Functional Copolymers of *p*-Cumyl Phenyl Methacrylate and Glycidyl Methacrylate: Synthesis, Characterization, and Reactivity Ratios

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Received 15 April 2004; accepted 20 September 2004
DOI 10.1002/app.21732
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Free-radical polymerization of *p*-cumyl phenyl methacrylate (CPMA) was performed in benzene using bezoyl peroxide as an initiator at 80°C. The effect of time on the molecular weight was studied. Functional copolymers of CPMA and glycidyl methacrylate (GMA) with different feed ratios were synthesized by free-radical polymerization in methyl ethyl ketone at 70°C, and they were characterized by FTIR and ^{1}H-NMR spectroscopy. The molecular weights and polydispersity indexes of the polymers and copolymers were determined by gel permeation chromatography. The copolymer composition was determined by ^{1}H-NMR. The glass-transition temperature of the polymer and the copolymers was determined by differential scanning calorimetry. The reactivity ratios of the monomers were determined by the Fineman–Ross and Kelen–Tudos methods. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 336–347, 2005

Key words: copolymerization; functionalization of polymers; glass-transition; synthesis

INTRODUCTION

Alkyl esters of methacrylic acid are important monomers used in the preparation of a variety of polymers. Because these polymers have a wide range of applications in different fields, such as automotives,[1] optics,[2] and biomedicals,[3] they are considered as industrially important polymers. They also serve as building blocks for several other applications. In recent years there has been enormous activity on aromatic acrylate based polymers. A variety of copolymers of aromatic acrylates with other acrylic/methacrylic monomers have been synthesized and utilized in the fields of biology,[4] pharmacy,[5] photochemistry,[6] and so forth.

The presence of an aromatic group in an acrylate monomer improves the thermal stability and facilitates the introduction of a functional group. In our previous work we have observed a significant increase in the glass-transition temperature (T_g) of poly(methyl methacrylate) (PMMA), when the methyl group in the ester carbonyl of MMA is substituted by a sterically bulky cumyl phenyl group.[7]

Copolymers based on GMA have found applications in various fields, which include chromatography,[8] for immobilization of enzymes,[9] catalysis,[10] the electronics industry, such as negative electron beam resist,[11] UV radiation curing surface coatings,[12] and so forth. Recently, the use of GMA–phenyl acrylate copolymers in the leather industry as an adhesive on leather–leather bonding and leather–rubber bonding with maximum peel strength is reported.[13]

In continuation of our previous work on (CPMA), in the present work functional copolymers of CPMA with GMA were synthesized and characterized by ^{1}H-NMR, IR, the reactivity ratio of the monomer, and the T_g of the copolymer. The composition of the copolymer was determined by ^{1}H-NMR.

EXPERIMENTAL

Materials

Methacrylic acid (MA) and GMA were procured from (Aldrich). MA was saturated with NaCl (to remove the bulk of the water), and then the organic phase was dried with $CaCl_2$ and distilled under a vacuum. GMA was distilled before use. *p*-Cumyl phenol [4-(2-phenyl isopropyl) phenol, mp 98–100°C), Herdillia Chemicals, Thane, India] was purified by recrystallization from petroleum ether. Benzoyl chloride, triethyl amine (s.d. Fine Chemicals), and hydroquinone (Loba Chemicals) were used without purification. Chloroform, methanol (s.d. Fine Chemicals), tetrahydrofuran (THF; Merck), and methyl ethyl ketone (SRL) were purified by distillation prior to use. Benzoyl peroxide (Merck) was recrystallized from a chloroform–methanol mixture.

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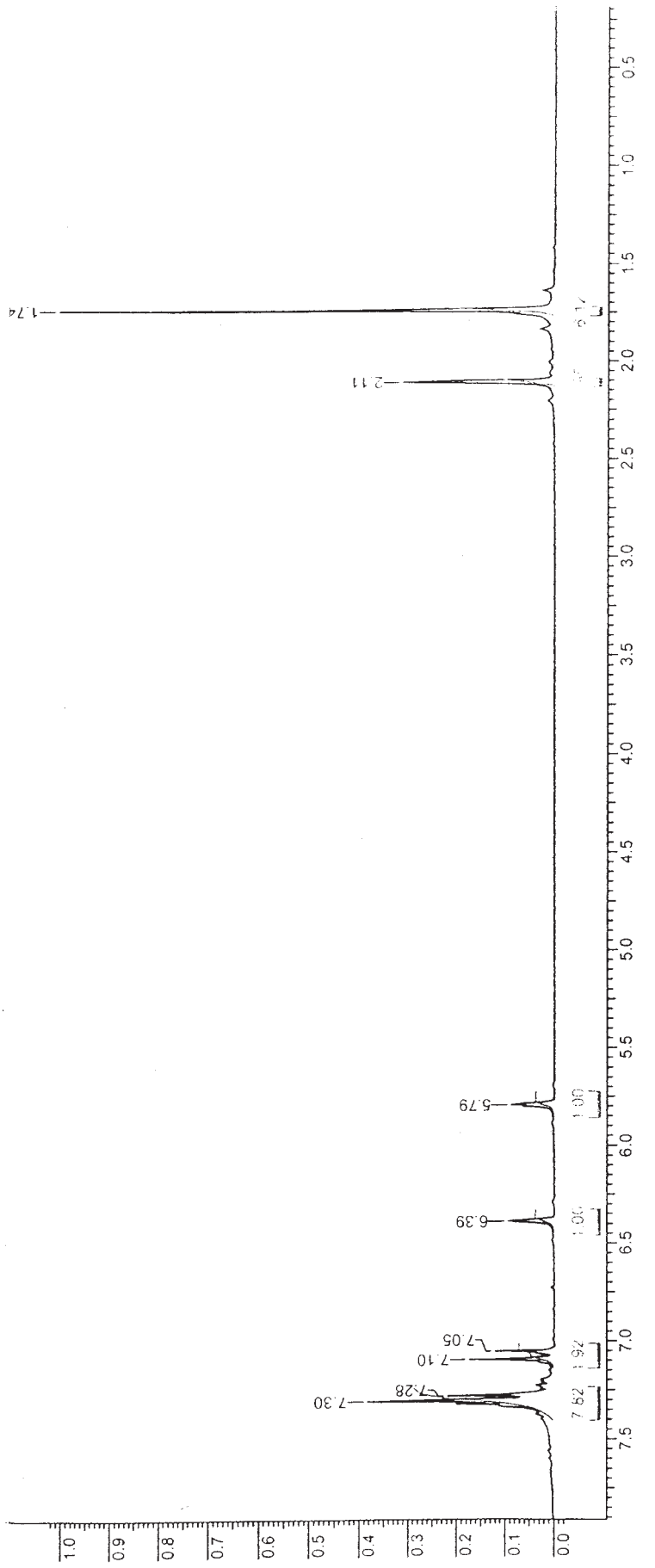


Figure 1 The ^{1}H-NMR spectrum of *p*-cumyl phenyl methacrylate.

