A STUDY OF COPOLYMERIZATION WITH 4-BROMOBENZYL METHACRYLATE AND ETHYL METHACRYLATE

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ABSTRACT

4-Bromobenzyl methacrylate [BrBMA] monomer was synthesized from a reaction of sodium methacrylate with 4-bromobenzylbromide. The copolymerization of this monomer with ethyl methacrylate (EMA) and its homopolymerization were carried out in a 1,4-dioxane solution at 60°C using 2,2′-azobisisobutyronitrile [AIBN] as initiator. The monomer and the polymers were characterized by IR, ^{1}H and ^{13}C-NMR techniques. The composition of monomeric units in the copolymer system was calculated using ^{1}H-NMR spectroscopy by comparing the integral values of well separated aromatic and aliphatic proton peaks. The monomer reactivity ratios of copolymerization were determined by using the Kelen-Tüdös (K-T), Inverted Fineman-Ross (IFR) and Yezrielev-Brokhina-Roskin (YBR) methods, and were found to be $r_1 = 0.44$, $r_2 = 0.63$ and $r_1 = 0.24$, $r_2 = 0.47$ and $r_1 = 0.37$, $r_2 = 0.64$, respectively (r_1 is the monomer reactivity ratio of BrBMA). Based on the experimental data of the K-T method, triad analysis was performed. It is concluded that this copolymerization results in statistical-type macromolecules. The solubility parameters and the glass transition temperature of the copolymers were determined as a function of copolymer composition.

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Key Words: Monomer reactivity ratios; Ethylmethacrylate

INTRODUCTION

Methacrylic and acrylic polymers find extensive applications due to the combination of durability and versatility, and their ability to tailor-make molecules for specific end use.[1−3] Determination of monomer reactivity ratios is important by means of quantitative values to predict the copolymer composition for any starting feed in batch preparation and to understand the kinetic and mechanistic aspects of copolymerization. The order of reactivity of monomers toward free radicals not only is a function of the reactivity of the monomers, but also depends on the nature of the attacking radicals. This is illustrated by the tendency of many monomers to alternate in a copolymer chain.[4] The results obtained for the same systems by different methods or by different investigators are usually inconsistent with each other. Monomer reactivity ratios are generally determined at low conversion.[5−8]

Estimation of the copolymer composition and determination of monomer reactivity ratios of its consistuents assume importance in evaluating and applications of a copolymer. ^{1}H-NMR spectroscopy is well established as a convenient method for determining the compositions and monomer reactivity ratios in this type of copolymer system due to the similarity of structural units. The use of NMR spectroscopy has sequence distributions and also of copolymer compositions in methacrylate systems.[9−11]

The monomer reactivity ratios of 4-bromobenzyl methacrylate and ethyl methacrylate for their free radical copolymerization were studied in this study. Triad analysis was performed from reactivity ratios for the copolymerization and the glass transition temperature of the copolymers were investigated as a function of copolymer composition.

EXPERIMENTAL

Materials

4-Bromobenzyl methacrylate and ethyl methacrylate (Merck), were purified by conventional methods and finally distilled under vacuum. Sodium methacrylate (Merck) and acetonitrile (Merck) were used as received without further purification. 2,2′-Azobisisobutyronitrile (Fluka) (AIBN), was purified by crystallization from methanol and dried.

Synthesis of 4-Bromobenzylmethacrylate [BrBMA, Monomer]

The monomer was prepared via the method given in the literature.[12] For the synthesis of BrBMA, 10 gr (0,040 mol) of 4-bromobenzylbromide and 4.75 gr (0.044 mol) of sodium methacrylate was stirred in 100 mL aceto-

nitrile at 80−85°C with a reflux condenser for 20 h in the presence of hydroquinone as inhibitor. Then the solution was cooled to room temperature and neutralized with a 10% NaOH solution. The organic layer was washed with water several times. Diethylether was evaporated.

