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COPOLYMERIZATION OF METHYL METHACRYLATE WITH 2-METHYLBENZYL METHACRYLATE AND 4-METHYLBENZYL METHACRYLATE: SYNTHESIS, CHARACTERIZATION, AND MONOMER REACTIVITY RATIOS

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ABSTRACT

Two types of copolymers based on 2-methylbenzyl methacrylate and 4-methylbenzyl methacrylate with methyl methacrylate were synthesized. Several copolymers of 2-methylbenzyl methacrylate (2-MBZMA) and 4-methylbenzyl methacrylate (4-MBZMA) with methyl methacrylate (MMA) having different copolymer compositions were performed in 1,4-dioxane using 2,2′-azobisisobutyronitrile (AIBN) as a free radical initiator at 60 ± 1°C. The copolymers were characterized by FT-IR, ^{1}H- and ^{13}C-NMR spectroscopic 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 reactivity ratios were calculated by employing Fineman-Ross and Kelen-Tüdös methods. The values of r_1 and r_2 obtained by the Fineman-Ross and Kelen-Tüdös methods appear to

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be in close agreement with each other, i.e., r_1(2-MBZMA):1.03 ± 0.039 and r_2(MMA): 0.77 ± 0.012 for the copoly(2-MBZMA-MMA) system, r_1(4-MBZMA): 0.97 ± 0.040 and r_2(MMA):0.77 ± 0.050 for the copoly(4-MBZMA-MMA) system.

Thermal stabilities of the homo- and co-polymers were investigated using thermogravimetric analysis, while differential scanning calorimetry was used to determine the glass transition temperature.

Key Words: Reactivity ratios; Methyl methacrylate; 2-Methylbenzyl methacrylate; 4-Methylbenzyl methacrylate

INTRODUCTION

A great deal of work has been published on the structure-reactivity relationship of vinyl monomers in their radical homo- and copolymerization.[1–6]

Incorporation of activated acrylates or methacrylates into polymers provides a versatile route for the preparation of reactive polymer.[7] Copolymers of these activated monomers have been employed to study the kinetic aspects of macromolecules reactions, preparation of macromolecular drug carriers, immobilized enzymes and polymeric reagents for peptide synthesis and transition metal catalysis.[8,9] The finishing stage in the leather making consumes almost a complete range of (co)polymers. The finishing operation is meant to make leather natural, durable, and beautiful. The reguirements of leather finish in respect of adhesion, flexibility, and mechanical strength[10,11] (abrasion and stretch) are quite high. The use of acrylics in textile finishing[12–14] and acrylic ester emulsions in leather finishing[15] are well documented.

Lacquer, vinyl, and polyurethane finishes are the main non-aqueous finishes employed in leather finishing. Aqueous dispersed resins mainly used are acrylic, methacrylic and synthetic rubbers based on butadiene. Synthetic rubbers from butadiene give a very soft resinous finish, which is not acceptable for leather finishing. However, copolymerization of butadiene to give a hard polymer with a monomer such as styrene, methyl methacrylate and acrylonitrile, or use of suitable copolymers of definite composition based on activated acrylates with a suitable (soft or hard) segment, results in a coating material having the desired softness for finishing.

Copolymerization of monomers containing aromatic and aliphatic acrylates facilitates the determination of copolymer composition by NMR techniques.[16,17] The NMR spectrocopy is well established as a convenient method for determining the compositions of constituent monomer units in a copolymer.[18–20] The use of ^{1}H-NMR spectroscopy has become more important not only for the determination of sequence distributions, but also of copolymer compositions in methacrylate systems.[21–23]

Poly(methyl methacrylate) (PMMA) is known for its glass-like transparency, good mechanical properties and easy processability. However, in many cases, applications of PMMA are limited by its low glass transition temperature (Tg ~ 105°C).[24]

Thermogravimetric analysis (TGA) is widely used to investigate the thermal decomposition of polymers.[25–27]

The present work is undertaken with a view to develop a suitable topcoat leather finish based on activated acrylates. The present work describes the free-radical copolymerization of methyl methacrylate with 2-methylbenzyl methacrylate and 4-methylbenzyl methacrylate. Determination of copolymer composition was achieved by ^{1}H-NMR spctroscopy and the reactivity ratios calculated by Fineman-Ross[28] and Kelen-Tüdös[29] methods. Thermal properties of the homo- and copolymers were analysed by TGA and DSC.

