

# Synthesis and characterization of homopolymer of 3,5-dimethylphenyl methacrylate and its copolymers with glycidyl methacrylate

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## Abstract

The acrylic monomer, 3,5-dimethylphenyl methacrylate was synthesized by reacting 3,5-dimethylphenol dissolved in ethyl methyl ketone (EMK) with methacryloyl chloride in the presence of triethylamine. The homopolymer and various copolymers with glycidyl methacrylate were synthesized using free radical polymerization in EMK solution at  $70 \pm 1$  °C using benzoyl peroxide as initiator. The copolymers were characterized by FT-IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR techniques. The molecular weights ( $\overline{M}_n$  and  $\overline{M}_w$ ) and polydispersity indices were determined using gel permeation chromatography. The glass transition temperatures were determined by differential scanning calorimetry. Thermogravimetric analysis were performed in air. The solubilities of the polymers were tested in various polar and non-polar solvents. Copolymer compositions were determined using <sup>1</sup>H-NMR spectra. The monomer reactivity ratios were determined by application of conventional linearisation methods such as Fineman–Ross, Kelen–Tüdös and extended Kelen–Tüdös. © 2002 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Polymer supports based on glycidyl methacrylate (GMA) have been used for the binding of drugs and biomolecules [1] and in electronic industries as negative electron beam resists [2]. Compounds containing epoxy groups are used as excellent thermosetting adhesives which are heat resistant and decrease flow cracking in the manufacture of semiconductor packaging [3,4]. Methacrylic copolymers have been used in the leather industry for the formulation of base and top coats [5] and leather–leather bonding [6]. Copolymers formed from substituted phenyl methacrylate are used in the production of printing plates and electrical circuits [7,8].

Phenyl(meth)acrylates have been used as weather-resistant high gloss top coats for automobile finishes [9].

The accurate estimation of copolymer composition and determination of monomer reactivity ratios are significant for tailor-made copolymers. In the past few decades, <sup>1</sup>H-NMR spectroscopic analysis has been established as a powerful tool for the estimation of copolymer composition [10–14]. The present paper reports the synthesis, characterization and determination of reactivity ratios for the comonomers 3,5-dimethylphenyl methacrylate (DMPMA) and GMA.

## 2. Experimental

### 2.1. Materials

3,5-Dimethylphenol (Lancaster, for synthesis) was used as received. GMA (Emerk) was purified by distillation

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under reduced pressure [15]. Benzoyl peroxide (BPO) was recrystallized from a chloroform–methanol (1:1) mixture. All solvents were purified by distillation.

## 2.2. Synthesis of 3,5-dimethylphenyl methacrylate

Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride using the procedure of Stampel et al. [16]. For the synthesis of DMPMA, 3,5-dimethylphenol (15 g, 0.12 mol) and triethylamine (18.8 ml, 0.12 mol) were dissolved in 250 ml of ethyl methyl ketone (EMK) and the reaction mixture was stirred in a bath at 0–5 °C. Methacryloyl chloride (13.1 ml, 0.12 mol) dissolved in 25 ml of EMK was added dropwise over a period of 30 min. After the addition the reaction mixture was stirred for 1 h. The cooling bath was removed and the reaction mixture was stirred at room temperature for a further period of 1 h. Then the precipitated triethylammonium chloride was filtered off and the solvent in the filtrate was removed using a rotary evaporator. The residue was dissolved in ether and was washed twice with 0.1% solution of NaOH and then with distilled water. The ether solution was dried using  $\text{Na}_2\text{SO}_4$ . The ether solution was evaporated to a residue which was distilled under reduced pressure to give pure DMPMA (yield 16.35 g) (70%).

The monomer was examined by FT-IR and  $^1\text{H-NMR}$  spectra.

IR  $\text{cm}^{-1}$ : 3090 and 3050 ( $=\text{C-H}$ ), 2972 and 2820 ( $\text{C-H}$  stretching), 1730 ( $\text{C=O}$ ), 1625 ( $\text{CH}_2=\text{C}<$ ), 1500 and 1400 (aromatic  $\text{C=C}$ ), 1375 ( $\text{CH}_3$  symmetrical bending), 1125 ( $\text{C-O}$ ), 840 and 685 ( $\text{C-H}$  out of plane bending).