Characteristic FT-IR bands: $1637 \, cm^{-1}$ (olefinic stretch), $1720 \, cm^{-1}$ (C=O stretch), $1595 \, cm^{-1}$ (aromatic stretch).

^{1}H-NMR (δ_{ppm}): 7.1−7.4 ppm (aromatic ring protons, 4H), 5.6 (CH_2=, 1H), 6,2 (CH_2=, 1H), 5.1 (-OCH_2-, 2H), 1.9 (CH_3-, 3H).

^{13}C-NMR (δ_{ppm}): 166.8 (C=O), 136.4 (=C), 132 (CH_2=) the other carbons in 122−136 (aromatic ring carbons), 65.6 (-OCH_2-), 18.3 (CH_3-).

Copolymerization of 4-Bromobenzylmethacrylate with Ethyl Methacrylate

The diethylether solutions of BrBMA and EMA were freed from inhibitor by washing with dilute KOH solution followed by distilled water, and drying over anhydrous $MgSO_4$. Diethylether was evaporated. Six copolymers of BrBMA and EMA were prepared in 1,4-dioxane at 60°C in the presence of 2,2′-azobisisobutyronitrile. Appropriate amounts of the monomers, AIBN and the solvent were mixed in a polymerization tube. The mixture was degassed with argon and kept in a thermostated oil bath at 60°C. Copolymerization was allowed to proceed to about 15% conversion. Copolymers were precipitated in excess ethanol, filtered, and washed repeatedly with fresh ethanol to ensure the complete removal of residual monomers. They were then dried at room temperature under vacuum. The homopolymers of both monomers were also prepared in a similar monomer.

Characterization Techniques

Infrared spectra were recorded by using a Mattson 1000 FT-IR spectrometer. The ^{1}H and ^{13}C NMR spectra were run on a Jeol FX 90Q 90 MHz NMR. The spectra were recorded at room temperature with 20−25% (w/v) solutions in $CDCl_3$. TMS was used as the internal standard. Thermogravimetric analysis (TGA) was performed in with a Shimadzu TGA-50 thermobalance with a sample size of 3.5 mg at a heating rate of 10 °C/min under a nitrogen atmosphere. Glass transition temperatures of the copolymers were determined by differential scanning calorimetry using a Shimadzu DSC-50 and samples were heated at a rate of 20 °C/min under an air atmosphere. The solubility parameters of the homopolymer and the copolymers were estimated from a solubility test using dichloromethane and non-solvents (n-hexane and ethanol) according to the method adapted from McCaffery.[12]

RESULTS AND DISCUSSION

Characterization of the Copolymer

Six copolymers of BrBMA and EMA having different composition were prepared according to the experimental details in Table 1 using AIBN as initiator in 1,4-dioxane solution under nitrogen atmosphere. The formula of poly(BrBMA-co-EMA) is illustrated in Sch. 1.

The IR spectra of poly(BrBMA) and poly(BrBMA-co-EMA) show absorption bands typical of the constituent monomeric units and their relative intensity depending on composition. Thus, as a function of BrBMA in copolymer, the band at $1600\,cm^{-1}$ (aromatic C=C stretching) strongly increased from 1 to 6.

The ^{13}C-NMR spectrum (Fig. 1) of copolymer (with BrBMA 20% units) has the most characteristic peaks of the monomeric units at 176−177 ppm (C=O in both units), 65.2 ppm (-OCH$_2$- in BrBMA units), 60.7 (-OCH$_2$- in EMA units).

The ^{1}H-NMR spectrum of the copolymer with two different compositions is shown in Fig. 2. The peaks at 7.1−7.4 ppm reveal the substituted phenyl ring protons, and the signal at 4.9 and 4.0 ppm are assigned to methylene in -OCH$_2$-Ar and -OCH$_2$CH$_3$, respectively. The other signals are due to the methyl, methylene protons of comonomeric units. Thus, the presence of the two monomer units in the copolymer is confirmed.