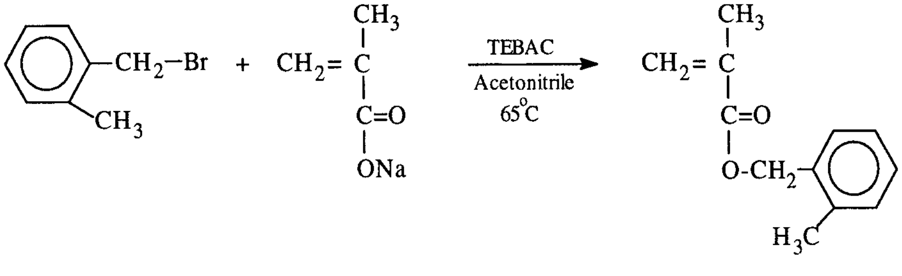
EXPERIMENTAL

Materials

Methyl methacrylate (Aldrich) was freed from the inhibitor by washing successively with NaOH (5% w/v solution) and distilled water, and finally distilled under reduced pressure. 2,2′-azobisisobutyronitrile (Merck) was recrystallized from a chloroform/methanol (1:1 v/v) mixture. 2-methylbenzyl bromide and 4-methylbenzyl bromide were supplied by Aldrich Chemicals. Sodium methacrylate and hydroquinone (Merck) were used without any further purification. All the solvents were purified by distillation prior to use.

Monomer Synthesis

2-Methylbenzyl methacrylate was synthesized (Sch. 1) as follows: a mixture of 2-methylbenzyl bromide (0.1 mol), sodium methacrylate (0.12 mol) in 100 mL acetonitrile and 2.0 g triethylbenzylamoniumchloride (TEBAC) was placed in a two-neck round bottom flask equipped with a magnetic stirrer,



Scheme 1.

thermometer, and dropping funnel. 100 ppm hydroquinone was added to this mixture to inhibit the polymerization of 2-methylbenzyl methacrylate monomer. The mixture was stirred at 65°C for 24 h. The reaction mixture was transferred to a separating funnel washed sequentially with distilled water diethylether mixture and NaOH solution (5%) to remove the unreacted reagents. It was then dried over anhydrous $MgSO_4$ and the solvent was evaporated. The resulting monomer was distilled under vacuum. Yield:80%, b.p.:132°C (2 mmHg).

IR (nujol, cm^{-1}):Ester carbonyl C=O 1740, Ar-CH 3050, olefinic $CH{=}CH_2$ band 1630 and 1540, mono-substitue ring 750, C = C streching vibrations 1280.

^{1}H-NMR (δ, ppm, $CDCl_3$):7.0–7.6 (4H, aromatic), 5.5–6.2 (3H, olefinic), 5.1 (2H, OCH_2), 3.6 (3H, OCH_3), 2.1 (3H, CH_3), 1.9 (3H, CH_3 between phenyl ring).

^{13}C-NMR (δ, ppm, $CDCl_3$):166 (O-$\underline{C}$=O), 130–121 (Ar-$\underline{C}$), 66 (O$\underline{C}H_2$-Ar), 54 ($CH_2{=}\underline{C}$), 21 ($\underline{C}H_3$), 44 ($\underline{C}H_2 = C$), 18 ($\underline{C}H_3$ between phenyl ring).

4-methylbenzyl methacrylate monomer was synthesized and characterized by the same methods.

Copolymerization

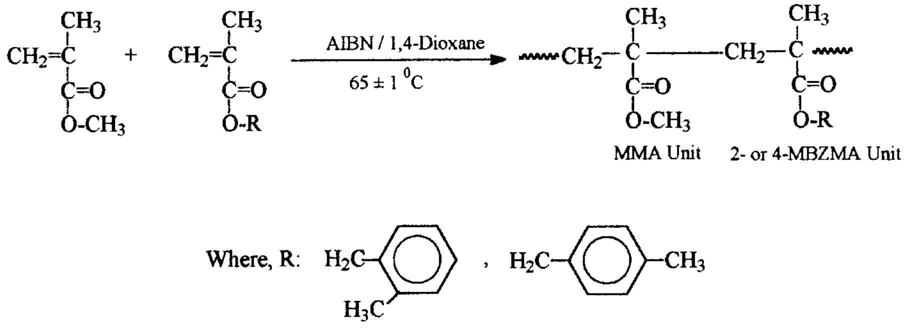
Copolymers of different molar ratios of 2-methylbenzyl methacrylate (M_1) and 4-methylbenzyl methacrylate (M_1) with methyl methacrylate (M_2) were synthesized using 2,2′ -azobisisobutyronitrile as an initiator (1% based on the weight of the monomers) in 1,4-dioxane solution at 60 ± 1°C. The reaction mixture was de-aerated by passing nitrogen gas for 20 min, then the tubes were tightly sealed and kept in a thermostatic oil bath at 60 ± 1°C. The copolymerization was terminated at low conversions (<10% wt) for estimating monomer reactivity ratios.

These copolymers were precipitated in excess methanol, purified by dissolution in 1,4-dioxane and reprecipitation in methanol. The samples were dried in vacuum to constant weight (Sch. 2).