TABLE I
Homopolymerization of *p*-Cumyl Phenyl Methacrylate

No.	Monomer [M]	Benzoyl peroxide [M] 10^{-5}	Initiator/ monomer ratio	Time (h)	η_{inh} (dL/g)	Conversion (%)	GPC M_n UV 10^4	GPC M_n RI 10^4	GPC M_W UV 10^4	GPC M_W RI 10^4	GPC M_W/M_n UV	GPC M_W/M_n RI	T_g by DSC (°C)
1	0.001785	1.785	0.01	6	0.073	26	1.13	1.83	2.47	2.49	2.24	2.11	—
2	0.001785	1.785	0.01	16	0.119	74	1.66	1.73	4.56	4.68	2.74	2.70	112
3	0.001785	1.785	0.01	24	0.134	82	1.43	1.52	5.05	4.94	3.53	3.25	130

The polymerization is carried out in benzene at 80 ± 2°C.

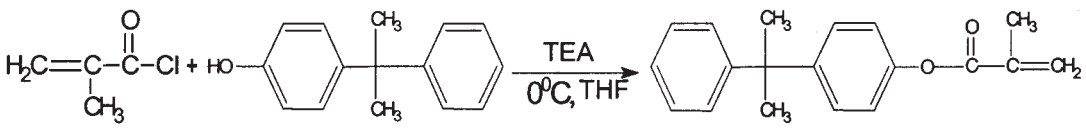
Measurements

FTIR spectra were recorded on a Perkin Elmer 16 PC FTIR instrument. The ^{1}H-NMR spectra were recorded on a Bruker 200-MHz NMR spectrometer in $CDCl_3$. Melting points (uncorrected) were determined in open capillary tubes using a melting point apparatus (Cambell Electronics). The inherent viscosity (η_{inh}) of a 1% (w/v) solution of polymer in $CHCl_3$ was determined at 30°C using an automatic Ubbelohde viscometer (Scott Gerate AVS 440). The molecular weights were determined by gel permeation chromatography (GPC; PSS Win GPC Scientific V 3.0 b-61). THF was used as an eluent at a flow rate of 1 mL/min, toluene was used as a stabilizer, and the calibration standard was PMMA. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer DSC-7 in aluminum pans at a heating rate of 10°C/min under a nitrogen atmosphere. The sample was heated to 200°C and cooled to room temperature, and the T_g was recorded using a second heating run.

Monomer synthesis

Methacryloyl chloride was prepared by reacting MA with benzoyl chloride using a reported procedure. The CPMA monomer was synthesized by condensing methacryloyl chloride with cumyl phenol according to a previously reported procedure [Eq. (1)], as follows. A mixture of *p*-cumyl phenol (6 g, 0.028 mol) and 2.83 g of triethylamine (4 mL, 0.028 mol) were placed in 15 ml of THF in a three-necked round-bottom flask equipped with a magnetic stirrer, dropping funnel, and thermometer. Then, the solution was cooled to 0°C. To this solution, 5.9 g of methacryloyl chloride (0.056 mol) was added dropwise with stirring. After complete addition of methacryloyl chloride the reaction was continued for a further period of 2 h. The reaction mixture was transferred to a separating funnel and washed sequentially with distilled water, 1% NaOH solution, and distilled water and dried over sodium sulfate. The solvent was evaporated and the resulting monomer was purified by column chromatography (neutral alumina) using petroleum ether as the eluent (yield- ≈80%). IR (nujol, cm^{-1}); 1730 (ester carbonyl); 1600, 1500, and 1461 (olefinic CH_2). ^{1}H-NMR ($CDCl_3$, δ); 7–7.07 (m, 2H aromatic) and 7.25–7.69 (m, 7H aromatic); 5.77–6.36 (m, 2H, olefinic), 2.08 (s, 3H, CH_3), 1.71 (s, 6H, $2CH_3$ between two benzene rings; Fig. 1).

preparation of CPMA



Polymerization

Free-radical polymerization was carried out in a sealed tube in the presence of benzoyl peroxide as an initiator in benzene at 80 ± 2°C for various intervals of time (Table I).

The polymer was synthesized by the following method. A pyrex glass ampoule was charged with the required amount of monomer, initiator, and solvent. The ampoule was evacuated and the mixture degassed by a number of freeze–thaw cycles (3 times). It was then sealed off and immersed in an oil bath at the appropriate temperature (Table I). The resulting polymer was dissolved in $CHCl_3$, isolated by precipitating in methanol, and dried under vacuum for 10 h. IR (nujol, cm^{-1}): 3050–2880 (aliphatic and aroatic stretch-

