Phenyl methacrylate–glycidyl methacrylate copolymers: synthesis, characterization and reactivity ratios by spectroscopic methods

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The free-radical polymerization of phenyl methacrylate and glycidyl methacrylate was carried out at 70°C in the presence of benzoyl peroxide using 2-butanone as the solvent. The copolymer compositions of seven copolymer samples with different feed compositions as well as the tacticities were determined by ^1H nuclear magnetic resonance spectroscopy. The results were used to calculate the reactivity ratios by the Kelen–Tudos method, which were found to be $r_1 = 1.57 \pm 0.56$ and $r_2 = 0.84 \pm 0.51$. The homo- and copolymers were also characterized by Fourier-transform infra-red and ^{13}C nuclear magnetic resonance spectroscopic methods. $\bar{M}_w$, $\bar{M}_n$ and polydispersity indices of the copolymers were determined using gel permeation chromatography.

(Keywords: copolymerization; phenyl methacrylate; glycidyl methacrylate; reactivity ratios; ^1H and ^{13}C nuclear magnetic resonance)

INTRODUCTION

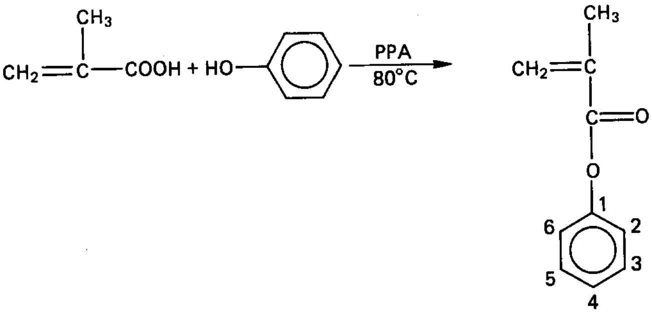
Copolymers based on glycidyl methacrylate (GMA) have wide applications in biology for the binding of enzymes, drugs and DNA[1–3]. Copolymers of GMA have also been used for immobilization of catalysts[4]. The epoxide group in the molecule is very reactive and has the ability to enter into a vast number of chemical reactions[5]. The presence of an aromatic ring in phenyl methacrylate (PhMA) polymers facilitates the introduction of the required functional group through chloromethylation. PhMA polymers are useful as basic polymeric supports in polymeric reagents. It is difficult by normal analytical techniques to estimate the composition of copolymers containing methacrylate monomers because of similarity in constituent units[6]. In recent years, the use of both ^1H and ^{13}C n.m.r. spectroscopy has shown many advantages not only for calculation of sequence distribution but also for composition determination[7–16]. This paper reports the estimation of composition of PhMA and GMA copolymers by the ^1H n.m.r. technique, and the reactivity ratios by the Kelen–Tudos method.

EXPERIMENTAL

Materials

Phosphoric acid (BDH), anhydrous phosphorus pentoxide (E. Merck), methacrylic acid (Sisco-Chem), phenol (BDH), 2-butanone (BDH), toluene (E. Merck), chloroform (E. Merck) and methanol (BDH) were used without further purification. Benzoyl peroxide (Fluka) was purified from chloroform/methanol mixture. Glycidyl methacrylate (Fluka) was distilled under reduced pressure before use.

Phenyl methacrylate was prepared by reacting phenol with methacrylic acid in the presence of polyphosphoric acid (PPA)[17]. Phenyl methacrylate was distilled under vacuum; b.p. 105–110°C/12 mmHg. The synthesis is outlined below:



I.r. (cm^{-1}): 3030, 2920, 1726, 1635, 1590, 1290 and 700.

^1H n.m.r. (δ, ppm): 7.35–7.26 (2H), 7.20–7.03 (3H), 6.29 (1H), 2.03 (3H) and 5.66 (1H).

^{13}C n.m.r. (δ, ppm): 135.68 (=C), 126.69 (=CH_2), 150.79 (C1), 129.06 (C3, C5), 125.36 (C4), 121.34 (C2, C6), 175.19 (C=O) and 16.00 (CH_3).

Copolymerization

Free-radical solution polymerization was used for preparing copolymers. Appropriate quantities of PhMA (1) and GMA (2) with 2-butanone and benzoyl peroxide were placed in a standard reaction ampoule (100 ml) and the mixture was flushed with a slow stream of oxygen-free nitrogen for about 5 min. The ampoule was tightly sealed and immersed in a thermostatic water bath for a suitable period at 70 ± 1°C. The copolymers were isolated by precipitation of the reaction mixture in excess methanol, filtered off and dried in a vacuum oven at 50°C for 12 h.