Measurements

IR spectra of the monomers and polymers were recorded on a Mattson 1000 FT-IR spectrometer as nujol. Fourier-Transform (FT) ^{1}H- and ^{13}C-NMR spectra were recorded using Jeol FX 90Q, 89.55 and 22.45 MHz spectrometer respectively. The monomers and homo- and copolymer samples were examined in about 20% (w/v) solutions of $CDCl_3$ using tetramethylsilane (TMS) as internal reference.

Thermogravimetric analysis (TGA) curves were recorded with a Shimadzu TGA-50 thermobalance. An aliquot sample weighting 6 mg was used



Scheme 2.

at a temperature rise of 10 min°C/min under nitrogen. The glass transition temperatures of polymers were determined by differential scanning calorimetry (DSC) using a Shimadzu DSC-50 thermal analyzer. Samples of 10 mg were heated at rate of 10°C/min in the presence of nitrogen atmosphere.

RESULTS AND DISCUSSION

IR Spectroscopy

The IR spectrum of the copolymer shows the same characteristic bands as that of poly(2-MBZMA). The ester carbonyl of poly (2-MBZMA) appeared at 1765 cm^{-1}, while that of copoly(2-MBZMA-MMA) and copoly(4-MBZMA-MMA) appeared at 1750 and 1745 cm^{-1}, respectively. A sharp band at 2850–3100 cm^{-1} is a characteristic peak of the aliphatic groups of copolymers. The peaks at 2800–3100 cm^{-1} may be assigned to the aliphatic and aromatic groups present in the system. The >C=C< stretching vibrations of o-methylbenzyl methacrylate and p-methylbenzyl methacrylate monomer peaks at 1630 and 1540 cm^{-1} disappeared in the copolymer spectra. The peaks due to MMA unit in copolymer system overlapped with those of the 2-methylbenzyl methacrylate and 4-methylbenzyl methacrylate monomeric unit in copolymers.

^{13}C-NMR and ^{1}H-NMR Spectroscopy

The proton – decoupled ^{13}C-NMR and ^{1}H-NMR spectra of copoly(2-MBZMA-MMA) are shown in Figs. 1(a,b), respectively. In ^{13}C-NMR spectra, the ester carbonyl of 2-MBZMA appeared at 176.0 ppm The aromatic carbons and the ipso carbon of the phenyl ring of 2-MBZMA unit in copoly(2-MBZMA-MMA) appeared at 131.8, 128.5, 127.8 and 124.5 ppm.

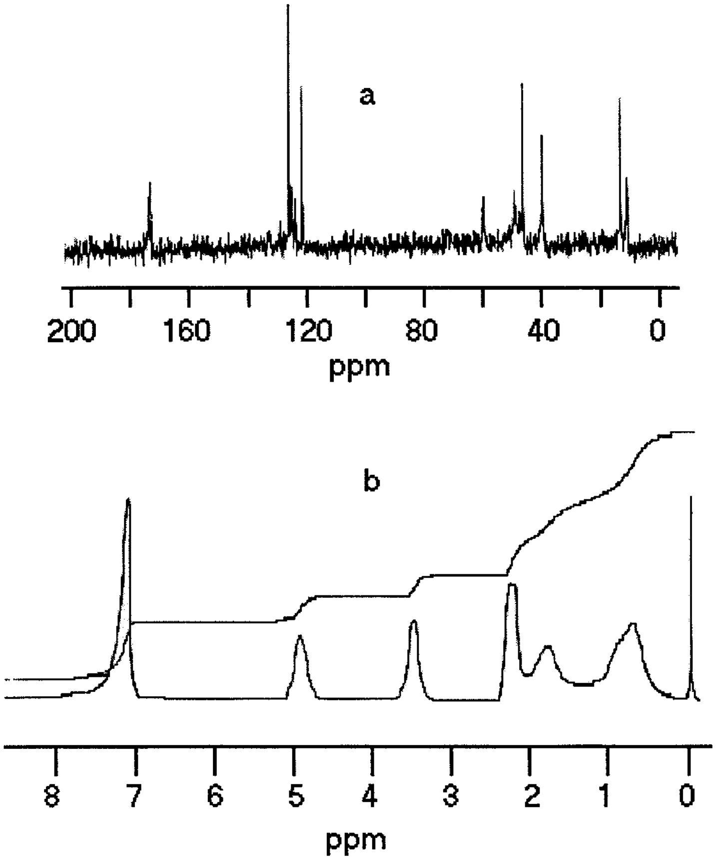


Figure 1. Proton decoupled ^{13}C-NMR spectra (a) and ^{1}H-NMR spectra (b) of copoly (2-MBZMA-MMA); m_1: $m_{2:}$ 0.52:0.48.

The ester carbonyl of MMA unit appeared at the same spot with the ester carbonyl of 2-MBZMA. The O-$\underline{C}H_2$-Ar carbon atoms appeared at 63.4 ppm The α-methyl and 2-methyl carbon atoms appeared at 19.0 and 17.2 ppm, respectively. The other broad peaks are due to the backbone carbons of the comonomer units.