Copolymer Composition

The composition of the BrBMA and EMA units in the copolymer was determined from the assignment of distinct and well separated resonance peaks in the ^{1}H-NMR spectra. Thus, the mole fraction of BrBMA in the copolymer was determined from the ratio of the integral values of the

Table 1. Some Properties of Homo and Copolymers BrBMA and EMA

Polymers	M_1	M_2	m_1	$W_1{}^a$	T_g (°C)	$\delta(cal/cm^3)^{1/2}$
Poly(EMA)		0.00	0.00		64	
1	0.10	0.90	0.17	.31	−	−
2	0.20	0.80	0.20	0.36	83	
3	0.35	0.65	0.34	0.54	87	9.4
4	0.50	0.50	0.45	0.65	93	9.8
5	0.70	0.30	0.66	0.81	84	9.6
6	0.90	0.10	0.91	0.96	−	−
Poly(BrBMA)		1.00	1.00	83	9.9	

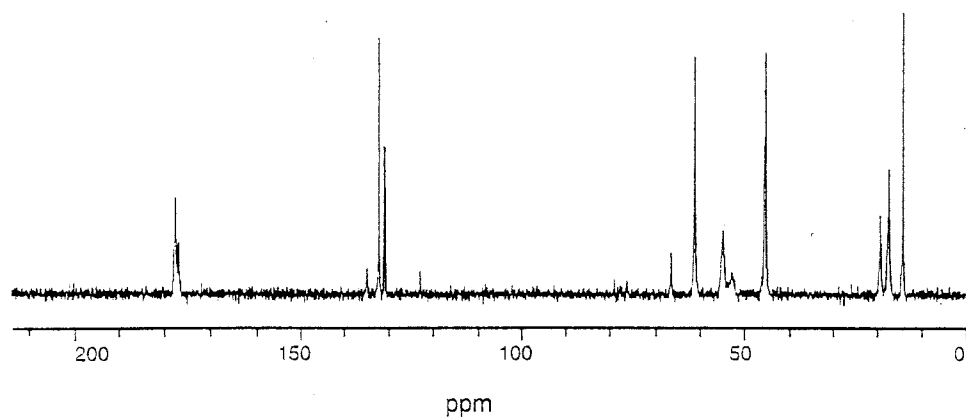$W_1{}^a$: weight fraction of BrBMA in the copolymer.
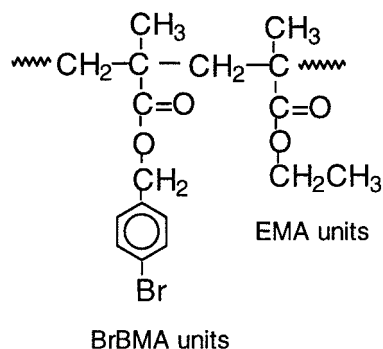
Scheme 1.

intensities of aromatic protons of BrBMA in 7.1−7.4 ppm and the aliphatic protons between 5.0 and 0.8 ppm. Thus, it was adopted for calculating the mole fraction of BrBMA in the poly(BrBMA-co-EMA) by taking into the ratio of the integral intensities of aromatic protons of BrBMA and total aliphatic protons of BrBMA and EMA units.

Let m_1 be the mole fraction of BrBMA and $m_2 = (1 - m_1)$ that of the EMA units.

$$C = \frac{\text{Integral intensities of aromatic protons } (I_{Ar})}{\text{Integral intensities of aliphatic protons } (I_{Alf})} = \frac{4m_1}{7m_1 + 10m_2}$$

On simplification; $\qquad m_1 = \dfrac{10C}{3C + 4}$

where m_1 = mole fraction of BrBMA and m_2 that of EMA in copoly(BrBMA-EMA). Values of m_1 are presented in Table 1. The value of **C** is