Measurements

^1H n.m.r. spectra for all the copolymer samples were run on a Bruker 270 MHz FTn.m.r. spectrometer. ^{13}C n.m.r. spectra of the copolymer were also run on a Bruker

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Table 1 Copolymerization[a] of phenyl methacrylate (PhMA) and glycidyl methacrylate (GMA)

Feed composition in mole fraction					Copolymer composition in mole fraction				
PhMA (M_1)	GMA (M_2)	Conversion (%)	Intensity of aromatic protons, I_A	Intensity of aliphatic protons, I_a	PhMA (m_1)	GMA (m_2)	$\bar{M}_n \times 10^3$	$\bar{M}_w \times 10^3$	$\bar{M}_w/\bar{M}_n$
0.206	0.794	8.95	3.60	20.80	0.295	0.705	4.59	14.32	3.12
0.306	0.694	13.50	6.00	26.70	0.367	0.633	4.77	15.31	3.21
0.401	0.599	9.26	7.20	23.00	0.477	0.523	5.02	12.99	2.59
0.498	0.502	12.37	9.80	24.70	0.568	0.432	5.20	14.15	2.72
0.595	0.405	6.48	14.80	27.10	0.706	0.294	5.46	15.51	2.84
0.805	0.198	9.34	12.40	16.20	0.867	0.133	5.72	17.23	3.01
0.907	0.093	8.84	16.00	18.05	0.940	0.060	5.96	20.61	3.46

[a] Temperature, 70 ± 1°C; solvent, 2-butanone; benzoyl peroxide, 0.2 g; non-solvent, methanol

270 MHz spectrometer operating at 67.80 MHz. In all cases $CDCl_3$ was used as solvent and tetramethylsilane (TMS) as internal standard. In ^{13}C n.m.r. the protons were decoupled by broad-band irradiation.

FTi.r. spectra of the copolymer were recorded on a Nicolet 20 DXB using a potassium bromide pellet. Weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights and polydispersity indices of the copolymers were determined by gel permeation chromatography (g.p.c.). Toluene was used as an eluant at a flow rate of 1 ml min^{-1}, and polystyrene standards were employed for calibration. The thermogravimetric analyses of homo- and copolymers were carried out under a nitrogen atmosphere at a flow rate of 200 ml min^{-1} with a Stanton Redcroft simultaneous t.g.–d.t.a. instrument, and the heating rate was maintained at 10°C min^{-1}.

RESULTS AND DISCUSSION

Synthesis and characterization

Copolymers and homopolymers were prepared in 2-butanone at 70°C using benzoyl peroxide as radical initiator. Copolymerization was allowed to proceed to $\approx$15% conversion in order to obtain polymer samples having as far as possible homogeneous composition (*Table 1*). All the polymers were characterized by ^1H n.m.r., making use of characteristic chemical shifts of the aromatic and aliphatic protons (*Figure 1*). The well resolved aromatic protons of PhMA appear at 7.0–7.5 ppm. In the case of GMA the $-OC\underline{H}_2$ protons appear as two separate peaks at 3.8 and 4.3 ppm respectively. The protons present in the epoxy group of GMA show a signal at 3.2 ppm due to $-C\underline{H}$ and at 2.6–2.8 ppm due to $-C\underline{H}_2$. The backbone methylene protons of the two monomer units in the copolymer gave a signal at 1.8–2.2 ppm. The α-methyl protons of the two units show a signal at 0.9–1.3 ppm, which is sensitive to tacticity.

I.r. spectroscopy

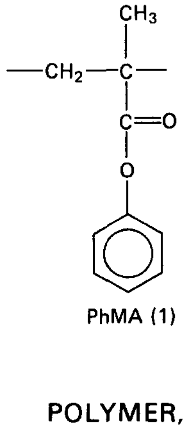
The FTi.r. spectrum of the copolymer (50/50 mol%, *Figure 2*) has the same characteristic absorption bands as that of the homopolymer mixtures. The bands at 3040 and 1591 cm^{-1} due to aromatic stretching and C=C stretching confirm the incorporation of PhMA unit in the copolymer. The carbonyl stretching of both acrylates appears at 1740 cm^{-1} and the appearance of the 909 cm^{-1} band not only explains the incorporation of GMA unit in the copolymer but also confirms the participation of the double bond in copolymerization. The stretching vibrations of CH_3 and CH_2 were also observed at 2920 and 2970 cm^{-1}.