In ^{1}H-NMR spectra of copoly(2-MBZMA-MMA), the resonance signals at 7.0–7.5 ppm are due to the aromatic protons of the 2-MBZMA unit. The signal at 3.6 ppm corresponds to the methoxy protons of the MMA unit. The signal at 4.9 ppm are assigned to methylene in -OCH_2-Ar. The resonance signals at 0.6–2.5 ppm are due to the α-methyl, 2-methyl and backbone protons of the comonomer units.

The proton – decoupled ^{13}C-NMR and ^{1}H-NMR spectra of copoly(4-MBZMA-MMA) are shown in Figs. 2(a,b), respectively. Similarly, in the copoly(4-MBZMA-MMA) spectrum shows characteristic peaks at 176.0 ppm which represent the ester carbonyl of both the units. The aromatic carbons of the 4-MBZMA unit appeared at 136.5, 130.9, 128.5, and 127.0 ppm The O-$\underline{C}H_2$-Ar carbon atoms appeared at 65.3 ppm The α-methyl and 4-methyl carbon atoms appeared at 19.4 and 17.6 ppm respectively.

In ^{1}H-NMR spectra of copoly(4-MBZMA-MMA), the resonance signals at 7.1–7.5 ppm are due to the aromatic protons of 4-MBZMA. The signal at 3.6 ppm is due to methoxy protons of MMA. The signal at 4.9 ppm is assigned to methylene in -OCH_2-Ar. The other signals are due to the methyl, methylene, and methine protons of the comonomeric units. Thus, the presence of the two monomer units in the copolymer is confirmed.

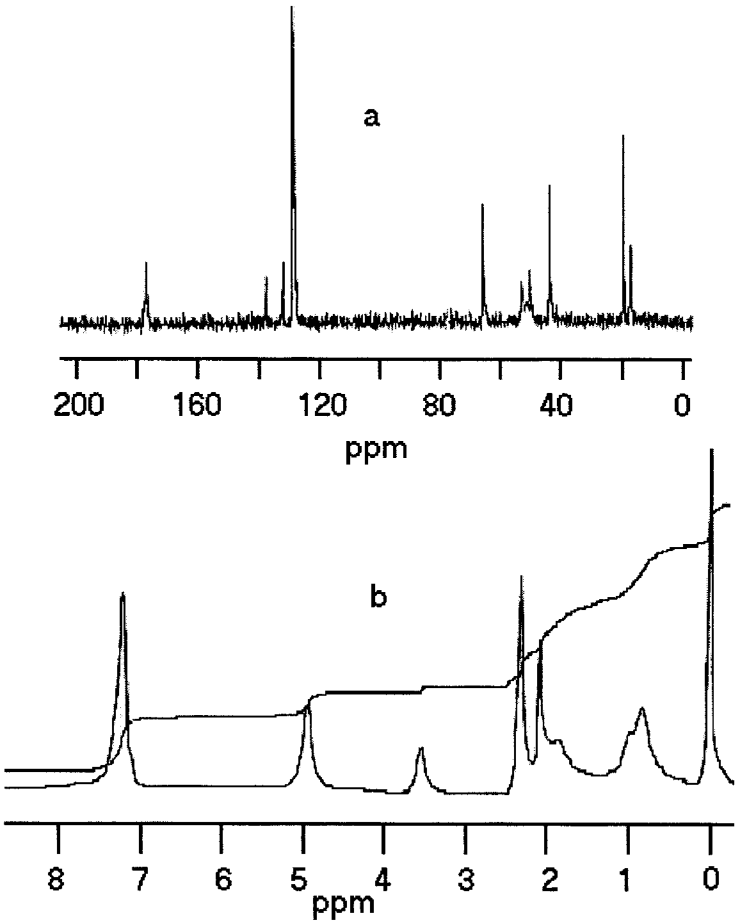


Figure 2. Proton decoupled ^{13}C-NMR spectra (a) and ^{1}H-NMR spectra (b) of copoly (4-MBZMA-MMA); m_1:m_2:0.53:0.47.

Copolymer Composition

The composition of the monomeric units in the copolymer was determined from the assinment of distinct and well separated resonance peaks in the ^{1}H-NMR spectra. Thus, the mole fraction of 2-MBZMA in the copolymer was determined from the ratio of the integrated values of the intensities of aromatic protons of 2-MBZMA (7.0–7.9 ppm) and methoxy protons (3.6 ppm) of MMA units.

Let m_1 be the mole fraction of 2-MBZMA and $m_2 = (1\text{-}m_1)$ that of the MMA unit.

$$\frac{\text{Integrated intensities of aromatic protons (IA)}}{\text{Integrated intensities of methoxy protons (Im)}} = \frac{4m_1}{3m_2} = C. \tag{1}$$

On simplification:

$$m_1 = \frac{3C}{3C + 4} \tag{2}$$

A similar approach was adopted for calculating the mole fraction of 4-MBZMA in the copoly(4-MBZMA-MMA) by taking the ratio of the integral intensities of aromatic protons (7.1–7.5) of 4-MBZMA and methoxy protons (3.6 ppm) of MMA units.

