

# Copolymerization of *N*-(4-bromophenyl)-2-methacrylamide with *n*-Butyl Methacrylate: Synthesis, Characterization and Monomer Reactivity Ratios

Ali Delibaş, Cengiz Soykan

Department of Chemistry, Faculty of Science and Arts, University of Bozok, Yozgat/Turkey

Received 27 March 2007; accepted 12 June 2007

DOI 10.1002/app.27054

Published online 19 September 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The monomer, *N*-(4-bromophenyl)-2-methacrylamide (BrPMAAm) has been synthesized by reacting 4-bromoaniline with methacryloyl chloride in the presence of triethylamine (NR<sub>3</sub>) at 0–5°C. Copolymerization of BrPMAAm with *n*-butyl methacrylate (*n*-BMA) has been carried out in 1,4-dioxane by free radical solution polymerization at (70 ± 0.1)°C utilizing 2,2'-azobisisobutyronitrile (AIBN) as an initiator in different in-feed ratios. The composition of the copolymer was determined by the elemental analysis. The comonomer reactivity ratios determined by Fineman-Ross (FR), Kelen-Tüdös (KT), and extended Kelen-Tüdös (EKT) methods. The copolymers were characterized by FTIR, <sup>1</sup>H-, and <sup>13</sup>C NMR spectroscopic technique. Gel permeation chromatography was employed for estimating the weight-average ( $M_w$ ) and number-average ( $M_n$ ) molecular weights and polydispersity index (PDI) of

the copolymers. Glass transition temperatures ( $T_g$ ) were determined by differential scanning calorimetry and found to be characteristic of copolymer composition. As the *N*-(4-bromophenyl)-2-methacrylamide content increases, the  $T_g$  increases from 339 to 437 K. Thermal stabilities of the homo- and copolymers were calculated using thermogravimetric analysis. Thermally stable copolymers were obtained by the incorporation of BrPMAAm units as the initial decomposition temperature of the copolymers increased with the increase in concentration of BrPMAAm units. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 364–371, 2008

**Key words:** *N*-(4-bromophenyl)-2-methacrylamide; monomer reactivity ratios; thermogravimetry; gel permeation chromatography

## INTRODUCTION

It has been well documented that copolymerization is one of the important techniques used in affecting systematic changes in the properties of the commercially important polymers. If primary or secondary amines are used in the reaction with methacryloyl chloride, acrylamides, or methacrylamides are formed. Because of the high nucleophilicity of amines, the reaction can be carried out at room temperature and is finished shortly after the addition of the polymeric acyl chloride to the amine solution. An excess of the amino nucleophile or a tertiary amine can be used to neutralize the hydrogen chloride.<sup>1</sup> Phenyl acrylates and phenylacrylamides are considered as reactive monomers primarily because of the presence of the aromatic ring.<sup>2</sup> The copolymers based on halogenated phenyl acrylate and phenyl acrylamide have been utilized for synthesizing electroactive polymers for the preparation of polymeric reagents carrying

piperazine and isonitrile functionalities.<sup>3–6</sup> Copolymers synthesized from 2,4,6-tribromophenyl acrylate showed higher reactivity due to the presence of electronegative bromine atoms in the aromatic ring.<sup>7</sup> The introduction of ester or amid linkages in the polymer backbone renders the resulting polymers hydrolytically, photo- or biodegradable. However, the polymers obtained by conventional radical polymerization generally have uncontrolled molecular weight and broad molecular weight distribution.<sup>8</sup> The chemical composition of the copolymers depends on the degree of incorporation of the comonomers and also on the relative reactivity between them. Monomer reactivity ratios are very important quantitative values to predict the copolymer composition for any starting feed and to understand the kinetic and mechanistic aspects of copolymerization. The accurate estimation of copolymer composition and determination of monomer reactivity ratios are significant for tailor-made copolymer with required physical, chemical properties, and in evaluating the specific end application of copolymers. Copolymerization modulates both the intramolecular and intermolecular forces exercised between like and the unlike polymer segments. Therefore, properties such as the glass transition temperature, melt point, solubility,

Correspondence to: C. Soykan (soykan@erciyes.edu.tr).

Contract grant sponsor: Erciyes University Research Fund; contract grant number: EÜBAP-FBT-04-54.