^{13}C n.m.r. spectroscopy

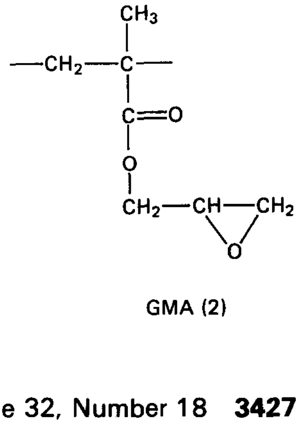
Figure 3 shows the proton-decoupled ^{13}C n.m.r. spectra of the homo- and copolymers of PhMA and GMA. The ^{13}C n.m.r. spectrum of the copolymers has the same characteristic peaks as the homopolymer mixture. The incorporation of two monomeric units into the copolymer was confirmed by their carbon chemical shifts. The appearance of multiple peaks from 16.90 to 19.90 ppm indicates the α-methyl groups of the two monomer units, which are sensitive to tacticity. Similarly the carbonyl groups of the two esters gave peaks at 175.50 and 171.65 ppm respectively. The appearance of aromatic C1 at 149.00 ppm is explained owing to the presence of the ester group adjacent to the C1 carbon. Carbons C2 and C6 gave peaks at 129.00 ppm followed by C4 at 124.00 ppm. These chemical shifts indicate the PhMA unit in the copolymer. In the case of GMA, the well resolved peak at 65.50 ppm is due to the $-O\underline{C}H_2$ group. The epoxy carbons of GMA unit gave peaks at 52.50 and 54.00 ppm. The chemical-shift difference of backbone methylene and tertiary carbons of the monomer units is less and appears at 45.00, 45.95 and 49.00 ppm respectively.

Estimation of copolymer composition and reactivity ratios

The constituent monomeric structural units of the copolymer are as follows:



PhMA (1)



GMA (2)

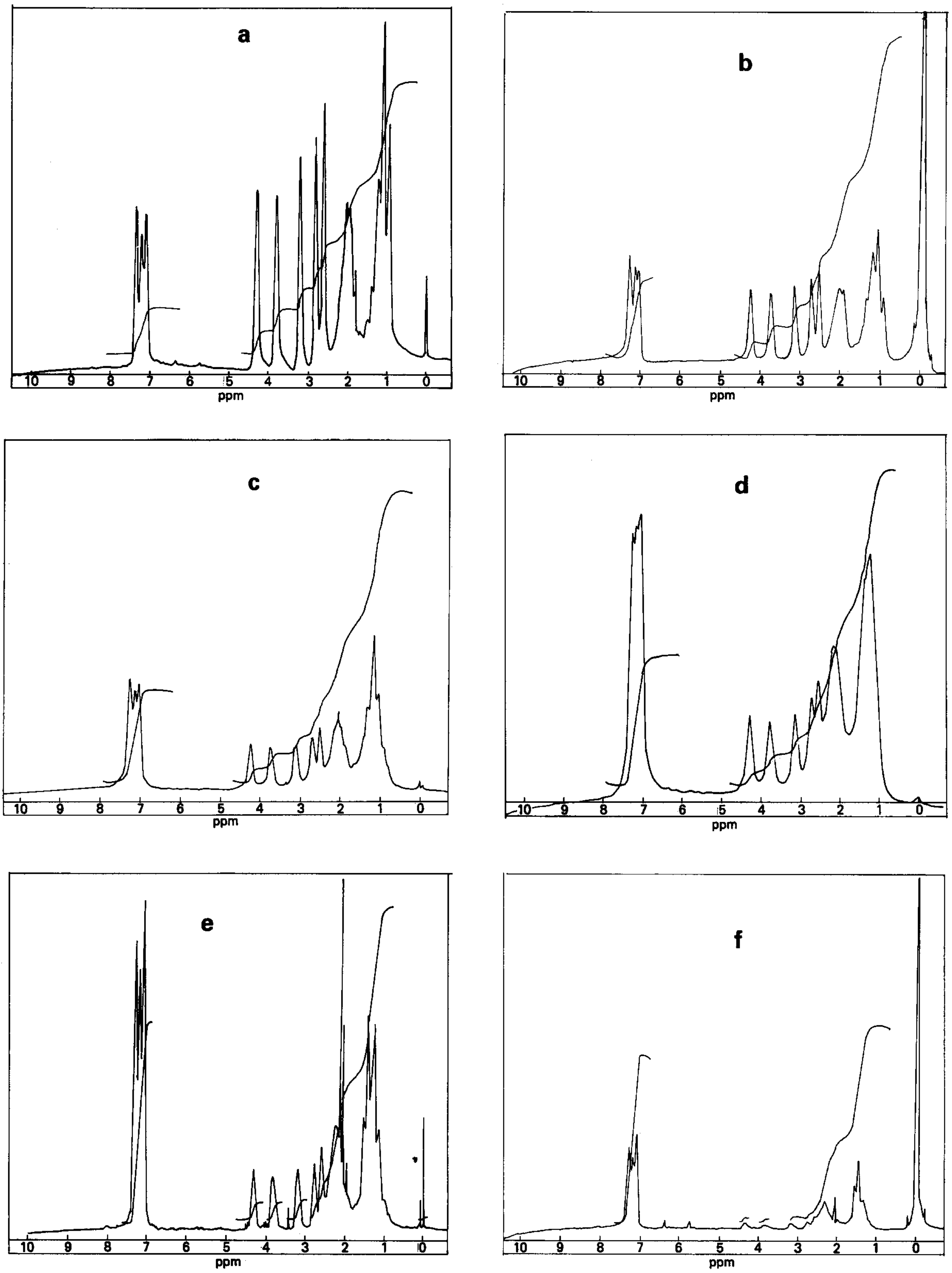
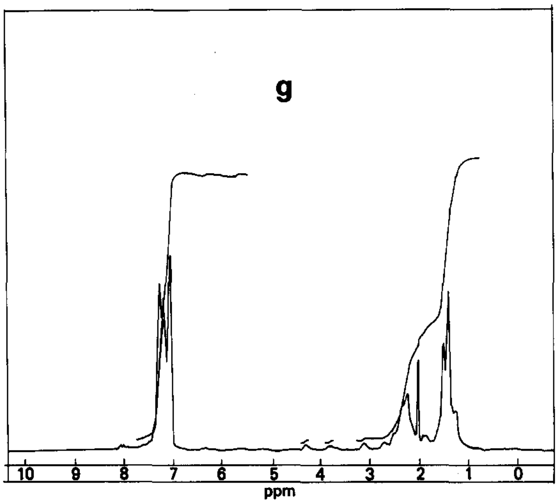