Where m_1: Mole fraction of 2-MBZMA and 4-MBZMA and m_2 that of MMA in copolymers.

From Eq. (2), the mole fraction of 2-MBZMA and 4-MBZMA in the copolymers was determined. The value of "C" and the corresponding mole fractions of 2-MBZMA and 4-MBZMA in the copolymer is presented in Table 1.

The solubility of the copolymers in various organic solvents were tested. The copolymers were soluble in polar aprotic solvents, namely tetrahydrofuran, dimethyl formamide, dimethyl sulphoxide, dimethylacetamide, etc., and chlorinated solvents such as chloroform and methylene chloride. They were insoluble in hydrocarbons (e.g., toluene, benzene, xylenes), and hydroxy group containing solvents such as methanol, ethanol, and 2-propanol.

Determination of Reactivity Ratios

To understand the copolymerization behavior, the reactivity ratios were calculated by the application of Fineman–Ross[28] (F–R), and Kelen–Tüdös[29] (K–T) methods. The composition of the monomer feed mixtures and that of the copolymers for the two investigated systems are compiled in Table 1.

Table 1. Copolymer Composition Data

Feed Composition in Mole Fraction		Conversion	Intensity of Aromatic Protons	Intensity of Methoxy Protons	Copolymer Composition in Mole Fraction			Weight (g)	
(M_1)	(M_2)	(%)	(I_A)	(I_m)	$C = I_A/I_m$	(m_1)	(m_2)	W_1	W_2
(a) Copoly(2-MBZMA-MMA) system									
0.90	0.10	9.20	4.5	0.5	9.00	0.87	0.13	0.93	0.07
0.75	0.25	9.38	3.5	1.1	3.18	0.70	0.30	0.82	0.18
0.50	0.50	8.66	2.6	1.8	1.44	0.52	0.48	0.67	0.33
0.25	0.75	9.13	2.0	3.0	0.67	0.33	0.67	0.48	0.52
0.10	0.90	8.80	1.0	4.5	0.22	0.14	0.86	0.24	0.76
(b) Copoly(4-MBZMA-MMA) system									
0.90	0.10	6.27	3.0	0.3	10.00	0.88	0.12	0.93	0.07
0.75	0.25	6.32	2.7	0.8	3.38	0.72	0.28	0.83	0.17
0.50	0.50	6.84	2.0	1.3	1.62	0.53	0.47	0.68	0.32
0.25	0.75	6.50	1.3	2.1	0.62	0.32	0.68	0.47	0.52
0.10	0.90	7.00	0.6	3.3	0.18	0.12	0.88	0.20	0.80

Solvent: 1,4-dioxane; Temperature: 60 ± 1°C; Initiator: AIBN (1% weight of the monomers); non-solvent:methanol.

The monomer reactivity ratios were calculated by the graphical methods of Fineman–Ross (F–R) and Kelen–Tüdös (K–T). The linear relations used are:

$$G = r_1H - r_2 \quad \text{(F–R equation)} \tag{3}$$

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \quad \text{(K–T equation)} \tag{4}$$

Where: $\eta = G/(\alpha + H)$, $\xi = H/(\alpha + H)$, $G = F(f-1)/f$, $H = F^2/f$, $F = M_1/M_2$, $f = m_1/m_2$, $\alpha = (H_{max}H_{min})^{1/2}$, M_1 = Mole fraction of 2-MBZMA or 4-MBZMA in feed, M_2 = Mole fraction of MMA in feed, m_1 = Mole fraction of 2-MBZMA or 4-MBZMA in copolymer, m_2 = Mole fraction of MMA in copolymer, r_1 = reactivity ratio of 2-MBZMA or 4-MBZMA and r_2 = reactivity ratio of MMA.

Fineman–Ross and Kelen–Tüdös plots were drawn as G vs H and η vs. ξ, respectively. The plot of G vs. H will give a straight line with r_1 as the slope and -r_2 as the intercept (Fig. 3(a)). A similar plot of η vs. ξ provides $[r_1 + (r_2/\alpha)]$ as the slope and $(-r_2/\alpha)$ as its intercept (Fig. 3(b)). The copolymerization reactivity ratios of by varius methods of 2-MBZMA and 4-MBZMA with MMA are presented in Table 2. The reactivity ratios determined up to 1990 were collected by Müller and Braun.[30,31] The recent work of Braun and Mott agrees with the values reported for the methyl methacrylate, somewhat higher $r_1$value of benzyl methacrylate (BZMA) confirms the higher reactivity of BZMA compared with that of methyl methacrylate (BZMA-MMA) system. In that system, the monomer benzyl methacrylate (BZMA) was the more active one ($r_{BZMA} = 1.06 \pm 0.13$, $r_{MMA} = 0.83 \pm 0.11$).[32] In our case, the monomer (2-MBZMA) and (4-MBZMA) were also more active. The reactivity ratios obtained from the two methods were in good agreement within the experimental error. Comparing BZMA, 2-MBZMA and 4-MBZMA to MMA, it should be stated that three monomers show similar copolymerization behavior. The reactivities of these monomers are close together, because the vinyl ester groups are directly attached to benzyl groups. Due to the presence of the benzyl groups, three monomers are highly susceptible to the addition of radicals leading to relatively stabile adducts. BZMA is a little more reactive than 2-MBZMA and 4-MBZMA to the MMA radical, because of its higher resonance stabilization. While there is a small decrease at monomer reactivity ratio values of 2-MBZMA-MMA and 4-MBZMA-MMA copolymers as monomers without methyl substitution, there is a question as to whether the ortho and para derivatives should behave similarly.