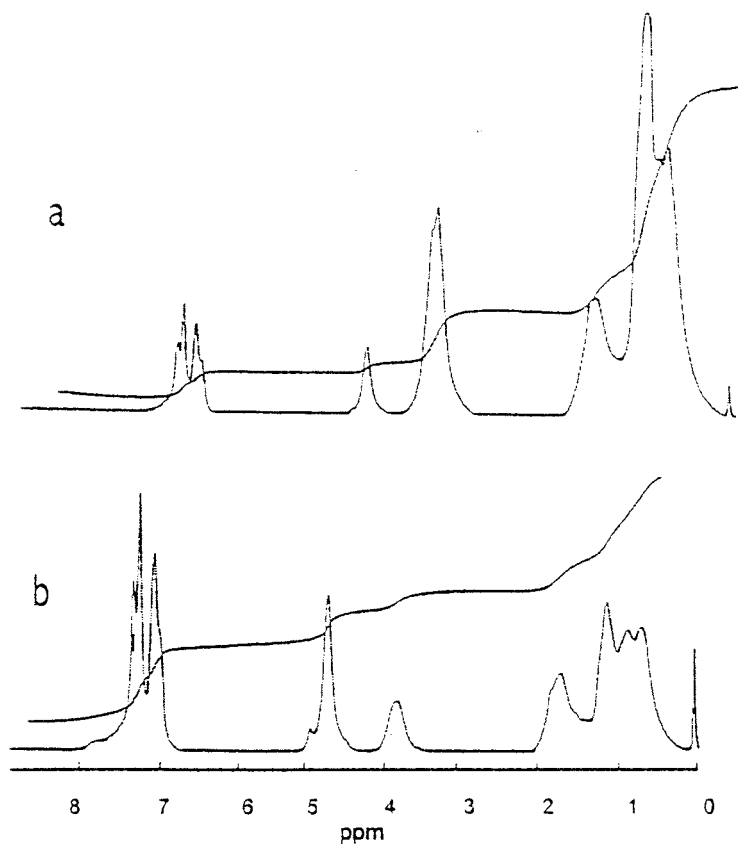*Figure 1.* ^{13}C-NMR spectrum of poly(BrBMA20%-co-EMA).

Figure 2. ^{1}H-NMR spectra of a) poly(BrBMA20%-co-EMA) and b) poly(BrBMA66%-co-EMA).

presented in Table 2. A plot of the mole fraction of BrBMA in the copolymer (m_1) against the feed composition is shown in Fig. 3.

Glass Transition Temperature

The glass transition temperatures of poly(BrBMA) and poly(BrBMA-co-EMA) were determined by a Shimadzu DSC-50 thermal analyzer. The Tg of poly(BrBMA) is 83°C, and that of poly(EMA) obtained under the same conditions is 64°C. In comparison to that of poly(EMA), the shift to higher temperature is also noted for all the copolymers studied and its magnitude is dependent on the increasing in BrBMA molar fraction in the copolymer chain. An increase in Tg of BrBMA-EMA copolymers may be due to the introduction of comonomer into EMA, BrBMA, which increases the inter-molecular polar interactions between the molecular chains due to structure stretching.

Table 2. Copolymer Composition of BrBMA and EMA

Sample No	Mole Fraction of BrBMA in Feed, M_1	Intensity of Aromatic Protons	Intensity of Aliphatic Protons	$C = Iar/Ialf$	Mole Fraction of BrBMA in Copolymer
1	0.10	8	110	0.073	0.17
2	0.20	12	140	0.086	0.20
3	0.35	14	91	0.154	0.34
4	0.50	17	80	0.213	0.45
5	0.70	24	72	0.333	0.66
6	0.90	32	63	0.508	0.91

Dependence on the copolymer composition of Tg, as weight fraction of BrBMA, has been shown in Fig. 4. It can be seen that the observed Tg increases with increasing BrBMA and presents a striking positive deviation with respect to linearity, which can be associated with a lower free volume, mobility and flexibility than a mixture of EMA and BrBMA units.