Figure 1 Fourier-transform ^1H n.m.r. spectra of phenyl methacrylate and glycidyl methacrylate copolymers

The distribution of protons in the two units is an important means of distinguishing monomers in the copolymer chain. The α-CH_3 group protons of both PhMA and GMA are almost indistinguishable. Grassie *et al.*[6] calculated the molar ratio of methyl methacrylate (MMA) to methacrylic acid (MA) in MMA–MA copolymer by the use of the total proton differences. The presence of equal numbers of protons in the two constituent monomeric units avoids the use of the above-mentioned method in the present study. Hence, we have chosen a new method for the determination of PhMA composition in the copolymer by comparing the intensities of aromatic protons ($\approx$7.5 ppm) of PhMA with the rest of the aliphatic protons present in the copolymer. Since the peak intensity corresponds to the total number of protons of a particular group, the mole



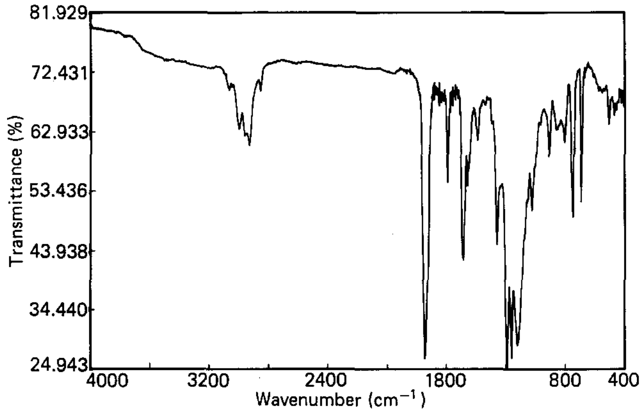


Figure 2 FTi.r. spectra of the phenyl methacrylate and glycidyl methacrylate copolymer (70:30)

fraction of the monomeric units in the copolymer was calculated by the following equation:

$$\frac{\text{intensity of aromatic protons } (I_A)}{\text{intensity of aliphatic protons } (I_a)} = \frac{5m_1}{5m_1 + 10m_2} \qquad (1)$$

This equation is based on the fact that there are ten protons each in PhMA and GMA, but five aromatic protons in PhMA. From this and $m_2 = 1 - m_1$, the following equation was derived:

$$m_1 = \frac{2I_A}{I_A + I_a} \qquad (2)$$

Integrated peak intensities were employed for this calculation, so m_1 is the mole fraction of PhMA and $1 - m_1$ is that of GMA.

Based on equation (2), the mole fraction of PhMA was calculated by measuring the intensities of aromatic protons and aliphatic protons from the spectra of all copolymer samples. ^1H n.m.r. spectra of all the copolymers of different feed compositions of M_1 from 0.21 to 0.91 mol were presented in *Figure 1*. All copolymer samples exhibit a content of PhMA units higher than that of the corresponding initial comonomer mixtures (*Table 1*). The reactivity ratios of PhMA (1) and GMA (2) were evaluated by least-squares evaluation of the Kelen–Tudos[18] parameters (*Table 2* and *Figure 4*) and the values are:

$$r_1 = 1.57 \pm 0.56 \qquad r_2 = 0.84 \pm 0.51 \qquad (3)$$

The errors were derived from the standard deviations in the slope and intercept of the straight line from *Figure 4*. The reactivity ratio values indicate that the PhMA radical slightly favours its own monomer rather than GMA, but the reverse happens for the GMA radical. However, since the product of the reactivity ratios is close to 1