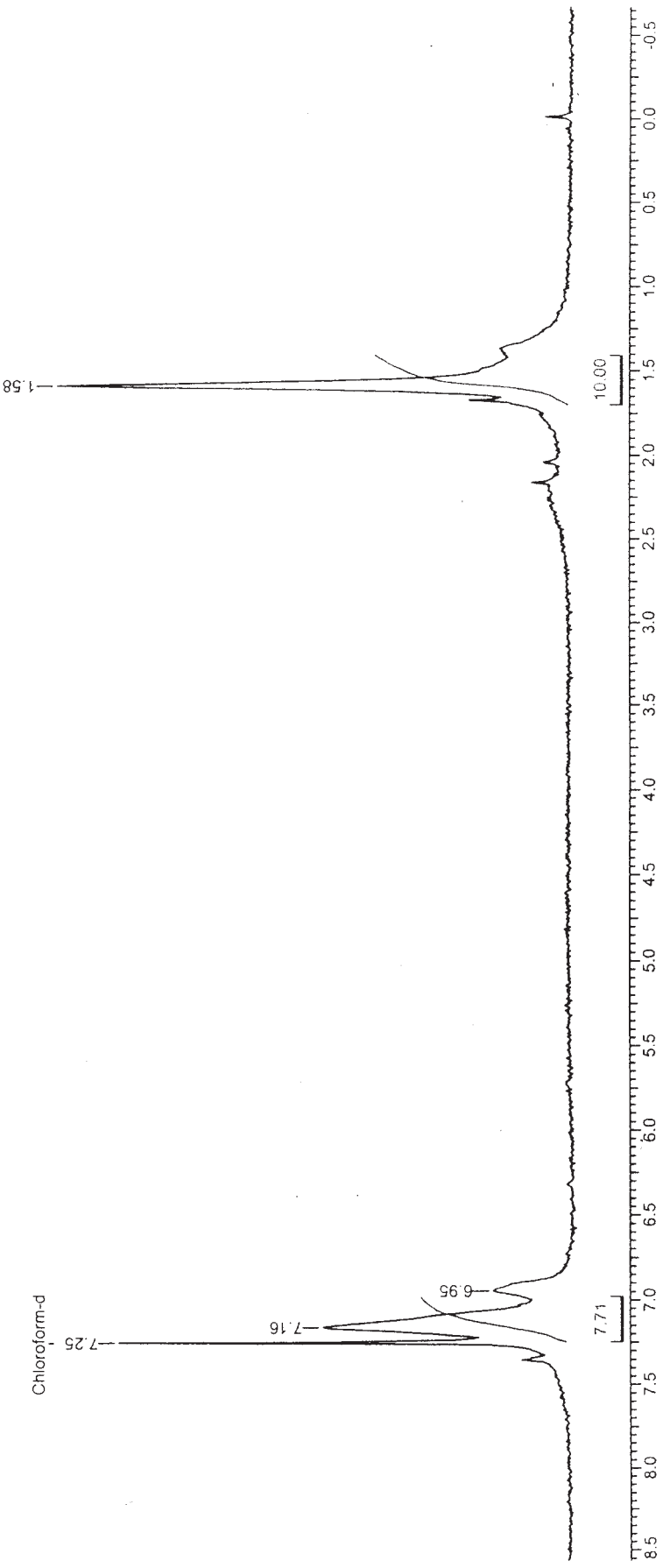


Figure 2 The ^{1}H-NMR spectrum of poly(*p*-cumyl phenyl methacrylate).

TABLE II
Copolymerization of *p*-Cumyl Phenyl Methacrylate (M_1) with Glycidyl Methacrylate Monomer (M_2)

No.	Mole fraction (feed) [M] M_1	M_2	Weight (g)	Benzoyl peroxide [M]	Conversion (%)	Mole fraction (copoly, by NMR) m_1	m_2	GPC M_n UV 10^4	M_n RI 10^4	M_W UV 10^5	M_W RI 10^5	M_W/M_n UV	M_W/M_n RI	η_{inh} (dL/g)	T_g (°C)
1	10	90	1.48	0.0286	34	14	86	7.63	8.35	2.32	2.44	3.04	2.93	0.571	90
2	20	80	1.70	0.0248	8	24	76	3.73	3.89	6.89	7.2	1.85	1.87	.478	103
3	30	70	1.835	0.024	30	32	68	4.74	5.05	1.39	1.43	2.95	2.85	0.345	105
4	40	60	0.982	0.012	43	54	46	3.52	3.91	9.80	9.76	2.78	2.49	0.265	113
5	50	50	1.059	0.012	32	52	48	4.26	4.56	1.01	1.09	2.38	2.39	0.247	118
6	60	40	1.34	0.012	15	60	40	2.52	2.57	5.19	5.33	2.05	2.07	0.243	121

ing), 1730 (carbonyl C═O); ^{1}H-NMR ($CDCl_3$, δ): peaks; at 7–7.07 (m, 2H aromatic) and 7.25–7.69 (m, 7H aromatic); 2.3 (d) 2H methylene CH_2); 2.08 (s, 3H CH_3); 1.71 (s, 6H, $2CH_3$ between two benzene rings; Fig. 2).

Copolymerization

The copolymerization of CPMA with GMA using different mole percentages of CPMA was carried out in a sealed tube at 70°C in methyl ethyl ketone (Table II) and terminated at less than 1% conversion (≈1.5 h). The resulting copolymers were purified by dissolving in chloroform and precipitation from methanol [Eq. (3)] IR (nujol, cm^{-1}): 1750 (C═O), 3050–2880 (aliphatic and aromatic stretching); 1260, 910 (oxirane ring; Fig. 3). ^{1}H-NMR ($CDCl_3$ δ): 7–7.28 (m 2H aromatic) and 7.3–7.8 (m 7H aromatic); 4.25–3.51, 3.5–3.14 (O═CH_2 of ester methylene and epoxy group protons of GMA); 2.2–1.2 (backbone CH_2; Fig. 4).

Molecular weight determination by GPC

The weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity indices (M_w/M_n) were determined by GPC (Fig. 5). The solvent THF was stabilized with toluene and used as an eluent at a flow rate of 1 mL/min. PMMA standards were used as calibration standards. The η_{inh} was determined at 30°C with an automated Ubbelohde viscometer (Schott Gerate AVS 440) using a 1% polymer solution in $CHCl_3$.

DSC analysis

DSC studies of the homopolymers and copolymers were performed on a Perkin Elmer DSC- 7 in aluminum pans at a heating rate of 10°C/min under a nitrogen atmosphere. The sample was heated to 200°C and cooled to room temperature and the T_g was recorded during the second heating run. DSC scans of the copolymers are given in Figure 6).