The solubility parameters were determined by means of the upper limits and lower limits of the solubility parameters using pairs of n-hexane (nonsolvent)-dichloromethane (solvent) and ethanol (nonsolvent)-dichloromethane (solvent) solvent-nonsolvent. As a function of BrBMA unit in
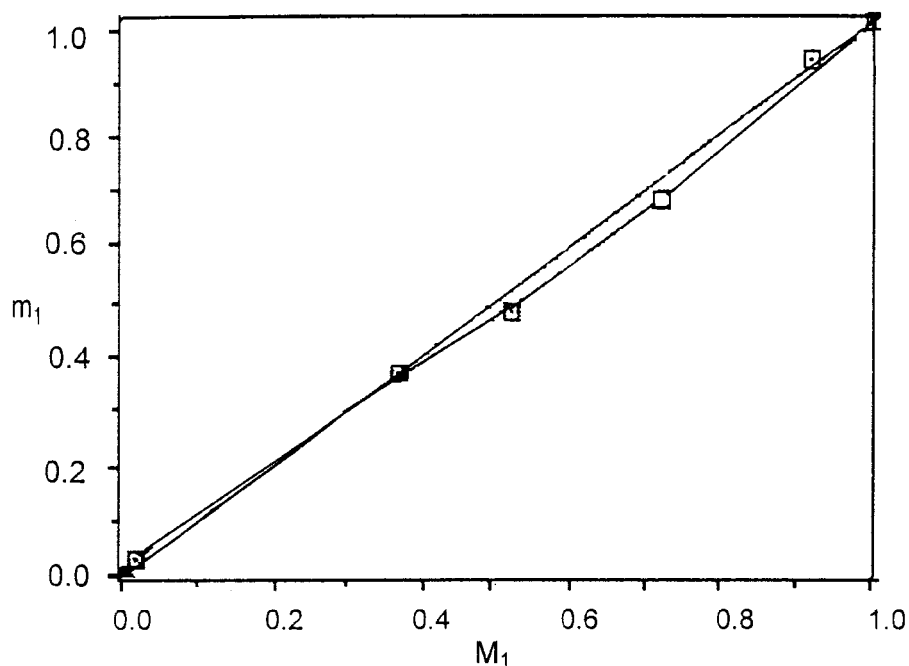
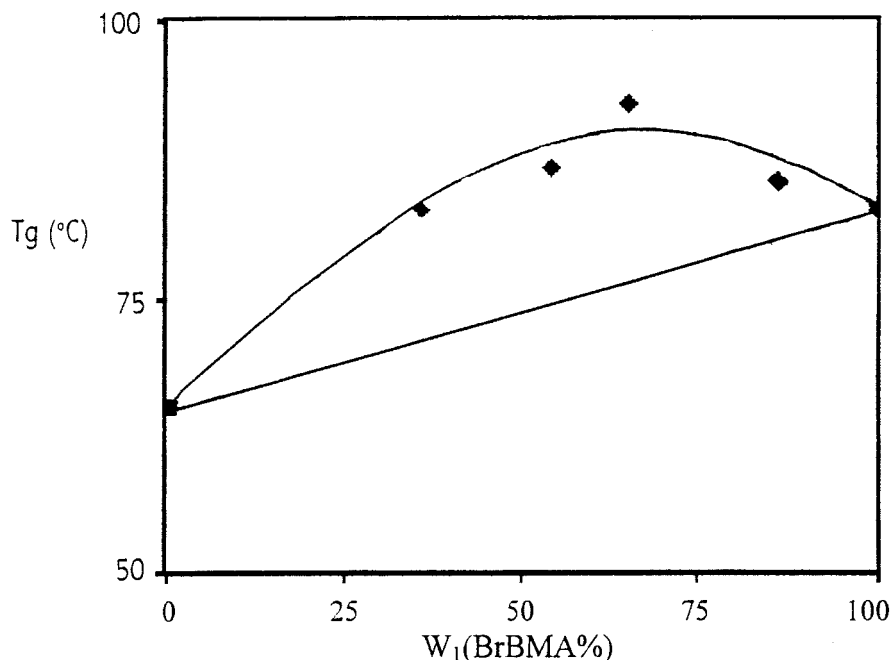***Figure 3.*** Composition diagrams of poly(BrBMA-co-EMA) systems.