$^1\text{H-NMR}$ : 6.85–6.73 (3H) ( $\text{Ar-H}$ ), 6.36 and 5.72 (2H) ( $\text{CH}_2=\text{C}$ ), 2.30 (6H) ( $\text{CH}_3\text{-Ar}$ ), 2.04 (3H) ( $\alpha\text{-methyl}$ ).

## 2.3. Homopolymerization

One gram of DMPMA and 50 mg of BPO were dissolved in 10 ml of EMK in a polymerization tube and  $\text{O}_2$  free  $\text{N}_2$  was purged through the solution for 20 min. Then the solution was thermostated at  $70 \pm 1$  °C. After 8 h the polymer was precipitated in methanol. It was purified by repeated reprecipitation by methanol from solution in EMK. The polymer was then dried in vacuum at 50 °C (yield 70%).

## 2.4. Copolymerization

Predetermined quantities of DMPMA, GMA, EMK and BPO were placed in a standard reaction tube (100 ml) and the mixture was flushed with  $\text{O}_2$  free  $\text{N}_2$  for 20 min. The tube was tightly sealed and immersed in a water bath at  $70 \pm 1$  °C. The polymer was precipitated in methanol. The precipitated polymer was filtered off and purified by repeated reprecipitation from chloro-

form solution using methanol and finally dried in vacuum at 50 °C for 24 h. The copolymer conversions were restricted to less than 10%.

## 2.5. Measurements

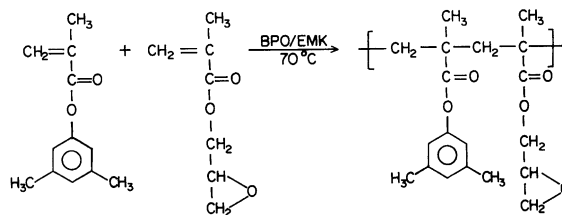
IR spectra were recorded with a Nicolet 360 FT-IR ESP spectrophotometer as KBr pellets.  $^1\text{H-NMR}$  spectra of all the monomer and polymer samples were recorded on a Bruker 270 MHz FT-NMR spectrometer at room temperature using  $\text{CDCl}_3$  and TMS as a solvent and internal standard respectively. The proton decoupled  $^{13}\text{C-NMR}$  spectrum was run on the same instrument operating at 22.63 MHz at room temperature and the chemical shifts were recorded under similar conditions. The molecular weights ( $\overline{M}_w$  and  $\overline{M}_n$ ) were determined using Waters 501 gel permeation chromatograph. Tetrahydrofuran was used as an eluent with polystyrene standards for calibration. Thermogravimetric analysis was performed with Mettler TA 3000 thermal analyser in air at a heating rate of 15 °C/min. The glass transition temperature was determined with a Perkin–Elmer DSC d7 differential scanning calorimeter at a heating rate of 10 °C/min in air.

## 3. Results and discussion

### 3.1. Synthesis of polymers

Poly(DMPMA) was obtained by the free radical solution polymerization of the monomer at  $70 \pm 1$  °C in EMK solvent using BPO as initiator. The copolymerization of DMPMA with GMA in EMK solution was carried out for mole fractions of DMPMA ranging from 0.15 to 0.9 in the feed. The reaction time was selected by trials to give conversions less than 10% in order to satisfy the differential copolymerization equation. The monomeric units of the copolymer are shown in the Scheme 1. The data on composition of feed and copolymers are presented in Table 1.

The homopolymer and the copolymers were soluble in chloroform, acetone, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, benzene,



Scheme 1. Synthesis of poly(DMPMA-co-GMA).

Table 1

Composition data for free radical copolymerization of DMPMA(1) with GMA(2) in EMK solution at 70 °C

Copolymer	$M_1^a$	Conversion (%)	Intensities of protons		C	$m_1^a$
			$I_{Ar}$	$I_{Al}$		
1	0.1480	8.84	6.281	93.183	0.0674	0.2298
2	0.3522	8.25	9.626	77.880	0.1236	0.4297
3	0.5906	7.13	13.562	86.438	0.1568	0.5514
4	0.6502	9.36	15.716	84.228	0.1866	0.6632
5	0.8042	8.52	17.712	81.586	0.2170	0.7797
6	0.9012	9.15	18.354	77.247	0.2376	0.8603

<sup>a</sup>  $M_1$  and  $m_1$  are the mole fraction of DMPMA in the feed and copolymer respectively.

toluene and xylene but insoluble in *n*-hexane and hydroxy-group-containing solvents such as methanol and ethanol.