*Journal of Applied Polymer Science*, Vol. 107, 364–371 (2008)  
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TABLE I  
Monomer Compositions in Feed and in Copolymer

Sample code no	Feed composition in mole fraction		Conversion (%)	Elemental (N, %)	Copolymer composition in mole fraction	
	BrPMAAm ( $M_1$ )	<i>n</i> -BMA ( $M_2$ )			BrPMAAm ( $m_1$ )	<i>n</i> -BMA ( $m_2$ )
1	1.00	–	–	–	1.00	–
2	0.90	0.10	13.8	4.907	0.76	0.24
3	0.75	0.25	14.6	4.510	0.67	0.33
4	0.60	0.40	12.4	3.940	0.55	0.45
5	0.40	0.60	10.8	2.207	0.26	0.74
6	0.25	0.75	10.2	1.148	0.13	0.87
7	0.10	0.90	13.4	0.336	0.04	0.96
8	–	1.00	–	–	–	1.00

crystallinity, permeability, adhesion, elasticity, and chemical reactivity may be varied within wide limits.<sup>9</sup> Most existing procedures for calculating reactivity ratios can be classified as linear least-squares (LLS), and nonlinear least-squares (NLLS) methods. It is accepted that LLS methods such as those proposed by Finemann and Ross<sup>10</sup> and by Kelen and Tüdös,<sup>11</sup> can only be applied to experimental data at sufficiently low conversion, because the calculation is based on the differential copolymerization equation.<sup>12,13</sup> The only LLS method, as an exception, is an extended Kelen-Tüdös method,<sup>14</sup> which involves a rather more complex calculation.

The copolymerizability of vinyl monomers with a bulky substituent that also carries a highly electronegative atomlike nitrogen and, electronegative halogenlike bromo is not discussed as yet. The possible effect of such a pendant group as the backbone with respect to reactivity is significant. Most of the polymers are produced by free-radical polymerization. This technology has advantages such as versatility, simplicity, compatibility with many functional groups, and tolerance to impurities as well as polar and nonpolar polymerization media. As disadvantage, the copolymers obtained are, in general, heterogeneous with very limited control over the molar mass, constitution, and chain architecture. The growing market of well-defined materials has become the driving force for the renaissance to study free-radical polymerizations in terms of both synthetic possibilities and mechanistic understanding.<sup>15,16</sup>

In our earlier study, the new methacrylamide monomer and the copolymers derived from 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) were investigated.<sup>17</sup> In this work, the synthesis and characterization of novel copolymers obtained from BrPMAAm and *n*-BMA and their reactivity ratios were evaluated for six different copolymer compositions by Fineman-Ross (FR), Kelen-Tüdös (KT), and extended Kelen-Tüdös (EKT) methods. The thermal properties investigated by thermogravimetry (TG)

and differential scanning calorimetry (DSC) for different polymer compositions are discussed.

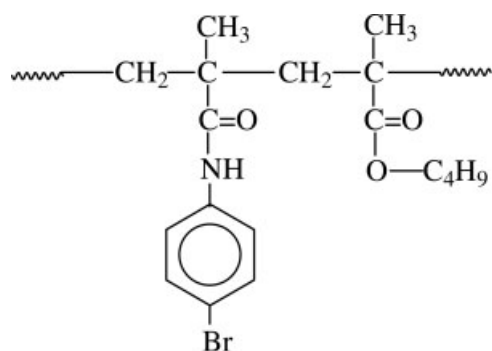
## EXPERIMENTAL

### Materials

BrPMAAm monomer was prepared as reported.<sup>17,18</sup> *n*-butyl methacrylate (*n*-BMA) monomer (Aldrich) were freed from the inhibitor by washing successively with 5% NaOH solution followed by distillation under reduced pressure. Triethylamine (Fluka) was distilled and the fraction boiling at 88–89°C was collected and used. 2,2'-Azobisisobutyronitrile (AIBN) (Merck) was recrystallized from chloroform methanol. 1,4-Dioxane, chloroform, tetrahydrofuran (THF), and ethanol (Merck) were analytical grade commercial products and used as received.