Figure 4. Plot of the Tg of a series of BrBMA-EMA copolymers obtained at low conversion as a function of BrBMA weight fraction in the copolymer chain.

copolymers, solubility parameters changed from 9.3 to 9.9 $(cal/cm^3)^{1/2}$. The solubility parameters of all the copolymers are between that of poly(EMA) $[\delta = 9.3 \ (cal/cm^3)^{1/2}]$ and that of poly(BrBMA) $[\delta = 9.8(cal/cm^3)^{1/2}]$. Consequently, all the copolymers and homopolymers are soluble in solvents such as 1,4-dioxane, dichloromethane, chloroform, tetrahydrofurane.

Determination of Monomer Reactivity Ratios

The composition of the poly(BrBMA-co-EMA) samples from various feed ratios of BrBMA and EMA were estimated by ^{1}H-NMR analysis, and are given in Table 2. To understand the copolymerization behavior, the monomer reactivity ratios of BrBMA and EMA were estimated by graphical methods according to the Finemann-Ross[13] equation, Kelen-Tüdös[14] and Yezrielev-Brokhina-Roskin[15] procedures using the data in Table 4 and the following equations:

$$G/H = r_1(1/H) - r_2 \qquad \text{(IFR)}$$
$$\eta = (r_1 + r_2/\alpha)(\xi - r_2/\alpha) \qquad \text{(K} - \text{T)}$$
$$G = r_1(H^{3/2}) - r_2 \qquad \text{(YBR)}$$

where G, F, η, α, ξ have been explained in Table 3.

Table 3. K-T, F-R, and YBR Parameters of BrBMA-EMA System (^{1}H-NMR Analysis)[a]

Sample No	$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f-1)/f$	$H = F^2/f$	$\eta = G/\alpha + H$	$\xi = H/\alpha + H$
1	0.111	0.204	-0.433	0.060	-0.577	0.080
2	0.250	0.250	-0.750	0.250	-0.800	0.266
3	0.538	0.515	-0.506	0.562	-0.404	0.449
4	1.000	0.818	-0.222	1.222	-0.116	0.640
5	2.333	1.941	1.131	2.804	0.323	0.802
6	9.000	10.100	8.109	8.019	0.930	0.920

[a]M_1: Mole fraction of BrBMA in feed; $M_2 = $ mole fraction of EMA in feed, $m_1 = $ mole fraction of BrBMA in copolymer, $m_2 = $ mole fraction of EMA in copolymer.
$(H_{min} \ H_{ma})^{1/2}. = 0.69$, H_{min}: lowest value of H, H_{max}: highest value of H.

r_1 is the reactivity ratios of BrBMA and r_2 is the reactivity ratio of EMA. The reactivity ratios of the monomers are obtained by plotting F-R, K-T and YBR parameters seperately using the reported methods. The values of r_1 and r_2 obtained from the Kelen-Tüdös, Finemann-Ross, Yezrielev-Brokhina-Roskin methods are given in Table 4.

The monomer reactivity ratios (r_1 and r_2) of copoly(BrBMA-EMA) are less than 1. This indicates that the system copolymerizes statistically. The relative reactivity of monomers towards the growing radicals with EMA ends are measured by $1/r_2$, which shows that the monomer propagation type M_{12} and M_{21} are preferred rather than M_{11} and M_{22}. The r_1r_2 value indicates that the system copolymerizes statistically in the polymer chain, although there is a possible tendency for alternation. Thus, the two factors, general reactivity and alternating tendency, are predominant in determining the behavior of monomers in copolymerization.[4] The plot of the mole fraction of BrBMA in feed vs. that of EMA in copolymer is shown in Fig. 3. The diagram shows an azeotropic composition at 32:68% (BrBMA:EMA).