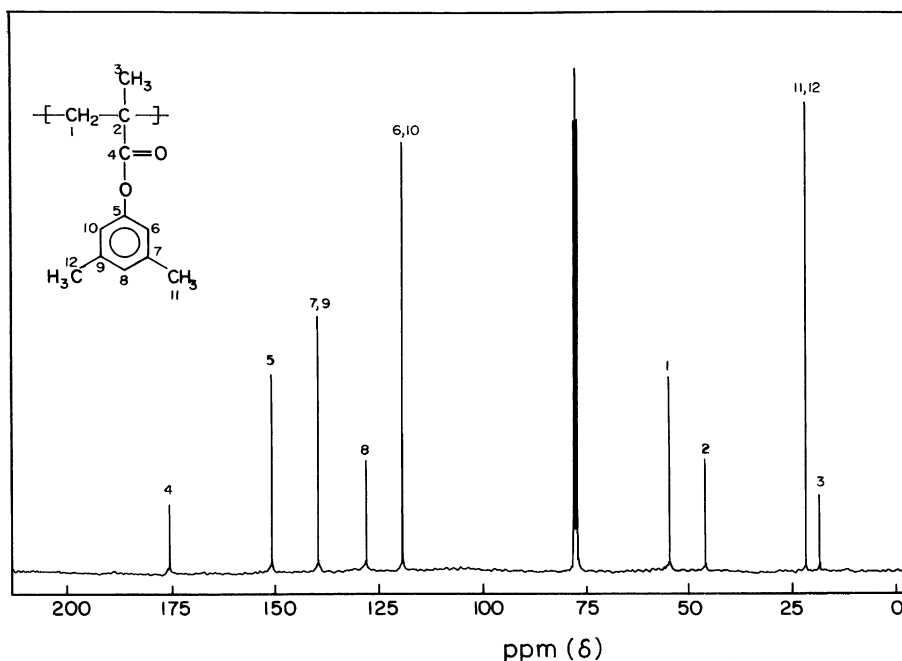
### 3.2. Characterization of polymers

The IR spectrum of the poly(DMPMA) shows a peak at 3025 cm<sup>-1</sup> due to the C-H stretching of the aromatic ring. The peaks at 2960, 2926, 2872 cm<sup>-1</sup> are attributed to the unsymmetrical and symmetrical C-H stretching of methylene and methyl groups. The ester carbonyl stretching is observed at 1750 cm<sup>-1</sup>. The ring stretching vibrations of the aromatic nuclei were observed at 1610, 1585 and 1475 cm<sup>-1</sup>. The symmetrical bending vibrations of methyl group is seen at 1375 cm<sup>-1</sup>. The peak at 1146 cm<sup>-1</sup> is due to the C-O stretching. The C-H out

of plane bending vibrations of the 1,3,5-trisubstituted aromatic nuclei are observed at 857 and 731 cm<sup>-1</sup>.

The <sup>1</sup>H-NMR spectrum of the homopolymer shows that the chemical shifts of the aromatic protons are shifted to upfield due to the electron-donating methyl groups attached to the aromatic nucleus and they appear at 6.79–6.69 ppm. The methyl groups attached to the aromatic nucleus show a signal at 2.19 ppm. The broad resonance signal at 1.87 and 1.07 ppm are due to the backbone methylene group and the  $\alpha$ -methyl group.

The proton decoupled <sup>13</sup>C-NMR spectrum of the homopolymer is given in Fig. 1. The ester carbonyl carbon shows a signal at 175.76 ppm. The aromatic carbon attached to the oxygen atom gave a signal at 151.02 ppm. The aromatic carbon atoms to which methyl groups are attached gave signals at 139.57 ppm (C<sub>7</sub> and C<sub>9</sub>). The other aromatic carbons gave signals at

Fig. 1. <sup>13</sup>C-NMR spectrum of poly(DMPMA).