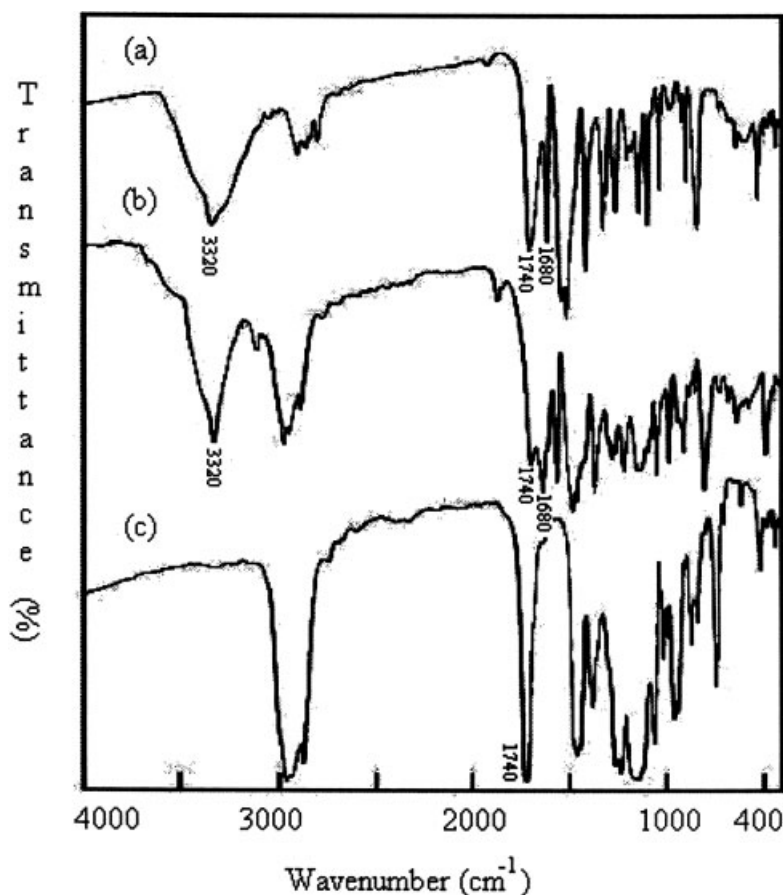
### Characterization techniques

Infra-red spectra were obtained with a Jasco 460 Plus FTIR spectrometer using KBr pellets in 4000–



Poly(BrPMAAm-co-*n*BMA)

Scheme 1 The structure monomeric units of the polymer.



**Figure 1** FTIR spectrum of (a) poly(BrPMAAm), (b) poly(BrPMAAm-co-nBMA) (0.26 : 0.74), and (c) poly(nBMA).

400  $\text{cm}^{-1}$  range, where 10 scans were taken at 4  $\text{cm}^{-1}$  resolution.  $^1\text{H}$  NMR spectra in  $\text{DMSO-}d_6$  solution were recorded on a Varian Gemini 200 MHz spectrometer with tetramethylsilane (TMS) as an internal reference. Thermal data were obtained using a Setaram DSC-131 instrument at a heating rate of 20  $^{\circ}\text{C min}^{-1}$  and Labsys TGA thermobalance at a heating rate of 10  $^{\circ}\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere. Elemental analyses were carried out by a LECO-932 microanalyzer. Molecular weight; ( $\bar{M}_w$  and  $\bar{M}_n$ ) of the polymers were determined using Waters 410 gel permeation chromatography equipped with a differential refractive index detector and calibrated with polystyrene standards.

### Copolymerization

Copolymerizations of BrPMAAm with *n*-BMA, having six different feed compositions, were carried out in 1,4-dioxane at ( $70 \pm 0.1$ )  $^{\circ}\text{C}$ , using AIBN (1%, based on the total weight of monomers) as an initiator. Appropriate amounts of BrPMAAm with *n*-BMA and 1,4-dioxane were mixed in a polymerization tube, purged with  $\text{N}_2$  for 20 min, and kept at ( $70 \pm 0.1$ )  $^{\circ}\text{C}$  in a thermostat. The copolymerization reac-