Based on the reactivity ratios obtained from the K-T method, $r_1 = 0.44$ and $r_2 = 0.63$, triad analysis was performed. Figure 5 shows how the triad probabilities vary as a function of M_1 (feed composition of BrBMA) for copolymerization of BrBMA and EMA. The probabilities of homotriads

Table 4. Comparison of Monomer Reactivity Ratios by Various Methods

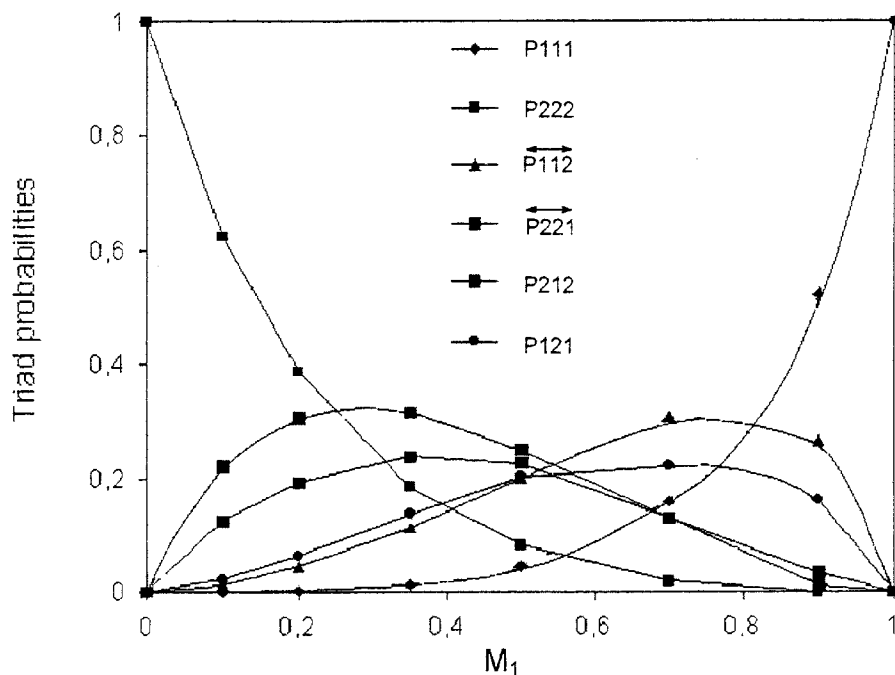| System	Methods	r_1	r_2	r_1r_2	$1/r_1$	$1/r_2$
Poly(BrBMA-co-EMA)	K-T	0.44	0.63	0.27	0.27	1.58
	YBR	0.37	0.64	0.27	2.70	1.56
	IFR	0.24	0.47	0.11	4.16	2.12

Figure 5.   Triad probabilities in BrBMA-EMA copolymer systems.

(P111 and P222) increase smoothly with their own mole fraction. The graphs show that the probabilities of alternating 1-centered triads and 2-centered triads reach a maximum of 0.24 at about $M_1 = 0.35$ and a maximum of 0.22 at about $M_2 = 0.30$, respectively. The probabilities of heterotriad having one BrBMA and EMA unit reach a maximum of 0.34 at $M_1 =$ about 0.27 and a maximum of 0.30 at about $M_2 = 0.25$, respectively.