RESULTS AND DISCUSSION

In continuation of our ongoing research on PMMA-based polymers, functional copolymers containing hydrophobic and hydrophilic groups. (i.e., copolymers of CPMA and GMA) have been studied. GMA-based functional polymers find applications ranging from solid-phase peptide synthesis to the adhesive and coating industries. The presence of an oxirane group in the copolymer provides further functionalization of the copolymer. The end use of the functional copolymer depends on the accurate estimation of the copolymer composition and the reactivity ratio of the monomers. The following sections discuss in detail the characterization of the homopolymers and copolymers by spectroscopy, DSC, molecular weight determination, and the reactivity ratio of the monomers.

Monomer synthesis

The monomer CPMA was synthesized in high yields (80%) by reacting methacryloyl chloride with *p*-cumyl phenol at 0°C. The resulting monomer was characterized by ^{1}H-NMR and IR. The ^{1}H-NMR shows signals at δ 7.7 and 7.5–7.3 (m, 9H) for aromatic protons and at δ 5.8–5.5 (2H) for olefinic protons of the MA group, at δ 2.3 (3H) for the methyl group of ester carbonyl, and at δ 1.7 (6H) corresponding to 2-methyl group between two phenyl rings. The IR spectrum shows a strong band at 1740 cm^{-1}, corresponding to the ester carbonyl group and bands for aromatic C═C stretching at 1600 and 1520 cm^{-1}. NMR and IR are in good agreement with the monomer structure.

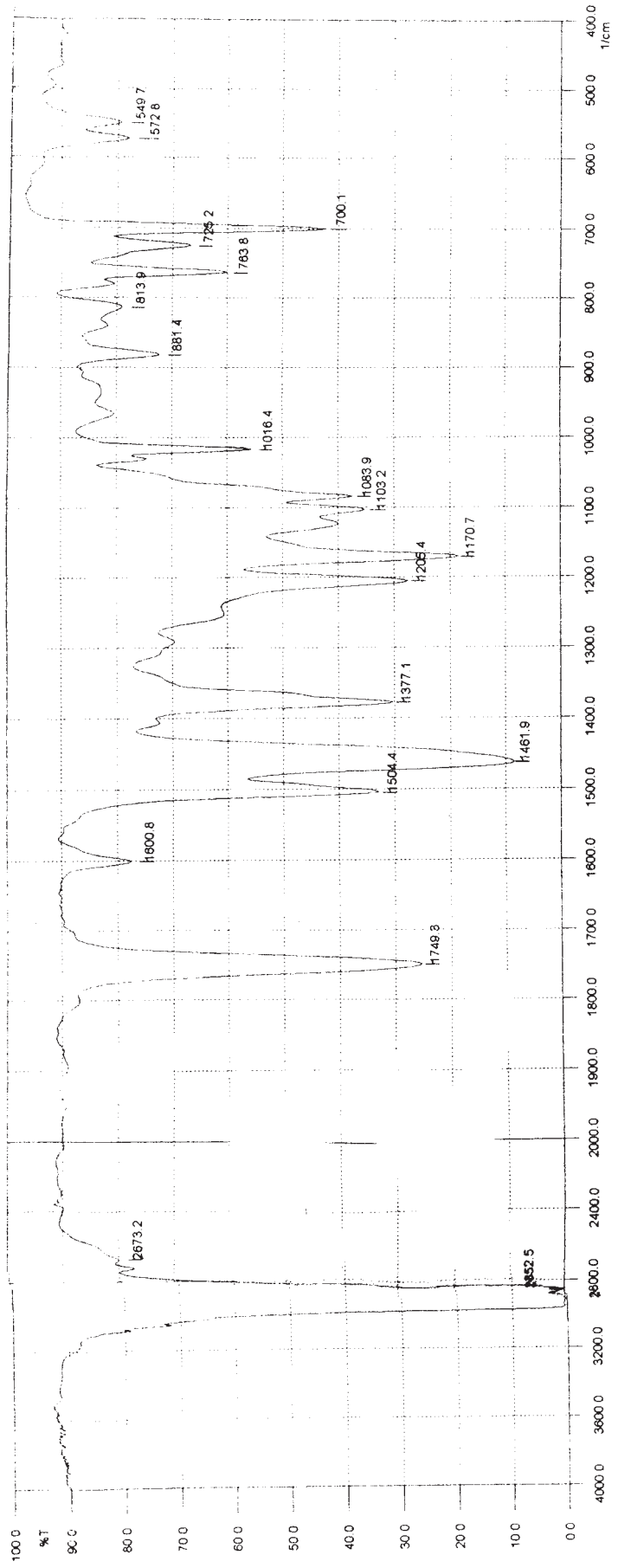


Figure 3 The IR spectrum of the copolymer of CPMA and GMA.