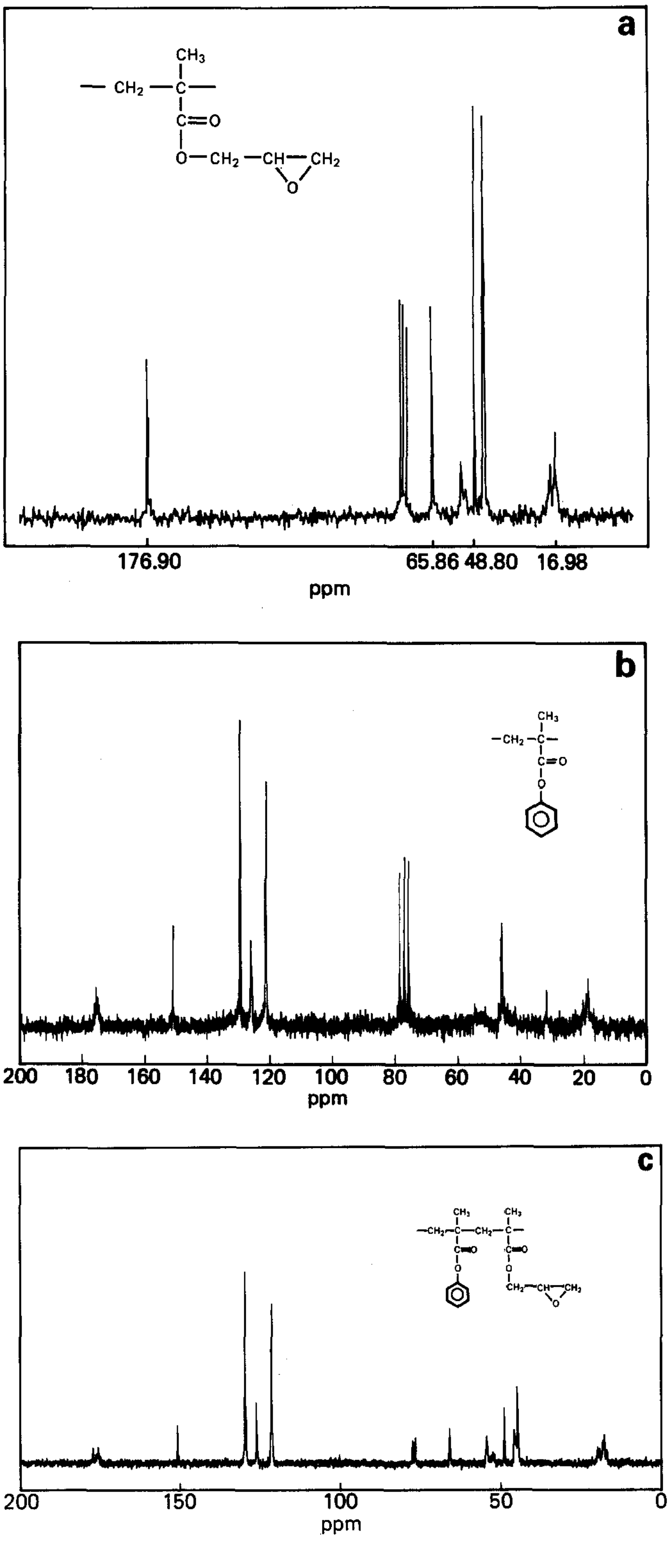


Figure 3 ^1H and ^{13}C n.m.r. spectra: (a) homopolymer of glycidyl methacrylate; (b) homopolymer of phenyl methacrylate; (c) copolymer of phenyl methacrylate and glycidyl methacrylate (70:30)

Table 2 Kelen–Tudos parameters of phenyl methacrylate (PhMA, M_1) and glycidyl methacrylate (GMA, M_2) copolymers

$X = M_1/M_2$	$Y = m_1/m_2$	$G = X(Y-1)/Y$	$F = X^2/Y$	$\xi = F/\alpha + F$	$\eta = G/\alpha + F$
0.2594	0.4184	−0.3604	0.0622	0.1093	−0.6691
0.4406	0.5795	−0.3196	0.3348	0.2524	−0.2409
0.6704	0.9113	−0.0652	0.4930	0.3320	−0.0439
0.9901	1.3148	0.2371	0.7455	0.4291	0.1365
1.4710	2.4059	0.8596	0.8993	0.4756	0.4546
4.0332	6.5240	3.4146	2.4926	0.7154	0.9800
9.7829	115.6112	9.1497	6.1217	0.8608	1.2863