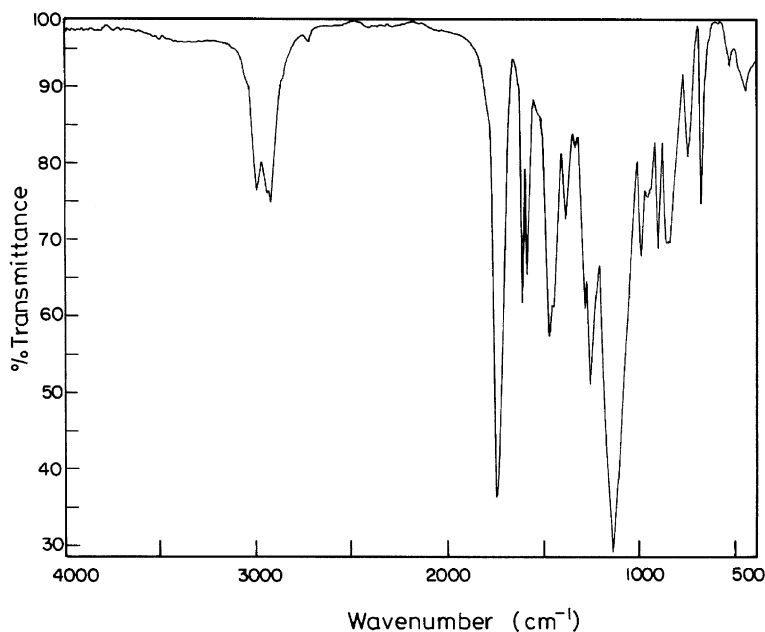


Fig. 2. IR spectrum of poly(DMPMA-co-GMA) (0.5514:0.4486).

119.16, 118.9 ppm ( $C_6$  and  $C_{10}$ ) and 127.90 ppm ( $C_8$ ). The backbone methylene and tertiary carbons gave signals at 54.93 and 46.25 ppm respectively. The peak at 21.60 ppm is attributed to the methyl carbons attached to the aromatic nucleus and that at 18.67 ppm is due to the  $\alpha$ -methyl group.

The IR spectrum of the copolymer, poly(DMPMA-co-GMA) (0.5514:0.4486) is shown in Fig. 2. The peak at 3054  $\text{cm}^{-1}$  corresponds to the C—H stretching of aromatic system. The symmetrical and unsymmetrical stretching due to the methyl and methylene groups are observed at 2970 and 2926  $\text{cm}^{-1}$ . The shoulder at 1789  $\text{cm}^{-1}$  and peak at 1751  $\text{cm}^{-1}$  are attributed to the ester carbonyl stretching of both DMPMA and GMA units. The aromatic C=C stretching are observed at 1610, 1585, 1475  $\text{cm}^{-1}$ . The symmetrical bending vibrations of methyl groups are seen at 1375  $\text{cm}^{-1}$ . The symmetrical stretching of the epoxy group is observed at 1250  $\text{cm}^{-1}$ . A band at 900  $\text{cm}^{-1}$  is due to the asymmetric stretching of the epoxy group. The C—O stretching is observed at 1135  $\text{cm}^{-1}$ . The C—H out of plane bending vibrations of the aromatic nuclei are observed at 854 and 733  $\text{cm}^{-1}$ .