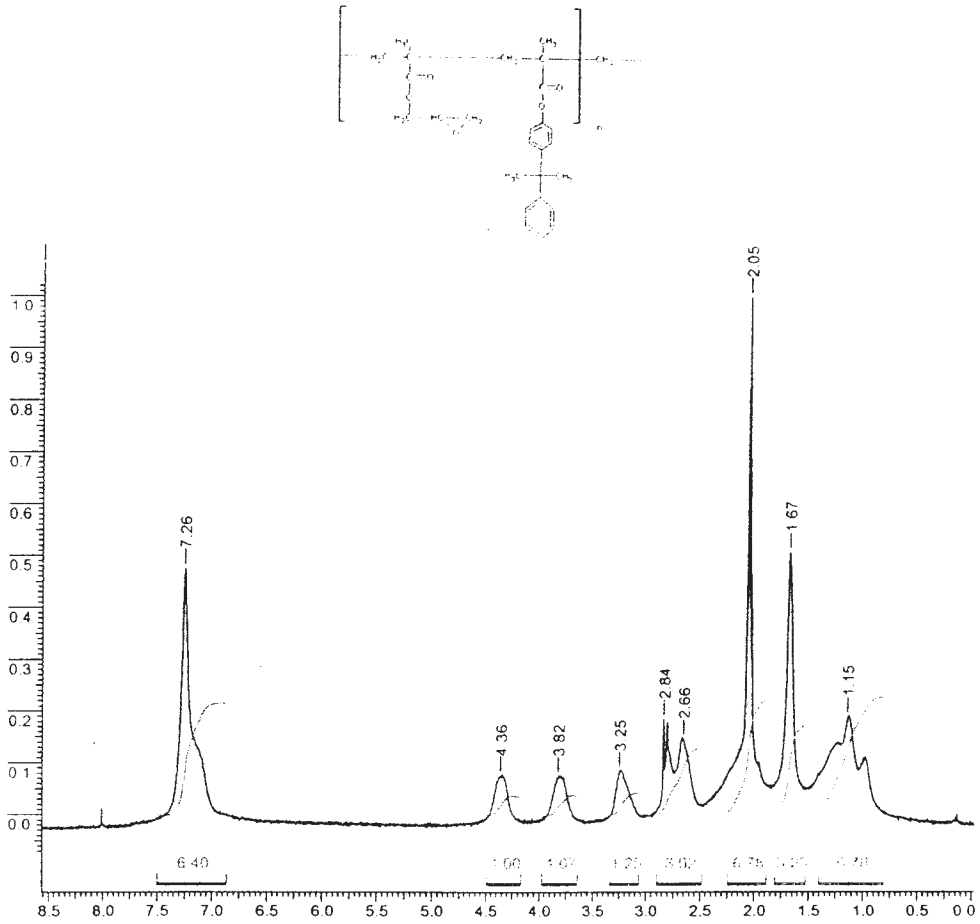


Figure 4 ^{1}H-NMR spectrum of the copolymer of CPMA and GMA.

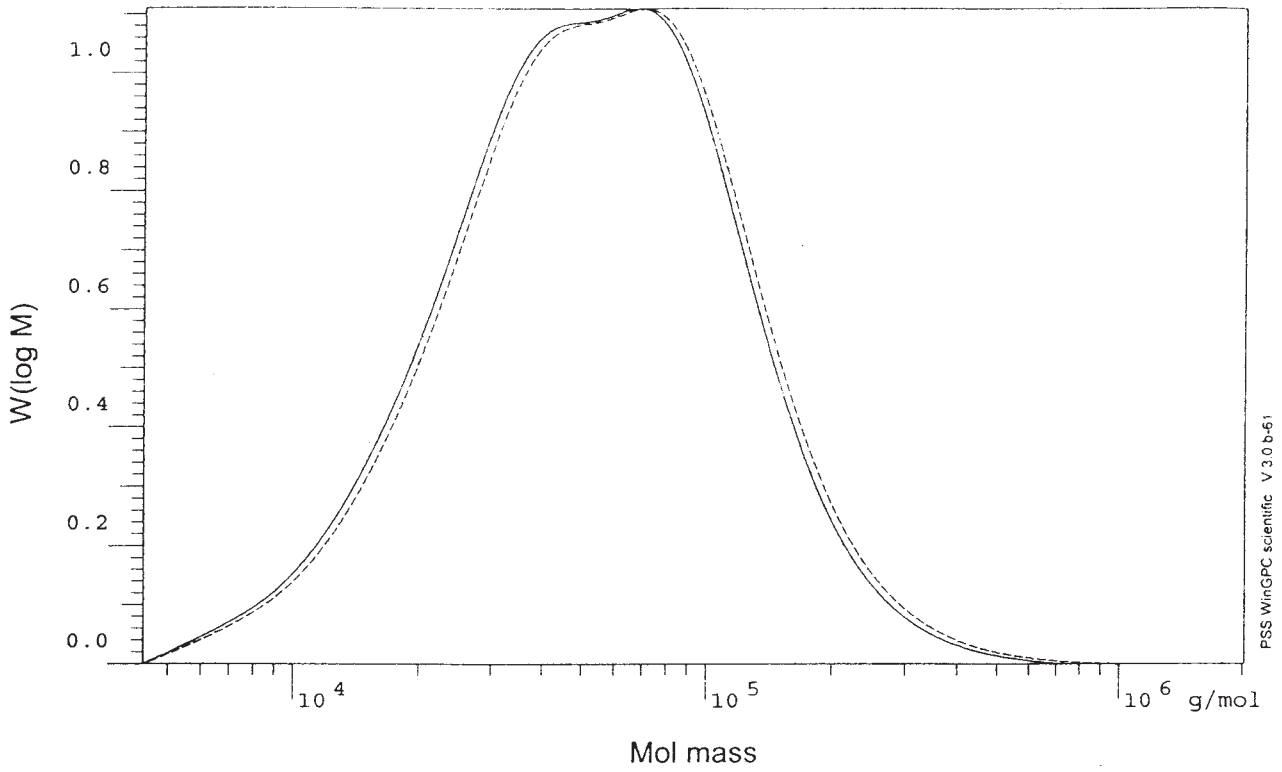


Figure 5 A GPC chromatograph of the copolymer.