$\alpha = 0.9917$

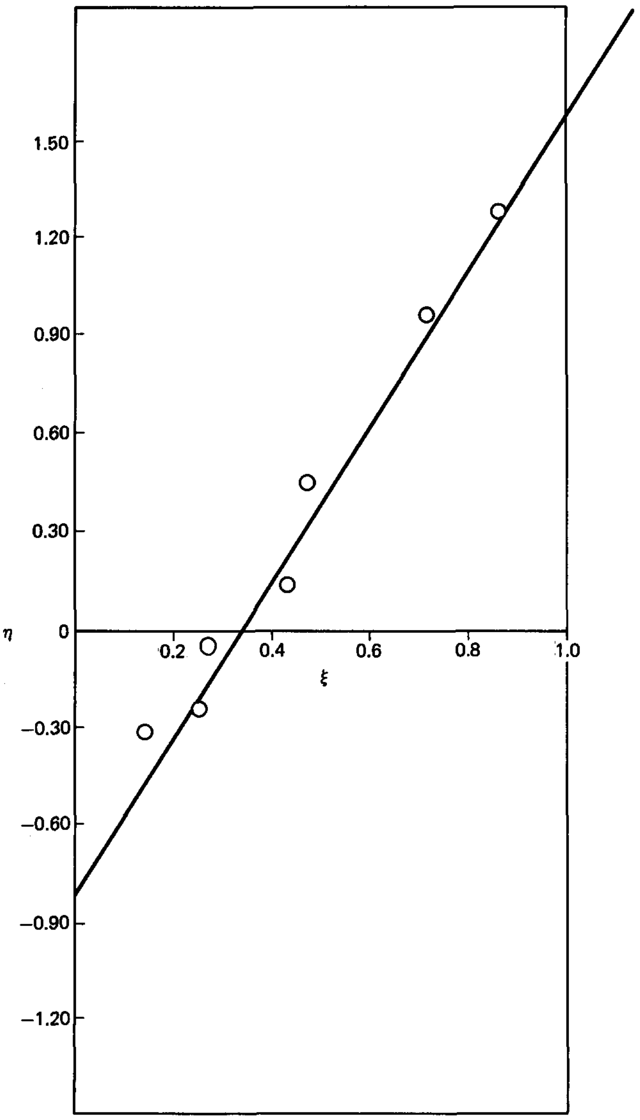


Figure 4 Kelen–Tudos plot

($r_1r_2 = 1.32$), the co-units are inserted into the copolymers in a substantially random manner[19].

The kinetic behaviour of the PhMA–GMA copolymer system has been studied at low conversions by a gravimetric method. The overall polymerization rate, expressed as conversion/time ratio, changes drastically with the feed composition, having values lower than those of the corresponding homopolymerization. It is noteworthy that a minimum value of the rate of polymerization is reached near an equimolecular monomer mixture in the feed. These results can be explained, as assumed earlier by other investigators for the polymerization of acrylic aromatic monomers[20–22], by π-complex formation between the electron-accepting acrylic/methacrylic double bonds and the electron-donating aromatic rings. The reactivity of the double bond participating in the π-complex formation with the aromatic ring decreases with respect to the free monomeric species, and therefore the overall activation energy in the polymerization increases[23].

Effect of copolymer composition on the tacticity of $-CH_3$

It is well known that the α-CH_3 resonance corresponding to poly(methyl methacrylate) shows three peaks around 0.82, 0.97 and 1.15 ppm from hexamethyldisilane (HMDS), which can be assigned to the syndiotactic, heterotactic and isotactic triads respectively[24]. Similar data were reported for the n.m.r. spectrum of poly(phenyl methacrylate)[25]. Both PhMA and GMA have α-methyl groups, and the chemical shifts representing the syndiotactic, heterotactic and isotactic effects of each monomeric unit in the copolymer were overlapped with each other. Therefore, the tacticity discussed here represents the net tacticity of both the monomeric units in the copolymer with respect to the chemical composition of PhMA. The spectra of all the samples analysed exhibit only three major peaks (0.96, 1.11 and 1.22 ppm) with the same chemical shift as poly(methyl methacrylate), but the peak intensities change with the copolymer composition. That is, the copolymer having $m_1 = 0.295$ and $m_2 = 0.705$ mol has 31.1%, 45.1% and 23.9% of syndiotactic (*rr*) heterotactic (*mr*) and isotactic (*mm*) triads respectively.

The tacticity of the copolymers can be explained by taking M-centred triads into account. The introduction of PhMA units in the macromolecular chain does not modify the diamagnetic effects of the carbonyl double bonds on the α-methyl groups as shown in *Figure 5*.

The configuration orientation of the carbonyl groups with respect to the α-CH_3 group is similar to that of poly(methyl methacrylate). The PhMA aromatic rings may be distributed along the copolymer chain in such spatial positions that they have slight influence on the chemical shift of the α-CH_3 resonance signals, considering GMA-centred triads. On the other hand, the stereochemical configuration of the copolymer chain is only finalized after the addition of the monomer molecules to the end unit of the group radicals, and depends on the relative positions of the substituents on the terminal C atom at the moment of bond formation.