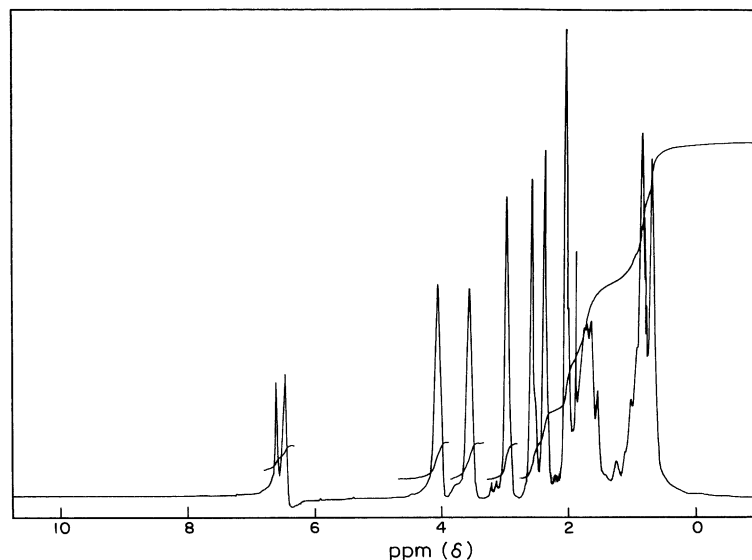
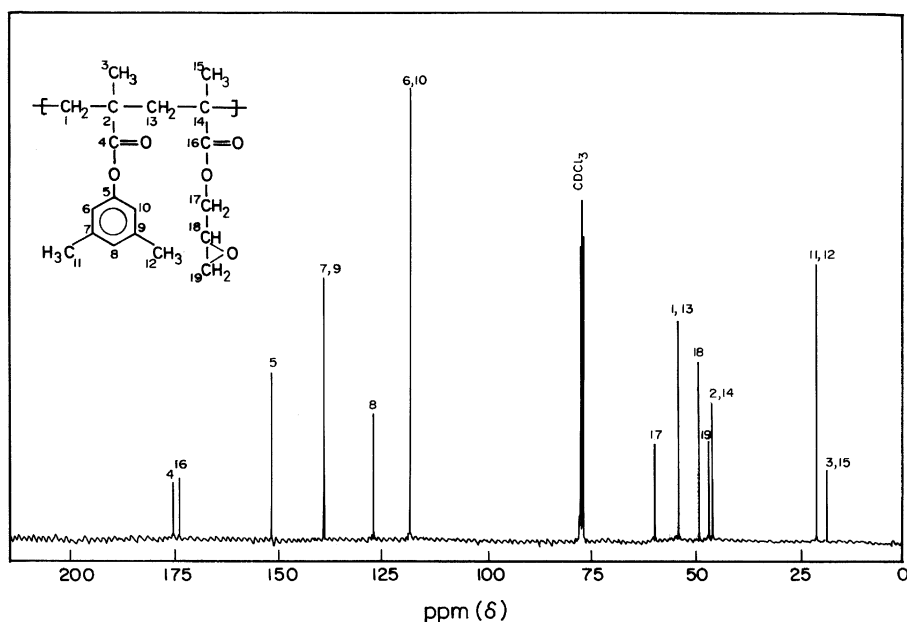
The  $^1\text{H}$ -NMR spectrum of the copolymer, poly(DMPMA-co-GMA) (0.5514:0.4486) is shown in Fig. 3. The chemical shifts assignments for the copolymers were based on the chemical shifts observed for the corresponding homopolymers. The aromatic protons show signals between 6.83 and 6.65 ppm. The spectrum shows two signals at 4.25 and 3.74 ppm due to the ester- $\text{CH}_2\text{O}$  group. The peak at 3.12 ppm is due to the methyne proton of the epoxy group. The methylene protons of

the epoxy group shows signals at 2.61 and 2.42 ppm. The signal at 2.30 ppm is due to the methyl protons attached to the aromatic nucleus. The methylene group of the backbone shows a broad signal between 1.88 and 1.44 ppm due to tacticity. The signals obtained at 1.01 and 0.82 ppm are due to the  $\alpha$ -methyl protons of both the monomeric units.

The proton decoupled  $^{13}\text{C}$ -NMR spectrum of poly(DMPMA-co-GMA) (0.5514:0.4486) is shown Fig. 4. It shows resonance signals at 175.76 and 173.2 ppm due to the ester carbonyl carbon of DMPMA and GMA units. The aromatic carbon attached to the oxygen atom shows a signal at 151.02 ppm. The other aromatic carbon signals are observed at 139.57 ppm ( $C_7$  and  $C_9$ ), 127.80 ppm ( $C_8$ ), 119.16 and 118.9 ppm ( $C_6$  and  $C_{10}$ ). The methylenoxy group flanked between the carbonyl group and epoxy group gives a signal at 59.9 ppm. The epoxy ring methyne and methylene carbon of GMA unit give signals at 49.12 and 47.13 ppm respectively. The signals due to the backbone methylene and tertiary carbon atoms are observed at 54.12 and 46.28 ppm respectively. The methyl group attached to the aromatic nuclei corresponds to the signal at 21.62 ppm. The  $\alpha$ -methyl group of both monomer units show a resonance at 18.31 ppm.