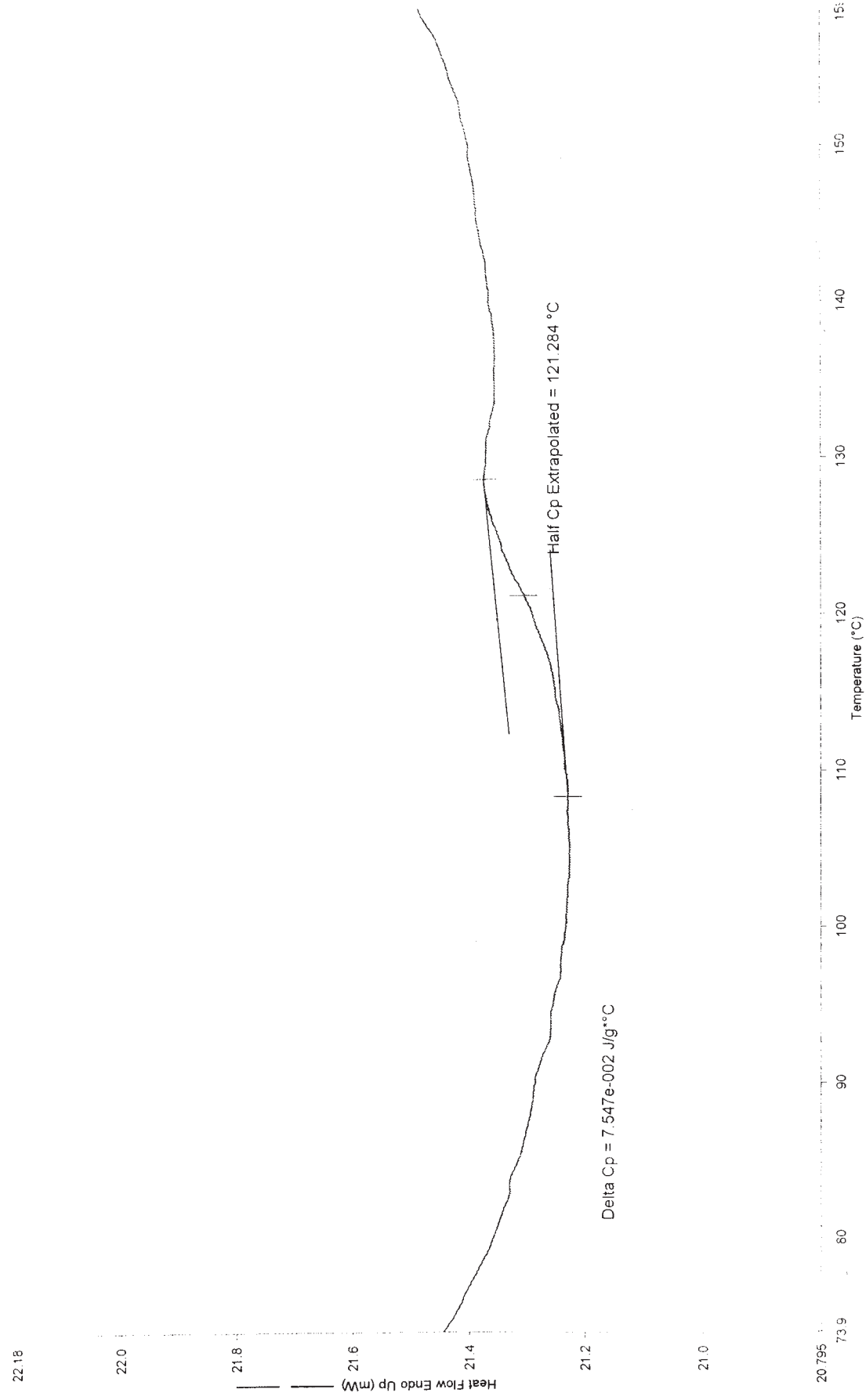
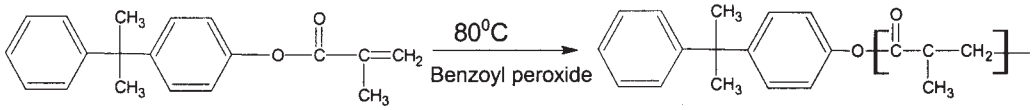


Figure 6 DSC scan of the 60:40 copolymer.

Polymer synthesis

Homopolymerization

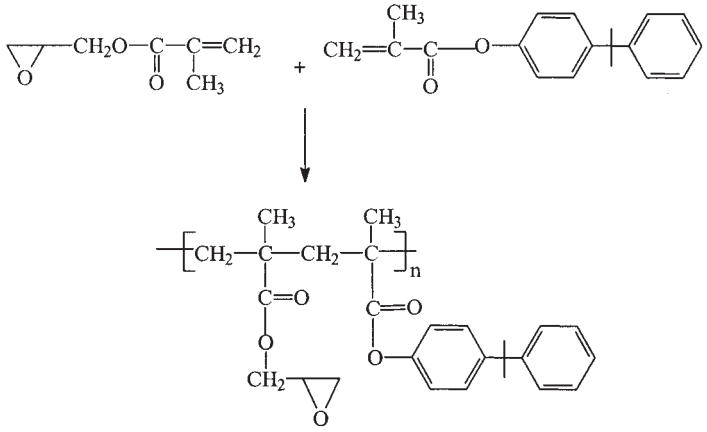
Homopolymerization of the monomer was performed in benzene using benzoyl peroxide as an initiator at 80 ± 2°C. The polymerization was terminated at various intervals of time [Table I, Eq. (2)] and was characterized by ^{1}H-NMR and IR. The ^{1}H-NMR spectrum of the polymer shows the absence of olefinic protons at δ 5.8–5.5 along with aromatic protons at δ 7.5–7.3 and a multiplet between δ 2.31 and 1.41 for backbone —CH_2 and —CH protons, indicating polymerization has occurred. The IR shows a strong band at 1730 cm^{-1} for the ester carbonyl.



The molecular weights were determined by the viscosity and GPC (M_w/M_n). The effect of time on the molecular weight buildup was studied by keeping the initiator concentration and temperature constant. An increase in the molecular weight was observed with an increase in the time of polymerization. The homopolymers obtained with 6 h of heating show lower molecular weights than the polymers prepared at 16 and 24 h of heating.

Copolymerization

Copolymerization of CPMA and GMA was performed with in different molar fractions of GMA in methyl ethyl ketone [Table II; Eq. (3)] at 70°C, and the copolymerization was terminated at low conversion.



The copolymers were characterized by IR and ^{1}H-NMR. The IR spectrum of the copolymer shows characteristic bands of both monomer units. The bands at 3050–2880 cm^{-1} are due to the aromatic and aliphatic stretching vibration of CH and CH_2. The ester carbonyl groups of GMA are seen at 1750 cm^{-1}. The incorporation of an aromatic ring of CPMA in the copolymer is confirmed by bands at 1600, 1500, cm and 1461 cm^{-1} in the IR spectrum of the copolymer. The presence of bands at 1260 and 910 cm^{-1} indicates the incorporation of an oxirane ring of GMA. This is also proved by the NMR of the copolymer (Fig. 4). Aromatic protons of CPMA are observed at δ 7–7.2 and δ 7.3–7.5 as multiplets and the signals at δ 4.25–3.51 and δ3.5–3.14 are due to the O—CH_2 of ester methylene and epoxy group protons of GMA. Overlapping of the backbone protons is observed at δ 2.2–1.2. The copolymer composition was also determined by the ^{1}H-NMR technique. The mole fractions of CPMA and GMA were calculated by comparing the intensities of well-separated aromatic and aliphatic protons of both units by the following equation[14]:

$$C = \frac{\text{integrated intensities of aromatic protons}(I_A)}{\text{integrated intensities of total aliphatic protons}}$$

