aromatic protons (7.1–7.9 ppm) of PMA and the intensity of the aliphatic protons (0.7–4.1 ppm) present in both the monomeric constituents in the copolymer.

Let m_1 be the mol fraction of PMA and $1 - m_1$ be that of MMA. There are five aromatic protons, five aliphatic protons in PMA, and 10 aliphatic protons in MMA. Therefore,

$$\frac{5m_1}{5m_1 + 10(1 - m_1)} = \frac{\text{intensity of aromatic protons}}{\text{intensity of aliphatic protons}} = C \rightarrow \quad (1)$$

On simplification, we have

$$m_1 = \frac{8C}{5 + 3C} \rightarrow \quad (2)$$

The mol fractions of PMA and MMA monomeric constituents in the copolymer calculated using eq. (2) are presented in Table I. To ascertain the normal co-

TABLE II
F–R and K–T Parameters for PMA–MMA Copolymers

Sample	F–R parameters		K–T parameters	
	$G = X(Y - 1)/Y$	$H = X^2/Y$	$\eta = G/(\alpha + H)$	$\xi = H/(\alpha + H)$
PMA–MMA ₁	2.293	18.430	0.118	0.946
PMA–MMA ₂	–1.888	4.836	–0.320	0.820
PMA–MMA ₃	–0.652	1.475	–0.257	0.582
PMA–MMA ₄	–0.510	0.703	–0.289	0.398
PMA–MMA ₅	–0.564	0.404	–0.384	0.276
PMA–MMA ₆	–0.904	0.312	–0.658	0.227
PMA–MMA ₇	–0.810	0.061	–0.721	0.055

$$\alpha = \sqrt{H_{\min}}; \Delta H_{\max} = 1.0614; X = M_1/M_2; Y = m_1/m_2.$$

TABLE V
Thermal Properties of the Copolymers of PMA-MMA

Sample	IDT (°C)	T_{\max} (°C)	FDT (°C)	Weight loss (%)				
				10	30	50	70	90
PMA-MMA ₁	295	437	495	318	370	409	438	445
PMA-MMA ₃	290	422	490	317	388	410	422	462
PMA-MMA ₄	286	410	488	344	370	398	410	430
PMA-MMA ₅	285	408	480	310	350	388	408	440
PMA-MMA ₆	282	407	475	311	354	382	407	419
PMA-MMA ₇	280	389	480	312	362	380	389	408

IDT, initial degradation temperature; FDT, final degradation temperature; T_{\max} , temperature at which the degradation is maximum.

polymer kinetic behavior, a plot was drawn (Fig. 3) between the mol fraction of the PMA in the feed and copolymer. These polymers somewhat followed the ideal copolymerization up to PMA mole fraction 0.35. Then the copolymers are richer with MMA units.

Copolymerization reactivity ratios

Reactivity ratios are the most important parameters for composition evaluation of copolymers, which can offer information such as the relative reactivity of monomer pairs and estimate the copolymer composition. From the monomer feed ratio and the resultant copolymer compositions, the reactivity ratios of monomers PMA and MMA were estimated by the methods of Fineman-Ross (F-R)⁴¹ and Kelen-Tudos (K-T).⁴²

The values of the F-R plot and the K-T plot are presented in Table II. The reactivity ratios of the monomers from the F-R and K-T methods are presented in Table III.

The reactivity ratios of PMA and of MMA indicate that PMA is less reactive than MMA. Thus, the copolymer formed is richer in MMA. The product of the reactivity ratios of PMA and MMA (0.136) infers that the copolymer should have a random distribution of monomeric units⁴³ in the copolymer chain. The reactivity of the growing radicals of both monomeric ends preferentially add to the MMA monomer, thus leading to the formation of a copolymer with a higher content of MMA, because the rate of homopropagation in the case

of MMA is higher than that of PMA and the rate of cross-propagation reaction is higher in the case of PMA.

MWD measurements

The number-average (M_n), weight-average molecular weights (M_w), and MWD of the copolymers, determined by GPC, are presented in Table IV. The theoretical values of the MWD for the polymers produced via radical combination and disproportionation are 1.5 and 2.0, respectively.⁴⁴ The values of the polydispersity index of the copolymers of PMA and MMA are nearly equal to 2, which infers a strong tendency for chain termination by disproportionation.