The number-average and weight-average molecular

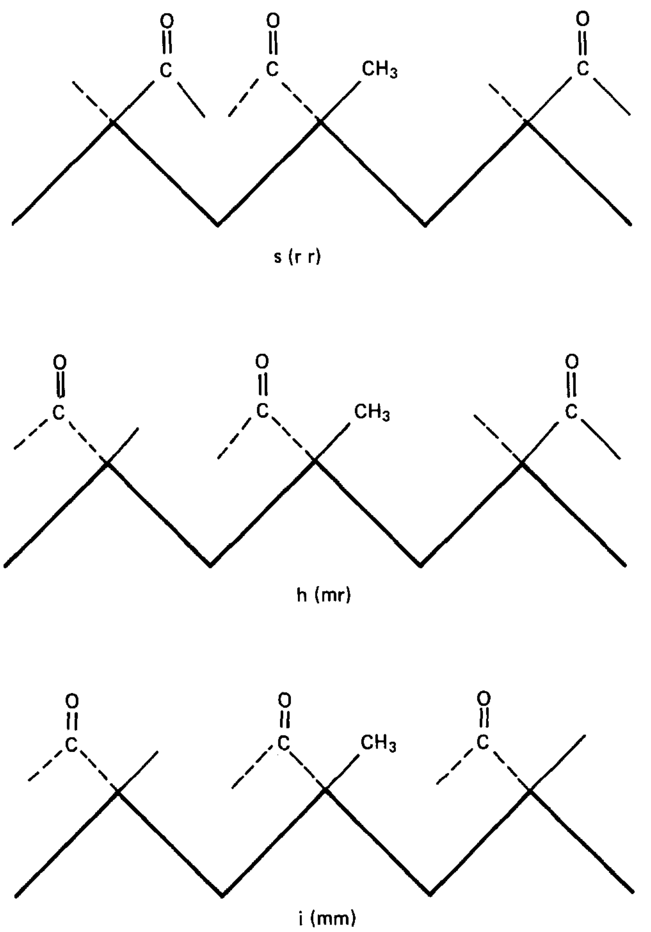


Figure 5 Tacticity of phenyl methacrylate–glycidyl methacrylate copolymer

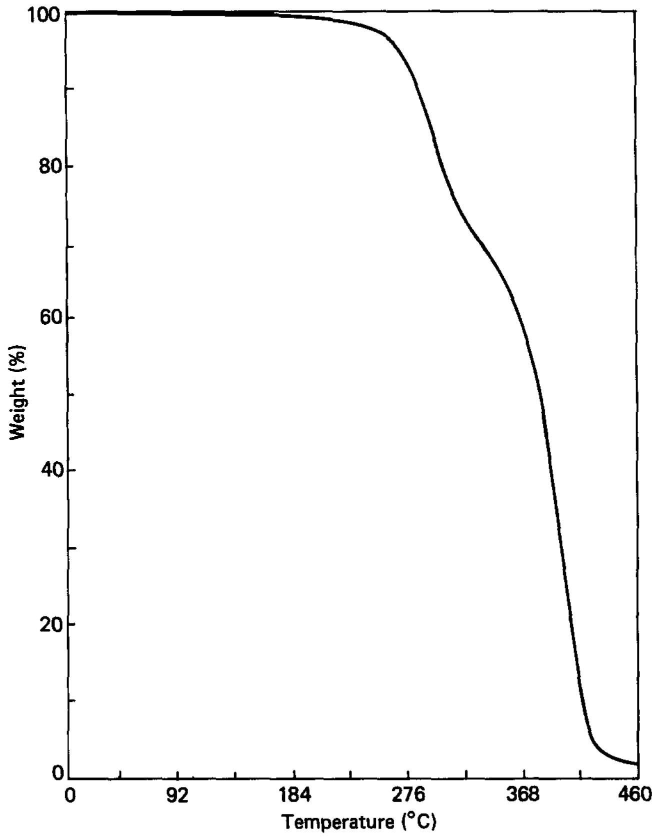


Figure 6 Thermogram of poly(phenyl methacrylate)

weights and polydispersity indices of the copolymers were shown in *Table 1*. The values show that the copolymers formed are polydisperse in nature.

Thermogravimetric analysis

The thermal decomposition curves of homo-PhMA, homo-GMA and copoly(PhMA–GMA) are shown in *Figures 6–8*. The weight losses of the respective homo/copolymers were determined from the t.g. curves and the stage of degradation was studied. The activation energies (E_a) involved in the degradation processes were calculated by the Coats and Redfern[26] and Doyle[27] methods. *Table 3* shows the decomposition temperature (*DT*) and activation energy values. The decomposition of the PhMA polymer occurred in a single stage with an activation energy of 62.4 kJ mol^{-1} (14.9 kcal mol^{-1}). The degradation of PhMA–GMA (56:44) occurred in two stages. The first stage was observed from 249.00 to 330.00°C with activation energy 26.8 kJ mol^{-1} (6.4 kcal mol^{-1}). The second stage of decomposition was found from 351.00 to 403.50°C and the activation energy in this stage was 79.5 kJ mol^{-1} (19.0 kcal mol^{-1}), which was substantially higher than for the first stage. In the case of the homopolymer of GMA the decomposition occurred in a single stage with activation energy of 75.3 kJ mol^{-1} (18.0 kcal mol^{-1}), which was higher than for PhMA homopolymer. The thermolysis curve of copoly(PhMA–