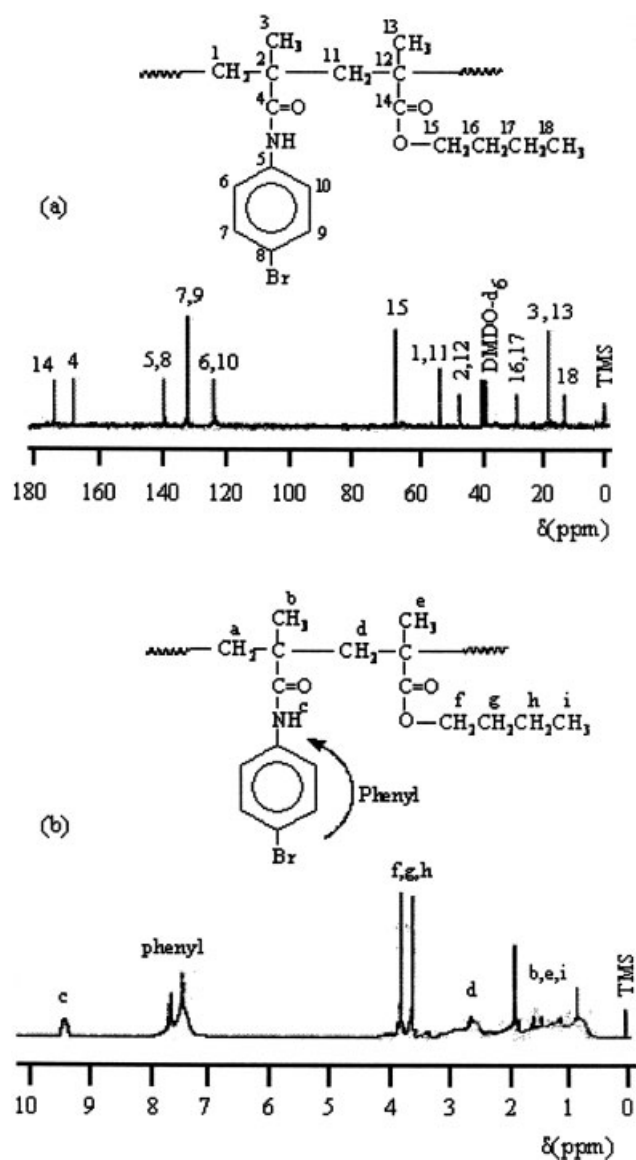
tions were carried out with different mole ratios of BrPMAAm and *n*-BMA (0.00 : 1.00 through 1.00 : 0.00). The reaction time (1 h) was selected to give conversions less than 10% to satisfy the differential copolymerization equation.<sup>15</sup> After the desired time the copolymers were separated by precipitation in ethanol-diethylether mixture and reprecipitated from 1,4-dioxane solution. The polymers were finally dried under vacuum at 40  $^{\circ}\text{C}$  to constant weight. The amounts of monomeric units in the copolymers were determined by elemental analysis (N content for BrPMAAm units). The results are presented in Table I.

## RESULTS AND DISCUSSION

The constituent monomeric units of the copolymer are shown in Scheme 1.

### Spectroscopic characterization

The FTIR spectra of the polymers are shown in Figure 1. The FTIR spectra confirmed the structure of polymers in all aspects. In the FTIR spectra of (a) and (b) the band at 3320  $\text{cm}^{-1}$  ( $-\text{NH}$  in the BrPMAAm unit) is the most characteristic for the



**Figure 2** (a)  $^{13}\text{C}$  NMR spectrum of poly(BrPMAAm-co-nBMA) (b)  $^1\text{H}$  NMR spectrum of poly(BrPMAAm-co-nBMA) [0.76 : 0.24].

polymer. The peak at  $3050\text{ cm}^{-1}$  corresponds to the C—H stretching of the aromatic system. The symmetrical and asymmetrical stretching due to the methyl and methylene groups are observed at 2985, 2940, and  $2865\text{ cm}^{-1}$ . The peak at  $1780\text{ cm}^{-1}$  is attributed to the ester carbonyl stretching of *n*-BMA units. The absorption at  $1720\text{ cm}^{-1}$  could be assigned for a complex stretching vibrations of C—O and C—N, while the strong absorption at  $1300\text{ cm}^{-1}$  could be attributed to predominantly C—O stretching. The broad band at  $1440\text{ cm}^{-1}$  could be due to the C—N scissoring vibration of the —N—C=O group. The ring-breathing vibrations of the aromatic nuclei are observed at 1600, 1505, and  $1470\text{ cm}^{-1}$ . The asymmetrical and symmetrical bending vibra-

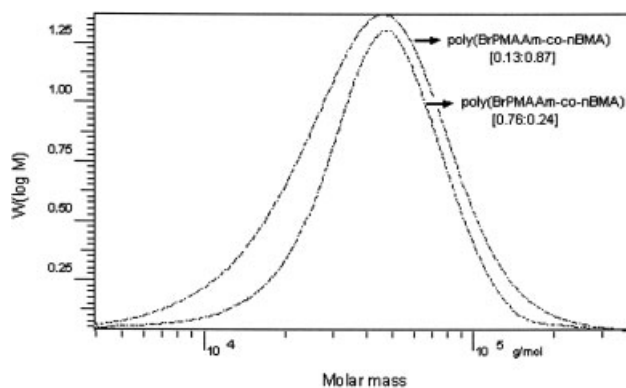
tions of methyl groups are seen at  $1455$  and  $1380\text{ cm}^{-1}$ . The C—H and C=C out of plane bending vibrations of the aromatic nuclei are observed at  $790$  and  $565\text{ cm}^{-1}$ , respectively. In the FTIR spectra (c) of *n*-BMA, the band at  $1780\text{ cm}^{-1}$  is the most characteristic for ester carbonyl of *n*-BMA units. The other characteristic bands confirmed the structure of *n*-BMA polymers in all aspects.