Thermal studies

The thermal stability of the copolymers was studied by TGA from room temperature to complete degrada-

TABLE IV
Molecular Weight Measurements
of PMA-MMA Copolymers

Sample	M_n	M_w	MWD
PMA-MMA ₁	21,020	41,980	1.997
PMA-MMA ₂	28,100	57,160	2.034
PMA-MMA ₃	24,630	49,670	2.017
PMA-MMA ₄	34,180	68,830	2.014
PMA-MMA ₅	30,370	60,480	1.992
PMA-MMA ₆	47,540	10,370	2.181
PMA-MMA ₇	42,910	88,810	2.070

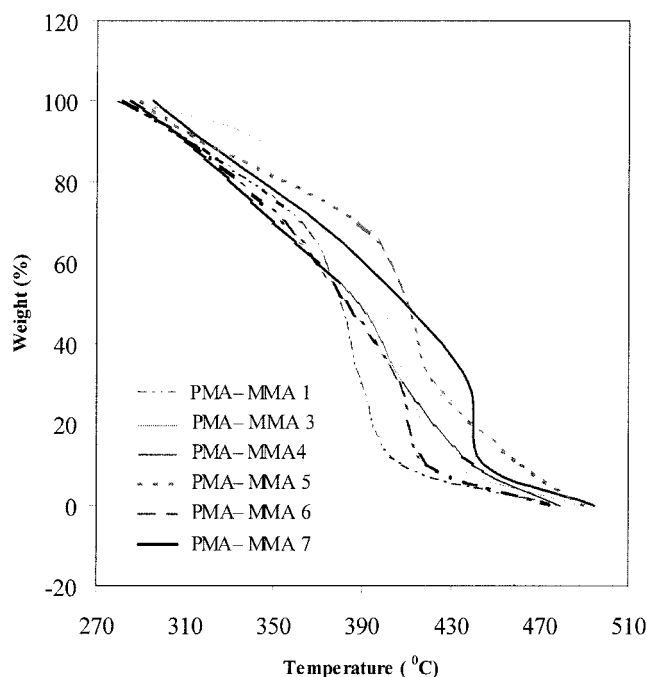


Figure 4 TGA plots of the copolymers of PMA and MMA.

TABLE VI
Activation Energy of the Copolymers of PMA and MMA

Sample	Temperature range (°C)	Activation energy (kJ/mol)		Glass transition temperature (°C)
		Broido's method	Horowitz's method	
PMA-MMA ₁	318-445	73.3	85.1	145.6
PMA-MMA ₃	317-462	78.5	88.3	143.9
PMA-MMA ₄	344-430	98.1	102.8	141.4
PMA-MMA ₅	310-440	80.4	89.5	140.9
PMA-MMA ₆	311-419	79.8	88.4	138.9
PMA-MMA ₇	312-418	105.1	116.6	135.5

tion. The degradation characteristics based on the TGA data are presented in the Table V. The TGA curves of the copolymers of PMA and MMA shown in the Figure 4 clearly indicate that the polymers undergo single-stage decomposition. The initial decomposition temperatures of the copolymers varied from 290 to 280°C, which depends on the PMA composition in the copolymer. As the PMA mol fraction in the copolymer composition increased, the thermal stability of the copolymers increased. The increment in the initial degradation temperature and final degradation temperature with increase of the PMA mol fraction in the copolymer may be attributed to the increase of phenyl groups in the copolymer. The activation energy of the copolymers using the TGA data was calculated by Broido's⁴⁵ and Horowitz's⁴⁶ methods and are presented in Table VI and the Broido and Horowitz's plots are presented in the Figures 5 and 6, respectively.

The glass transition temperatures of the copolymers are presented in Table VI. The glass transition temperature of the copolymers lies between the homopolymers of PMA (147°C) and MMA (105°C). All the copolymers show a single T_g , indicating the absence of the formation of the mixture of homopolymers or the

formation of a block copolymer. The increase of T_g with the mol fraction of PMA is due to the synergetic effect of the phenyl groups' restriction to the chain mobility and intermolecular force of attraction between the monomeric units of the copolymer. The plot (Fig. 7) drawn between the T_g and the mol fraction of the PMA monomer in the copolymer shows nonlinearity with positive deviation from simple additivity, because favorable specific interactions between PMA and MMA in the copolymers may cause a negative volume of mixing or densification; a reduction in the free volume may result in a higher T_g .^{47,48}