Thermogravimetric Measurement of Polymers

The effect of EMA units on the thermal stability of poly(BrBMA) was studied by thermogravimetric analysis. The decomposition of poly(BrBMA) and those of copolymers occurred in a single stage. Typical thermogram obtained by plotting percentage of residual weight against temperature for poly(BrBMA) and one copolymer (with BrBMA%17 units) are given in Fig. 6. The initial decomposition temperature of poly(BrBMA) and poly-(EMA) are 225°C and 243°C, respectively. However, that of poly-(BrBMA17%-co-EMA) was 238°C. TGA results show that the thermal stability of the copolymers increase with an increase of EMA units in the copolymer segments. The results of the thermogravimetric analysis are present in Table 5.
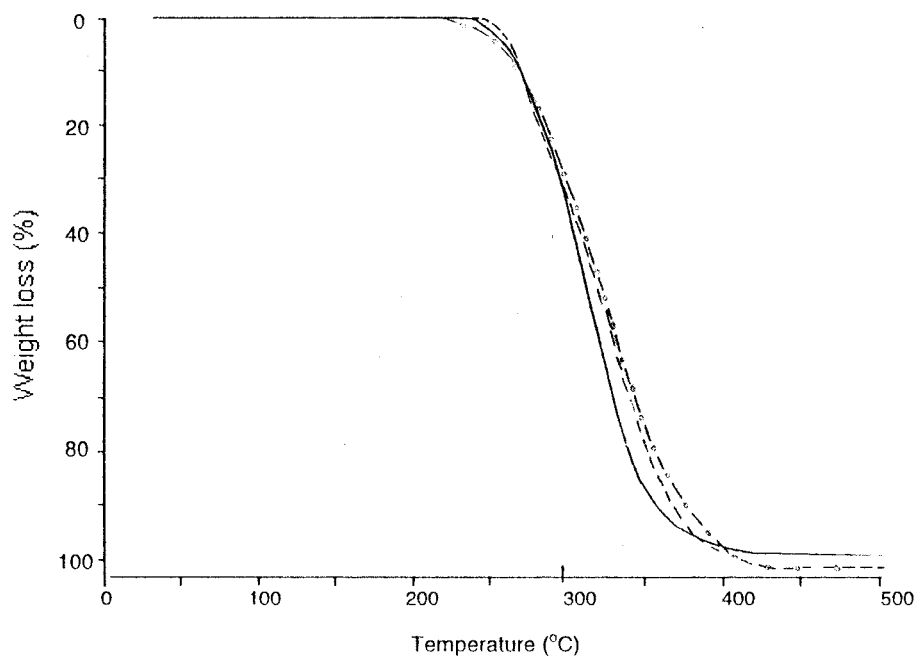
Figure 6. TGA curves for - - - - poly(BrBMA), ----- poly(EMA),——poly(BrBMA17%-co-EMA).

Table 5. TGA Data for Homopolymers and Copolymers

Polymer	T_{ID}[a] (°C)	T_{fD}[b] (°C)	50%Wt Loss (°C)	Residue (%)
Poly(EMA)	243	435	325	0
Poly(BrBMA)	225	435	330	0
[Poly(BrBMA-co-EMA)] (17:83)	238	435	320	2

[a]T_{ID}: Initial decomposition temperature.
[b]T_{fD}: Final decomposition temperature.

CONCLUSION

Six copolymers of BrBMA-EMA were prepared using AIBN as initiator in 1,4-dioxane at 60°C. ^{1}H, ^{13}C-NMR and FT-IR techniques revealed the presence of both monomeric units in the copolymer chain. The monomer reactivity ratios were calculated from feed composition and copolymer composition determined by ^{1}H-NMR analysis. The monomer reactivity ratios obtained by K-T, IFR and YBR methods agree well with each other. The values of the monomer reactivity ratios shows that the BrBMA radicals

prefer to be added on to EMA units, whereas the EMA radicals prefer to be added on BrBMA. The glass transition temperature of copolymers was found to increase with an increase in the mole fraction of BrBMA units. Based on the experimental data of the K-T method, triad analysis was performed. It is concluded that this copolymerization afford statistical type macromolecules.

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