In the proton-decoupled  $^{13}\text{C}$  NMR spectra [Fig. 2(a)] of poly(BrPMAAm-co-*n*-BMA) [0.76 : 0.24]; the amide carbonyl of BrPMAAm appeared at 168.1 ppm ( $\text{C}_4$ ) while the ester carbonyl of *n*-BMA appeared at 176.2 ppm ( $\text{C}_{14}$ ). The aromatic carbons of BrPMAAm unit in copolymer appeared at 140.1 ( $\text{C}_5$ ,  $\text{C}_8$ ), 135.6 ( $\text{C}_7$ ,  $\text{C}_9$ ), and 127.0 ( $\text{C}_6$ ,  $\text{C}_{10}$ ) ppm, respectively. The signals due to the backbone methylene carbons atoms are observed at 53.22 ppm ( $\text{C}_1$  and  $\text{C}_{11}$ ). The butyl, methylene, and methyl carbon atoms of *n*-BMA unit appeared at 64.4 ( $\text{C}_{15}$ ), 44.4 ( $\text{C}_2$ ,  $\text{C}_{12}$ ), and 16.31 ( $\text{C}_{18}$ ) ppm, respectively. The  $\alpha$ -methyl carbon atoms of BrPMAAm appeared at 18.36 ppm ( $\text{C}_3$ ,  $\text{C}_{13}$ ).

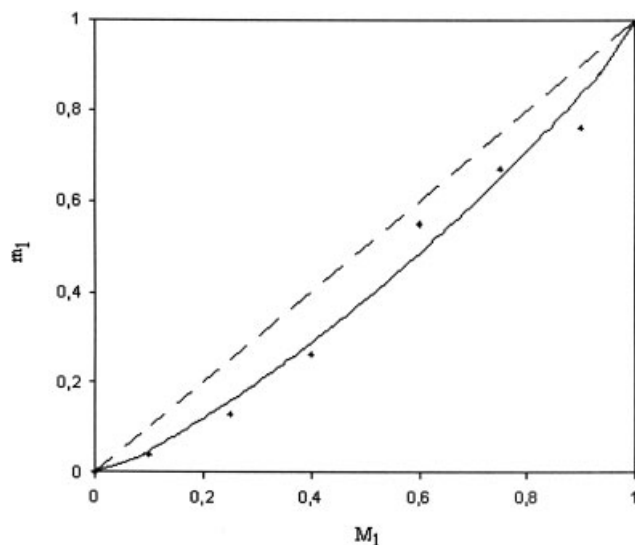
The  $^1\text{H}$  NMR spectrum [Fig. 2(b)] of poly(BrPMAAm-co-*n*-BMA) [0.76 : 0.24] is consistent with its chemical structure. The resonance signals at 9.5 ppm correspond to the NH protons of the BrPMAAm unit. The resonance absorptions at 7.8–7.2 ppm are due to the two types of aromatic ring protons of BrPMAAm unit. The signals at 3.6–3.8 ppm are due to the butyleneoxy protons of *n*-BMA. The backbone methylene protons of the two comonomer units are observed between 1.4 and 3.0 ppm. The  $\alpha$ -methyl protons of both types of monomer units are observed at 0.8–1.1 ppm.

### Determination of the solubility parameters

Solubility of the polymers was tested in various polar and nonpolar solvents. About 5–10 mg of the polymer was added to about 2 mL of different sol-



**Figure 3** The GPC curves of the investigated polymers.



**Figure 4** Copolymer composition diagram for poly (BrPMAAm-*co*-nBMA) system ( $M_1$ : Feed composition in mole fraction for BrPMAAm;  $m_1$ : Copolymer composition in mole fraction for BrPMAAm).

vents in a test tube and kept overnight with the test tube tightly closed. The solubility of the polymers was noted after 24 h. The polymers were soluble in chloroform, dimethylformamide, dimethylsulfoxide, tetrahydrofuran, and benzen, but insoluble in *n*-hexane, *n*-heptane, and hydroxyl group containing solvent such as methanol and ethanol.

The solubility parameters of the polymers were determined by using a titration method<sup>19</sup> at 25°C from a solubility test using THF as solvent and ethylalcohol and water as nonsolvent. The solubility parameters values of the copolymers are between 10.34 and 11.35 (cal/cm<sup>3</sup>)<sup>1/2</sup>. These values are close to 9.52 ± 1.5 (cal/cm<sup>3</sup>)<sup>1/2</sup>, which is tetrahydrofuran (THF) solubility parameter. The THF is the best solvent for all of the copolymers. The solubility parameters ( $\delta$ ) values are presented in Table III.