The relative reactivities of the 2- and 4-methylbenzyl methacrylates show that as the location of the methyl group in methylbenzyl methacrylate, the small high r_1 value for 2-MBZMA-MMA, compared with 4-MBZMA-MMA, suggests greater reactivity of 2-MBZMA than 4-MBZMA toward

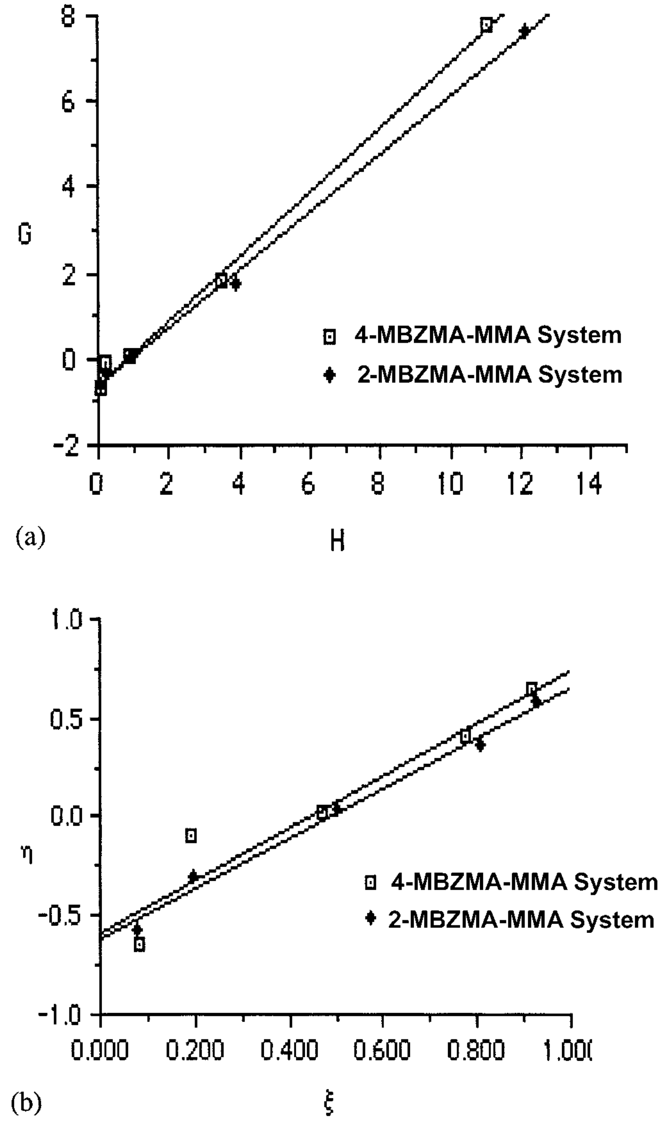


Figure 3. (a) F-R plot for 2-MBZMA-MMA and 4-MBZMA-MMA copolymer system; (b) K-T plot for 2-MBZMA-MMA and 4-MBZMA-MMA copolymer system.

MMA. The copolymer (2-MBZMA-MMA) and (4-MBZMA-MMA) will have a statistical arrangement of units in which 2-MBZMA and 4-MBZMA will tend to predominate.

Thermal Analysis

Thermogravimetric analysis (Fig. 4) was used in estimating the percent weight loss of the copolymer which undergoes decomposition. The thermo-