There are 9 aromatic protons and 11 aliphatic protons in CPMA (m_1) and 10 aliphatic protons in GMA (m_2). Thus, the composition m_1 is determined by

$$\text{mole fraction} = 9m_1/11m_1 + 10m_2 = m,$$

$$\text{then } m_2 = 1 - m_1$$

The mole fraction of m_1 (i.e., CPMA), which was determined by NMR, was plotted versus the mole frac-

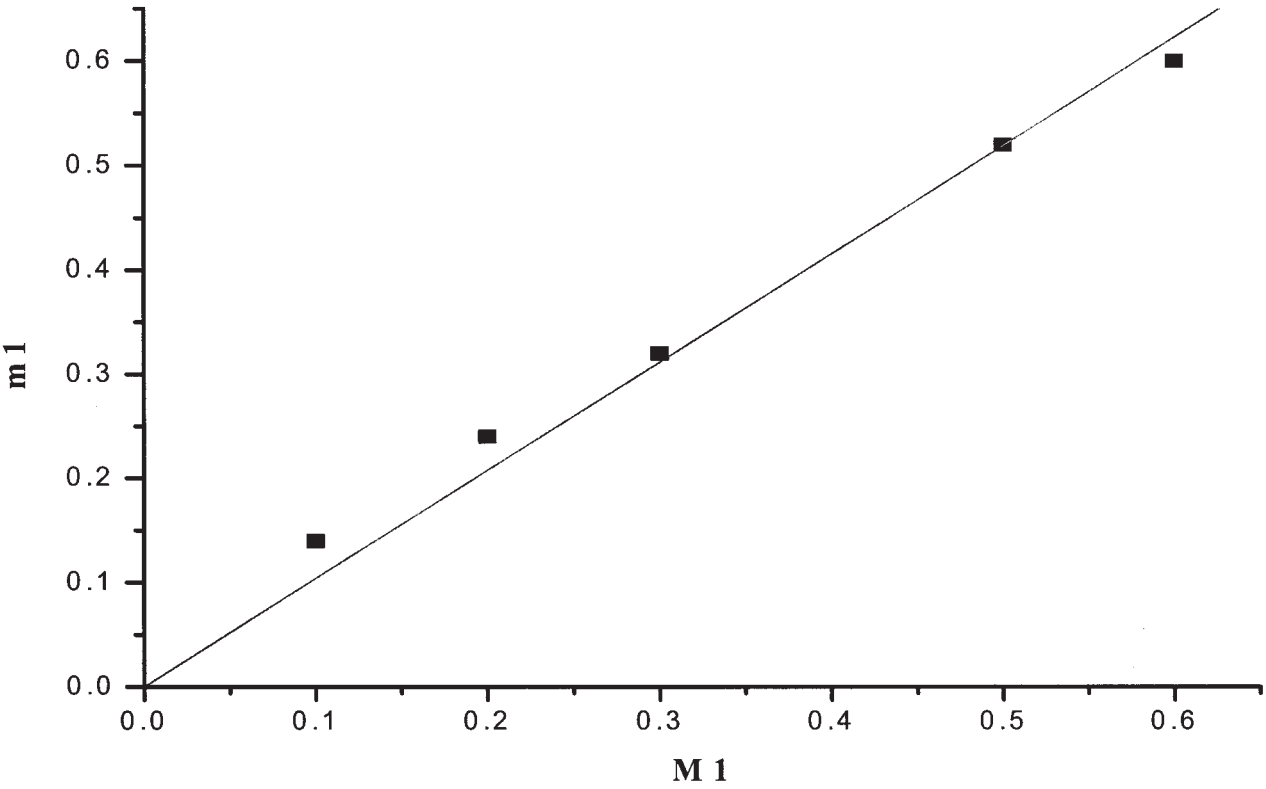


Figure 7 The plot of the mole fraction of CPMA in the copolymer (m_1) by NMR versus the mole fraction of CPMA in the feed.

tion (M_1) of CPMA in the feed. The graph is linear and passes through the origin, indicating the random nature of the copolymer (Fig. 7).

Reactivity ratios

To understand the copolymerization behavior, the reactivity ratios of the copolymer of CPMA and GMA were determined from the copolymer composition and monomer feed ratio by Fineman–Ross[15] (FR) and Kelen–Tudos (KT) methods.[16] The KT plot was drawn from the values of η and ξ (Table III, Fig. 8), and the values obtained by KT are $r_1 = 1$ and $r_2 = 0.504$ and by FR (Fig. 9) are $r_1 = 0.73259$ and $r_2 = 0.659$. The values obtained by the KT and FR methods are in good agreement with each other. The CPMA monomer has a higher reactivity ratio than GMA, which indicates the copolymer becomes richer in M_1 composition because of its reactivity.

GPC

The weight-average and number-average molecular weights and the polydispersity indices of the copoly-

TABLE III
Determination of Reactivity Ratio of Copolymer by Kelen–Tudos Method

	Monomer composition		Copolymer composition							
No.	M_1	M_2	m_1	m_2	$X = M_1/M_2$	$Y = m_1/m_2$	$G = X(Y-1)/Y$	$F = X^2/Y$	$\eta = G/\alpha + F$	$\xi = F/\alpha + F$
1	10	90	14	86	0.11	0.16	−0.5775	0.0756	−1.4031	0.1836
2	20	80	24	76	0.25	0.32	−0.5436	0.1984	−1.0172	0.3713
3	30	70	32	68	0.42	0.47	−0.4736	0.3753	−0.6686	0.5276
4	40	60	54	46	0.66	1.17	0.0958	0.3723	0.1353	0.5256
5	50	50	52	48	1	1.08	0.0740	0.9259	0.0586	0.734
6		40	60	40	1.5	1.5	0.5	1.5	0.2723	0.817

Copolymerization was carried in methyl ethyl ketone at 70 ± 2 for 2 h. M_1, mole ratio of *p*-cumyl phenyl methacrylate; M_2, mole ratio of glycidyl methacrylate; m_1, mole ratio of *p*-cumyl phenyl methacrylate in the copolymer; m_1, mole ratio of glycidyl methacrylate in the copolymer.