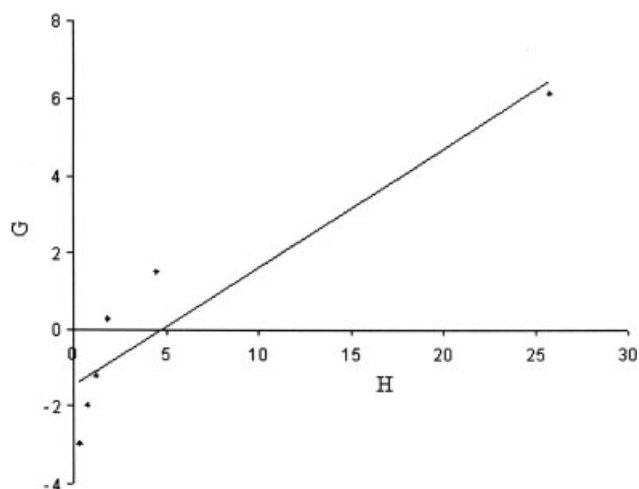
### Molecular weights of the polymers

The gel permeation chromatography (GPC) curves of the copolymers are shown in Figure 3. The GPC system calibrated with polystyrene in tetrahydrofuran (THF) showed that the weight-average molecular mass of the BrPMAAm-*co*-nBMA (13% BrPMAAm) was 74,913 (polydispersity index, PDI : 1.92). The weight-average molecular mass of the BrPMAAm-*co*-nBMA (76% BrPMAAm) was 52,838 (polydispersity index, PDI : 1.79). The PDIs of the polymers are close to 2.0. The theoretical values of PDI for polymers via radical recombination and disproportionation are 1.5–2.0, respectively.<sup>20,21</sup> This suggest that the polymers were produced mainly via termination of growing chain by disproportionation.

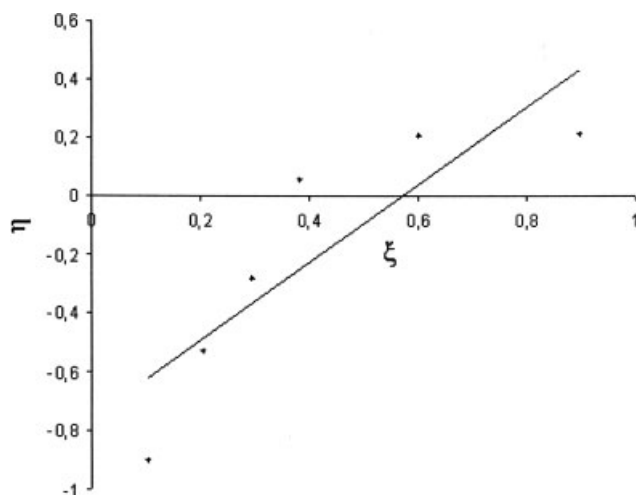
### Copolymer composition and monomer reactivity ratios

The monomer reactivity ratios for the copolymerization of BrPMAAm with *n*-BMA were determined from the monomer feed ratios and the copolymer composition. The classical approach for acquiring copolymer data was to isolate the copolymers from each of six feed compositions at early conversions and analyze the copolymer compositions by elemental analyses. The analytical data for copolymerization of BrPMAAm with AMPS as an example are illustrated in Table I. The plot of the mole fractions of BrPMAAm ( $M_1$ ) in the feed versus that in the copolymer ( $m_1$ ) is shown in Figure 4. It clearly indicates that the composition of BrPMAAm in the copolymer is always lower than that in the feed. The FR<sup>10</sup> and KT<sup>11</sup> methods were used to determine the monomer reactivity ratios. The graphical plots concerning the methods previously reported are given in Figures 5–7, whereas the reactivity ratios are summarized in Table II. The monomer reactivity ratios determined by conventional linearization methods are only approximate and are usually employed as good starting values for nonlinear parameter estimation schemes. In determination of the monomer reactivity studies, the curves of the FR, KT, and EKT methods are quite different from straight lines. Because, these methods are conventional linearization methods.

Because the value of  $r_1$  is less than 1 and the value of  $r_2$  is greater than 1, this indicates the presence of a lower amount of BrPMAAm units in the copolymer than in the feed. However, the product of  $r_1$  and  $r_2$  is greater than 1, which indicates that the system leads to random distribution of monomer units with a longer sequence of *n*-BMA units in the copolymer chain. Generally, neutral olefin molecules and