### 3.3. Molecular weights

The number- and weight-average molecular weights of poly(DMPMA), poly(GMA) and six samples of copolymers, determined by gel permeation chromatography, are presented in Table 2. The polydispersity

Fig. 3.  $^1\text{H}$ -NMR spectrum of poly(DMPMA-co-GMA) (0.5514:0.4486).Fig. 4.  $^{13}\text{C}$ -NMR spectrum of poly(DMPMA-co-GMA) (0.5514:0.4486).

indices of poly(DMPMA) and poly(GMA) are 1.78 and 1.97 respectively. The theoretical value of  $\overline{M}_w/\overline{M}_n$  for polymers produced via radical combination and disproportionation are 1.5 and 2.0 respectively [17]. In the homopolymerization of GMA the growing chains undergo termination by disproportionation. The polydispersities of poly(GMA) and poly(DMPMA) suggest that the tendency for chain termination by dispro-

portionation is greater for GMA than for DMPMA. The values of  $\overline{M}_w/\overline{M}_n$  in copolymerization is also known to depend on chain termination in the same way as in homopolymerization [18]. The values of  $\overline{M}_w/\overline{M}_n$  of the copolymers suggest a strong tendency for chain termination by disproportionation when the mole fractions of GMA is higher than that of DMPMA in the feed.

Table 2  
Molecular weight data for homo and copolymers of DMPMA and GMA

Polymer	$m_1^a$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
Poly(DMPMA)	1.000	3.03	1.70	1.78
Poly(DMPMA-co-GMA)	0.229	2.61	1.45	1.80
	0.430	2.87	1.57	1.83
	0.551	2.75	1.52	1.81
	0.663	2.93	1.58	1.85
	0.780	3.56	1.89	1.88
	0.860	3.89	2.02	1.93
Poly(GMA)	0.000	4.02	2.04	1.97

<sup>a</sup>  $m_1$  is the mole fraction of DMPMA in the copolymer.

### 3.4. Glass transition temperature

The glass transition temperatures ( $T_g$ ) of the copolymers were determined using differential scanning calorimetry (see Table 3). All the copolymers show a single  $T_g$ , showing the absence of formation of mixture of homopolymers or the formation of a block copolymer. The  $T_g$  of poly(DMPMA) is 85 °C and that of poly(-GMA) is 74 °C [19].

### 3.5. Thermogravimetric analysis

TGA curves for poly(DMPMA), poly(GMA) and a sample of poly(DMPMA-co-GMA) (0.5514:0.4486) are shown in Fig. 5. The results of the differential thermogravimetric analysis are presented in Table 3. The thermograms clearly indicate that poly(DMPMA) and poly(DMPMA-co-GMA) undergo two stage decomposition while poly(GMA) undergoes single stage decomposition. The initial decomposition temperatures of poly(DMPMA), poly(DMPMA-co-GMA), and poly(-GMA) are 242, 219 and 188 °C respectively. TGA results indicate that the thermal stability of the copolymer increases with rising DMPMA content.

### 3.6. Copolymer composition

The chemical structure of copolymers may be represented as in Scheme 1. The average compositions of the copolymer samples were determined from the <sup>1</sup>H-NMR spectra. The assignment of the resonance peaks in the <sup>1</sup>H-NMR spectrum leads to the accurate evaluation of the content of each kind of monomeric unit in the copolymer chains.

Thus, the mole fraction of DMPMA in the copolymer chain was calculated from measuring the integrated intensities of aromatic protons of DMPMA and aliphatic protons of DMPMA and GMA.

The following expression is used to determine the composition of copolymers. Let  $m_1$  be the mole fraction of DMPMA and  $(1 - m_1)$  be that of GMA. DMPMA contains 3 aromatic protons and 11 aliphatic protons and GMA contains 10 aliphatic protons.

$$C = \frac{\text{Intensities of aromatic protons } (I_{Ar})}{\text{Intensities of aliphatic protons } (I_{Ali})} \quad (1)$$

$$= \frac{3m_1}{11m_1 + 10(1 - m_1)}$$

which on simplification gives

Table 3  
TGA and DSC data for DMPMA-GMA copolymer system

Polymers	$m_1$	IDT <sup>a</sup>	Temperature at weight loss (°C)					$T_g$ (°C)
			10%	30%	50%	70%	90%	
Poly(GMA)	0.000	188	263	292	307	322	375	74
Poly(DMPMA-co-GMA)	0.229	201	261	293	315	341	389	75
	0.430	206	266	294	331	356	407	78
	0.551	219	275	312	343	375	437	80
	0.663	228	293	324	362	398	450	82
	0.780	235	302	330	365	401	461	83
	0.860	239	309	337	368	404	466	84
Poly(DMPMA)	1.000	242	319	343	375	406	475	85

<sup>a</sup> IDT is initial decomposition temperature.