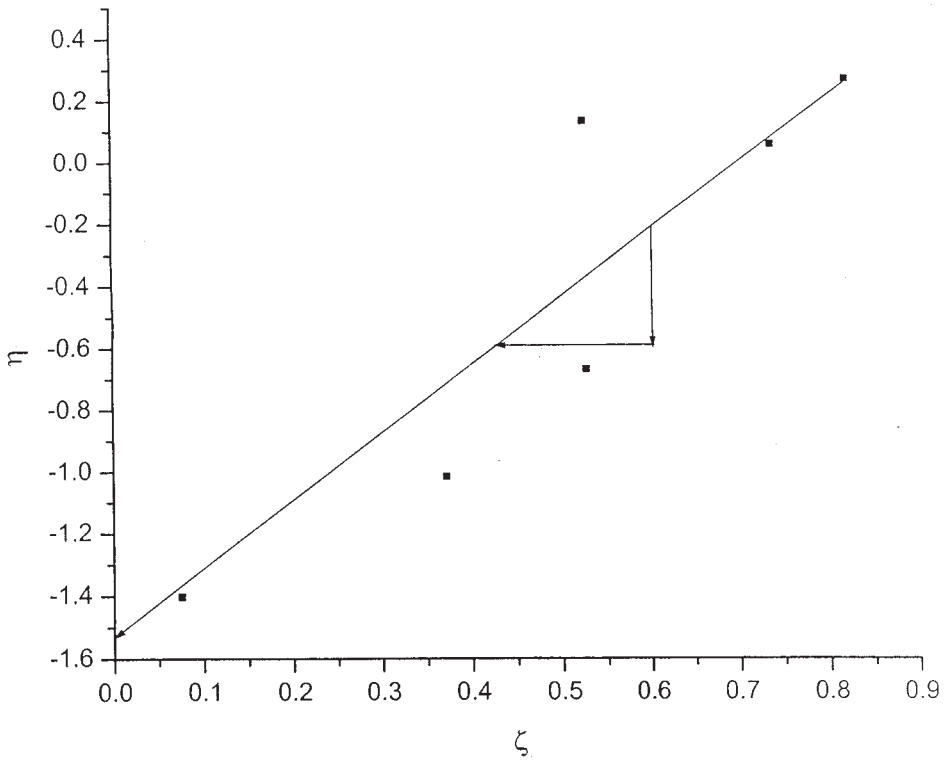


Figure 8 A Kelen–Tudo plot.

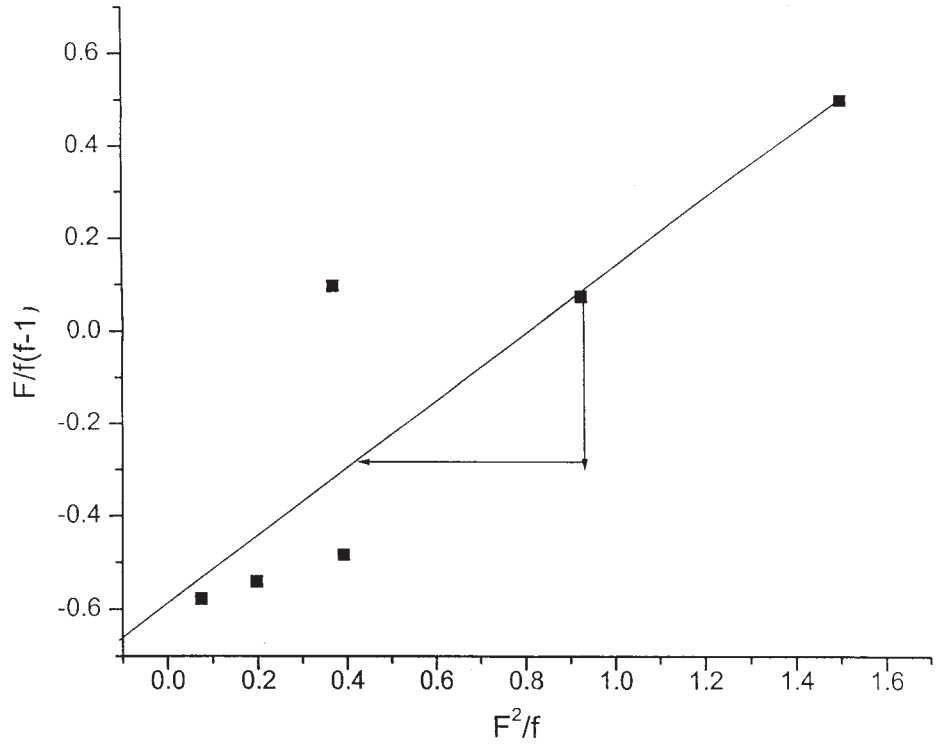


Figure 9 A Fineman–Ross plot.

mer were determined by GPC (Table II). The polydispersity indices of the copolymer are 2–3.5, which are typical for free-radical polymerization.[17]

DSC studies

The T_g values of the copolymers were determined using a DS calorimeter. It is observed that the T_g of poly(glycidyl MA) (PGMA) increases on incorporation of CPMA as a comonomer. Thus, the T_g of PGMA is 76°C whereas the T_g of the copolymer of GMA–CPMA (90:10) is 90°C. The gradual increase in the T_g of the copolymer was observed with an increase in the mol percent of CPMA in the copolymer (Table II) indicating that the presence of sterically bulky cumyl phenyl group in the copolymer increases the T_g of the copolymer.

CONCLUSIONS

The homopolymerization of the MA monomer containing aromatic groups (CPMA) yields a polymer with a higher T_g (130°C) than MMA (100°C). The copolymerizations of CPMA with a functional monomer like GMA also showed higher T_g than the corresponding PGMA. Thus, the copolymers containing a hydrophobic groups (i.e., cumyl phenyl) and a hydrophilic epoxy group will find application in diversified fields of polymer science by opening the epoxy ring or by substitution in the aromatic ring.

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