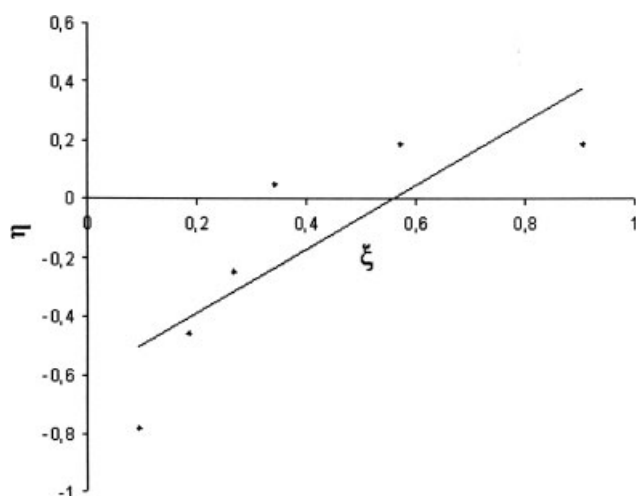


**Figure 5** FR plots for determining monomer reactivity ratios in copolymerization of BrPMAAm ( $M_1$ ) and AMPS ( $M_2$ ) data of elemental analysis.



**Figure 6** KT plots for determining monomer reactivity ratios in copolymerization of BrPMAAm ( $M_1$ ) and *n*BMA ( $M_2$ ) data of elemental analysis.

those olefin molecules containing moderately electron-donating or electron-withdrawing groups favor free radical polymerization. *n*-BMA consists of an electron-withdrawing ester group and electron-donating methyl group and attached to an olefin molecule, while BrPMAAm consists of electron withdrawing phenyl amide group and an electron-donating methyl group attached to an olefin molecule. But the net charge on the *n*-BMA molecule is less when compared with BrPMAAm, and therefore, the reactivity of *n*-BMA is more than that of BrPMAAm. Moreover, the relative reactivity of the comonomers has to be decided not only in terms of the electronic effects, but also in terms of the steric effects and the overall polarity of the molecule.



**Figure 7** Ext.KT plots for determining monomer reactivity ratios in copolymerization of BrPMAAm ( $M_1$ ) and *n*BMA ( $M_2$ ) data of elemental analysis.

**TABLE II**  
Copolymerization Parameters for the Free-Radical Copolymerization of BrPMAAm with *n*-BMA

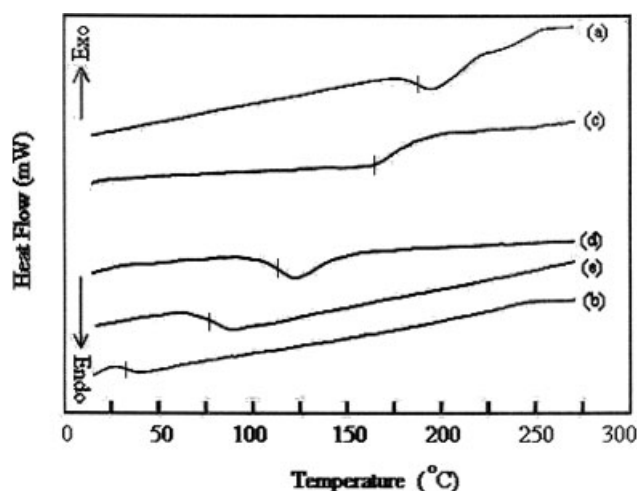
Method	$r_1^a$	$r_2^a$	$r_1 r_2$
Fineman-Ross	0.3068	1.4546	0.4463
Kelen-Tüdös	0.5722	2.2304	1.2762
Ext.Kelen-Tüdös	0.4869	2.2096	1.0758

<sup>a</sup>  $r_1$  and  $r_2$  are the monomer reactivity ratios of BrPMAAm and *n*-BMA, respectively.

### Differential scanning calorimetry experiments

The glass transition ( $T_g$ ) temperatures were determined by a Setaram 131 DSC. Samples of about 5–8 mg held in sealed aluminum crucibles and the heating rate of 20°C/min under a dynamic nitrogen flow (5 L h<sup>-1</sup>) were used for the measurements. From DSC measurements,  $T_g$  was taken as the midpoint of the transition region. All the copolymers show a single  $T_g$ , showing the absence of a mixture of homopolymers or the formation of a block copolymer. The  $T_g$  of poly(BrPMAAm) is 185°C and that of poly(*n*-BMA) is at 34°C. The result clearly indicates that the  $T_g$  values of copolymers depend on the composition of comonomers, and the value increases with increases in the mole fraction of BrPMAAm in copolymer. High  $T_g$  of the copolymers (Table III) in comparison with that of polystyrene ( $T_g = 95^\circ\text{C}$ ) indicates the substantial decrease of chain mobility of the copolymer due to bulky bromophenyl structural unit. The change in the  $T_g$  value of the copolymer is due to the substitutional effects of different groups in the backbone.