Table 2. Comparision of Reactivity Ratios by Various Methods

System	Methods	r_1	r_2	$r_1 \times r_2$	$1/r_1$	$1/r_2$
Copoly(2-MBZMA-MMA)	F-R	1.01 ± 0.054	0.77 ± 0.010	0.78	0.99	1.30
	K-T	1.04 ± 0.025	0.76 ± 0.013	0.79	0.96	1.32
	Average:	1.03 ± 0.039	0.77 ± 0.012	0.79	0.98	1.31
Copoly(4-MBZMA-MMA)	F-R	0.98 ± 0.020	0.72 ± 0.070	0.71	1.02	1.39
	K-T	0.96 ± 0.050	0.81 ± 0.030	0.78	1.04	1.23
	Average:	0.97 ± 0.04	0.77 ± 0.050	0.75	1.03	1.31

gram of poly(MMA) is compared with that of poly(2-MBZMA), poly-(4-MBZMA), poly(2-MBZMA-co-MMA) (0.52:0.48) and poly(4-MBZMA-co-MMA) (0.53:0.47) in Fig. 4. All of the polymers underwent decomposition in a single stage. Table 3 shows the values of the initial decomposition temperature (°C) for each polymer taken from the first strong change in the slope of the thermogravimetric curve (see Fig. 4). The actual decomposition temperature range depends upon the composition of the constitutional monomeric units in the copolymer. The initial decomposition temperature and thermal stability of the copolymers increases with an increase in MMA monomer concentration. Table 3 gives the range of decomposition temperatures for homopolymers and copolymers of different compositions.

Glass Transition Temperatures

The glass transition temperature (Tg) of poly(2-MBZMA), poly(4-MBZMA), poly(MMA), poly(2-MBZMA-co-MMA)s and poly(4-MBZMA-co-MMA)s were determined by DSC. The Tg's were calculated using the Fox-Flory[33] equation. A relationship for the dependence of glass transition temperature on composition for a copolymer may be derived from simple assumptions. From its limitation comes:

$$\frac{1}{\mathrm{Tg}} = \frac{w_1}{\mathrm{Tg}(1)} + \frac{w_2}{\mathrm{Tg}(2)} \tag{5}$$

For a copolymer, w_1 and w_2 refer to the weight fraction of the two comonomers, whereas Tg(1) and Tg(2) refer to the glass transition temperatures of the two corresponding homopolymers. This equation may be expected to apply to a system which are compatible and not too strongly polar. Data on copolymers on polymer-diluent systems illustrate this is substantially true.

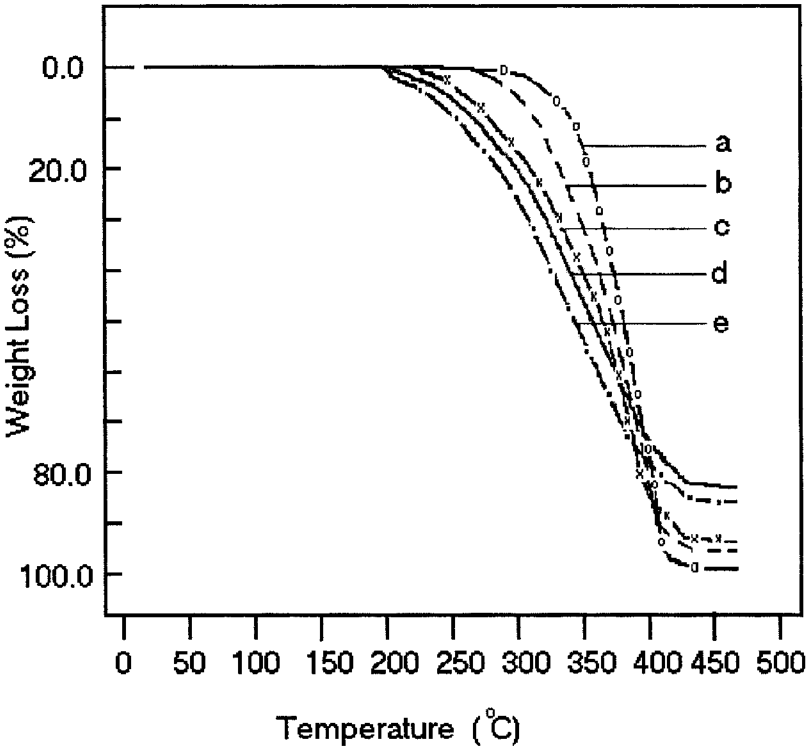
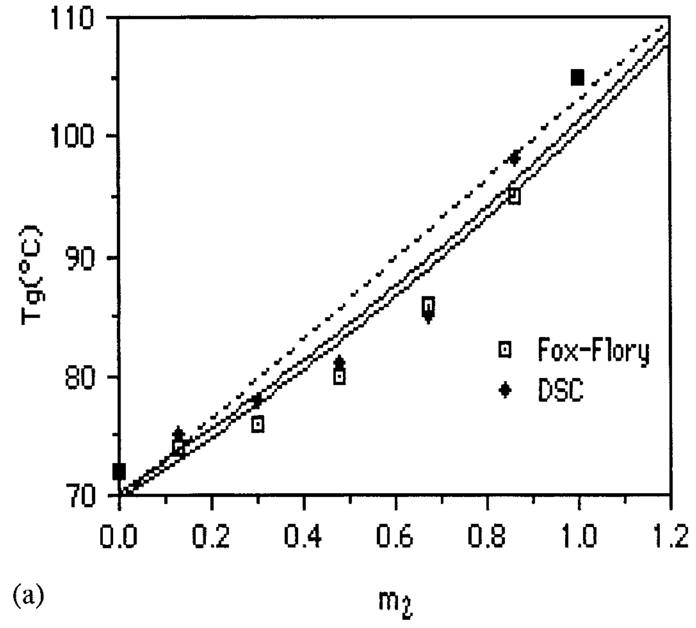