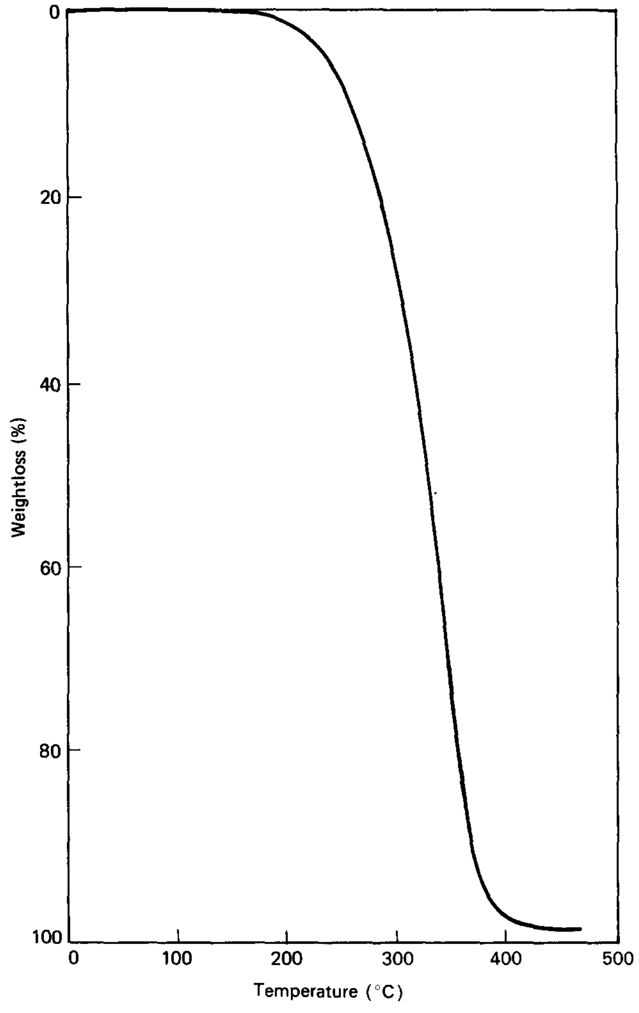


Figure 7 Thermogram of poly(glycidyl methacrylate)

Table 3 Thermal decomposition temperatures and activation energies of phenyl methacrylate (PhMA) and glycidyl methacrylate (GMA) homo- and copolymers

Polymer	Decomposition temperature, *DT* (°C)			Stage of decomposition	Temperature range (°C)	Correlation coefficient *r* and activation energy E_a (kJ mol^{-1})			
						C & R		Doyle	
	30%	50%	70%			*r*	E_a	*r*	E_a
PhMA	342.77	382.77	403.61	Single	286.38–408.95	0.98	55.3	0.98	62.4
GMA	365.00	395.00	415.00	Single	305.00–445.00	0.99	64.9	0.99	75.3
PhMA-*co*-GMA	291.00	351.00	381.00	Stage I	249.00–330.00	0.99	17.6	0.99	26.8
				Stage II	351.00–403.50	0.98	69.1	0.99	79.5

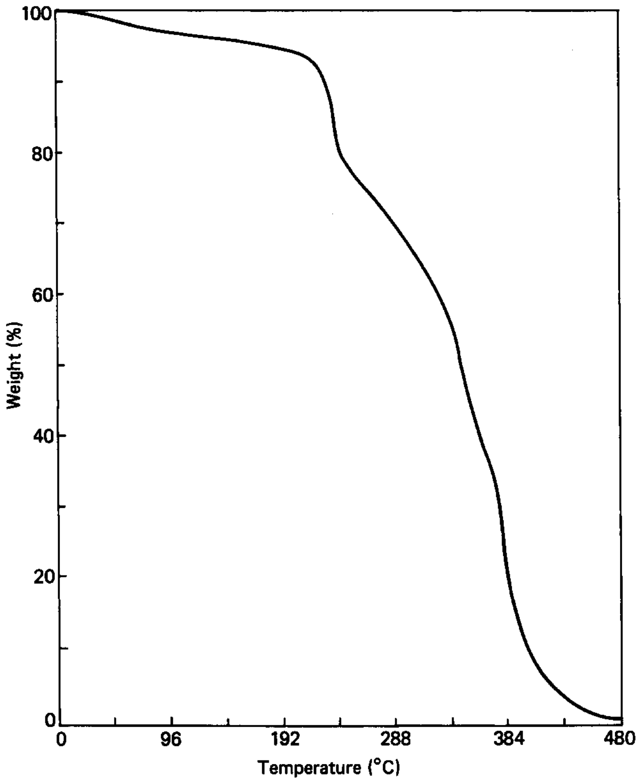


Figure 8 Thermogram of phenyl methacrylate–glycidyl methacrylate copolymer (70:30)

GMA) shows that the incorporation of PhMA polymer reduces the thermal stability of GMA considerably.

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