The DSC thermograms of polymers indicated endothermic degradation. Representative DSC ther-



**Figure 8** DSC thermograms of investigated copolymers; (a) poly(BrPMAAm), (c–e) poly(BrPMAAm-co-*n*-BMA): [0.76 : 0.24], [0.55 : 0.45], and [0.13 : 0.87], (e) poly(*n*-BMA).

TABLE III  
Summary of Solubility Parameters, DSC Parameters, and TGA Parameters of the Poly(BrPMAAm-co-*n*-BMA) System<sup>a</sup>

Sample	DSC				TGA % weight loss at		
	$\delta(\text{cal}/\text{cm}^3)^{1/2}$	$T_g$ (°C)	$\Delta H_o^d$ (J/g)	$\Delta C_p$ (J/gK)	250°C	350°C	450°C
1	12.58	185	5.4642 (Endo)	-0.0742	10	40	72
2	10.74	164	2.6629 (Endo)	-0.1124	-	38	61
3	10.54	141	2.3140 (Endo)	-0.1510	-	4	65
4	10.34	118	3.7475 (Endo)	-0.0494	-	6	68
5	10.40	98	2.1080 (Endo)	-0.3100	-	17	73
6	10.63	80	2.1426 (Endo)	-0.1628	-	26	80
7	11.35	66	2.6290 (Endo)	-0.1790	-	32	81
8	10.80	34	1.4281 (Endo)	-0.2592	-	35	82

<sup>a</sup> Polymerization conditions: 1,4-dioxane solution; temperature:  $(70 \pm 1)^\circ\text{C}$ ; initiator:AIBN (0.1%, based on total molar of monomers).

mograms of polymers are given in Figure 8. Data analysis was carried out with the Setaram software package. The enthalpy changes  $\Delta H_o^d$  and heat capacity  $\Delta C_p$  during thermal degradation obtained from the DSC thermograms of polymers are given in Table III.

### Thermogravimetric analysis

The thermal stabilities of the polymers were investigated by thermogravimetric analysis (TGA) under nitrogen stream at a heating rate of  $10^\circ\text{C min}^{-1}$ . The data obtained from this study are given in Table III, and the thermograms are reproduced in Figure 9. The TGA results indicate that the thermal stability of the copolymer do not depend on the copolymer composition. The temperature versus loss of sample mass indicates some interesting results. The TG curves for poly(BrPMAAm and poly(*n*-BMA) are different. So, the TG of copolymers has the characteris-

tic lines of each homopolymer. But the thermograms clearly indicate that the residue of the copolymers increases with an increase in the BrPMAAm content in the copolymer.

It is clear that three degradation stages for poly(BrPMAAm) and poly(BrPMAAm-co-*n*-BMA)s while poly(*n*-BMA) undergoes two-stage decomposition. The first decomposition may be due to the rupture of weak linkages and volatilization of low molecular weight species. The decomposition of polymers at higher temperature may be due to the breakage of main chain accompanied by volatilization of the cleaved products.

### CONCLUSIONS

Poly(BrPMAAm) and the copolymers of BrPMAAm with *n*-BMA were synthesized by free-radical polymerization in 1,4-dioxane at  $(70 \pm 0.1)^\circ\text{C}$ . Characterization of copolymers were performed by FTIR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR techniques. The glass transition temperature increases with BrPMAAm content. The  $r_1$  value is less than 1, and  $r_2$  is greater than 1. This indicates that the BrPMAAm is less reactive than *n*-BMA. The value of the product of  $r_1r_2$  is greater than 1, which indicates that the system forms a random copolymer with a longer sequence of *n*-BMA units in the copolymer chain.

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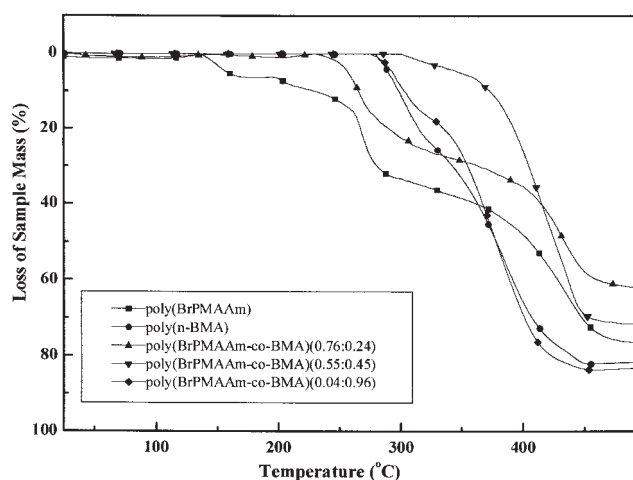


Figure 9 TGA curves of the investigated homo-and copolymers.

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