Figure 4. Thermogravimetric analysis (TGA) curves in nitrogen atmosphere of polymers a) Poly(MMA); b) Poly(2-MBZMA-co-MMA) m_1:m_2:0.52:0.48; c) Poly(4-MBZMA-co-MMA) m_1:m_2:0.53:0.47; d) Poly(2-MBZMA); e) Poly(4-MBZMA).

Table 3. TGA Data of Homo- and Co-polymers

System	Copolymer Composition m_1	Copolymer Composition m_2	Decomposition Temperature °C (Range) State 1	% Weight Loss of Polymers at (°C) 10	25	50	75	90
Poly(2-MBZMA-MMA)	0.52	0.48	273–425	315	342	373	398	407
Poly(4-MBZMA-MMA)	0.53	0.47	228–428	278	322	366	385	414
Poly(MMA)			300–420	344	358	380	397	404
Poly(2-MBZMA)			210–465	265	310	353	405	–
Poly(4-MBZMA)			202–460	252	297	345	390	–



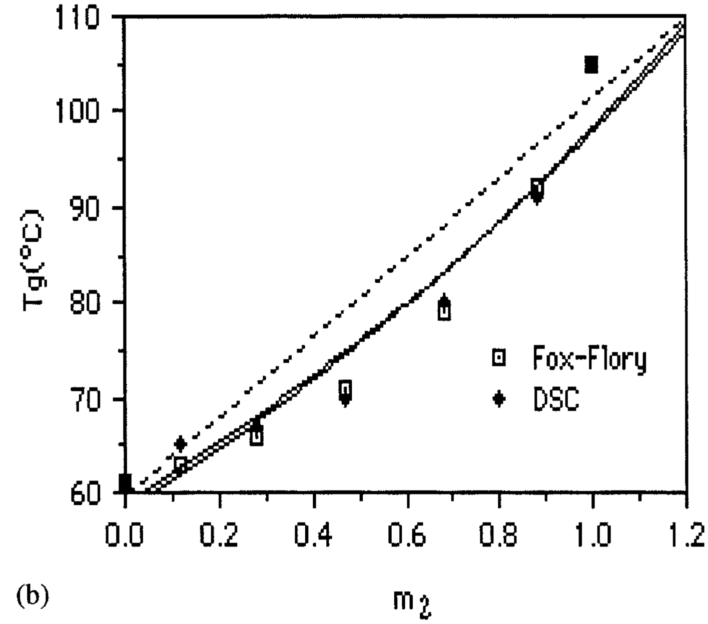


Figure 5. (a) Plot of glass transition temperature vs copolymer composition for copoly(2-MBZMA-MMA) system; m_2:mole fraction of MMA in copolymer; (b) Plot of glass transition temperature vs copolymer composition for copoly(4-MBZMA-MMA) system; m_2:mole fraction of MMA in copolymer.

The Tg of poly(MMA) is 105°C. The Tg of poly(2-MBZMA) is 72°C and poly(4-MBZMA) is 61°C under conditions similar to that of poly-(MMA). The Tg of poly(2-MBZMA) is greater than poly(4-MBZMA). This may be due to the chain flexibility and free movement associated with the side methyl group. The glass transition temperature (Tg) of the copolymers ranged between the values of the two homopolymers. The Tg's calculated by Fox-Flory equation were in good agreement with the experimentally observed values (Figs. 5(a,b)).

CONCLUSION

A knowledge of copolymer composition is an important step in the evaluation of their utility. Copolymer composition and its distribution are dependent on the reactivity ratios. The calculation of the monomer reactivity ratios requires the mathematical treatment of experimental data on the compositions of copolymers and monomer feed mixtures. 2-Methylbenzyl methacrylate and 4-methylbenzyl methacrylate was synthesized and characterized. Copolymers of 2-MBZMA and 4-MBZMA with MMA having different copolymer compositions were prepared. The reactivity ratio values have been discussed. The reactivity ratio values were derived from the F-R and K-T methods were in good agreement with each other. The reactivity of 2-MBZMA and 4-MBZMA is greater than MMA, which means the copolymer is always richer in the 2- and 4-MBZMA unit.

The TGA curves of the copolymers show an increase in the initial decomposition temperature with the increase in concentrations of the MMA unit in the copolymer. From the results of the DSC analysis, it is obvious that when MMA was copolymerized with 2-MBZMA and 4-MBZMA, the Tg of copolymer was significantly improved.

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