CONCLUSIONS

Poly(PMA) and the copolymers of PMA and MMA were synthesized by free-radical solution polymerization using the benzoyl peroxide initiator. The copolymers were structure-elucidated by IR and ¹H-NMR spectroscopic techniques. The solubilities of the polymers were tested in different organic solvents. Copolymer compositions were determined by ¹H-NMR analysis. F-R and K-T methods were used to evaluate

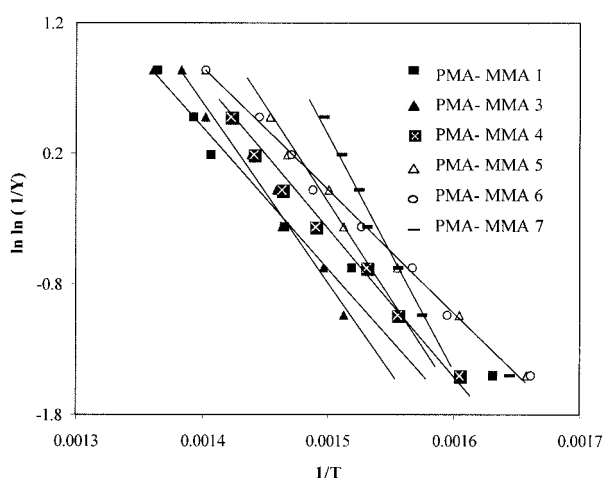


Figure 5 Broido's plots for the copolymers of PMA and MMA.

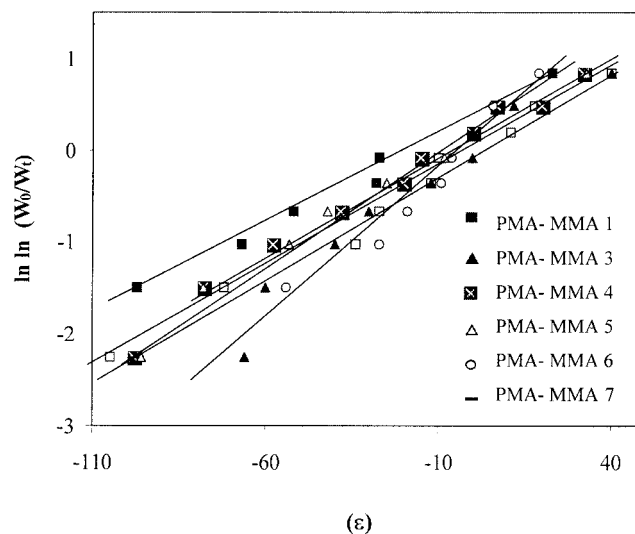


Figure 6 Horowitz's plots for the copolymers of PMA and MMA.

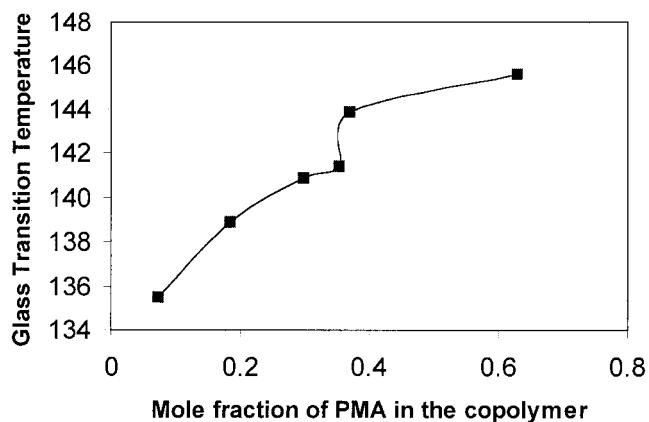


Figure 7 Variation of glass transition temperature with mol fraction of PMA.

the reactivity ratios of PMA and MMA and the values strongly suggest that the growing radicals of both monomeric ends preferentially add to the MMA monomer, thus leading to the formation of a copolymer with a higher amount of MMA. GPC data infer that the polydispersity index of the copolymers is nearly equal to 2, which infers a strong tendency for chain termination by disproportionation. Thermogravimetric studies indicated that the initial degradation temperature of the copolymers increases with increase of the PMA content in the copolymer. The activation energy of the decomposition of the copolymers was calculated by Broido's and Horowitz's methods using the TGA data. The glass transition temperature of the PMA-MMA copolymers lies between the homopolymers of PMA and MMA and glass transition temperature of the copolymer increases with increase of the mol fraction of PMA in the copolymer and the variation is nonlinear.

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