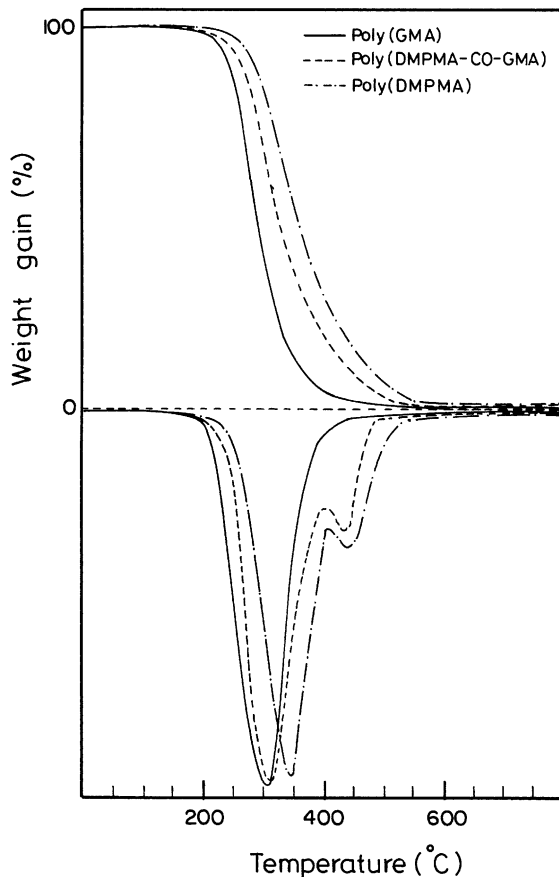


Fig. 5. TGA curves for poly(GMA), poly(DMPMA-co-GMA) (0.5514:0.4486) and poly(DMPMA).

$$m_1 = \frac{10C}{3 - C} \quad (2)$$

From Eq. (2), the mole fractions of DMPMA in the copolymers were determined by measuring the intensity of aromatic proton and aliphatic proton signals. Table 1 gives the values of  $C$  and the corresponding mole fractions of DMPMA in the copolymers. The plot of mole fractions of DMPMA ( $M_1$ ) in the feed vs that in the copolymer ( $m_1$ ) is shown in Fig. 6. It indicates that the system can form an azeotropic polymerization.

### 3.7. Reactivity ratios

From the monomer feed ratios and the copolymer compositions, the reactivity ratios of DMPMA and GMA were determined by application of the Fineman–Ross (F–R) [20], Kelen–Tüdös (K–T) [21] and extended Kelen–Tüdös (Ext K–T) [22] methods. The values of  $r_1$  and  $r_2$  from the F–R plot, K–T and Ext K–T plots (Fig. 7) are presented as follows.

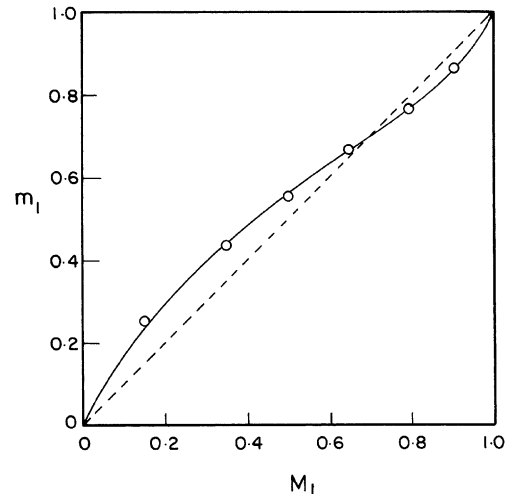


Fig. 6. Copolymer composition diagram of poly(DMPMA-co-GMA) system.

Fineman–Ross:  $r_1 = 0.63$ ;  $r_2 = 0.45$ ;  $r_1 r_2 = 0.29$

Ross:

Kelen–Tüdös:  $r_1 = 0.65$ ;  $r_2 = 0.43$ ;  $r_1 r_2 = 0.28$

Ext Kelen–Tüdös:  $r_1 = 0.64$ ;  $r_2 = 0.44$ ;  $r_1 r_2 = 0.28$

Tüdös:

Since  $r_1$  and  $r_2$  values are both less than unity the system gives rise to an azeotropic polymerization at a particular composition viz. 0.6502. The product  $r_1 r_2$  is very much less than 1 suggesting that the system shows strong alternating tendency.

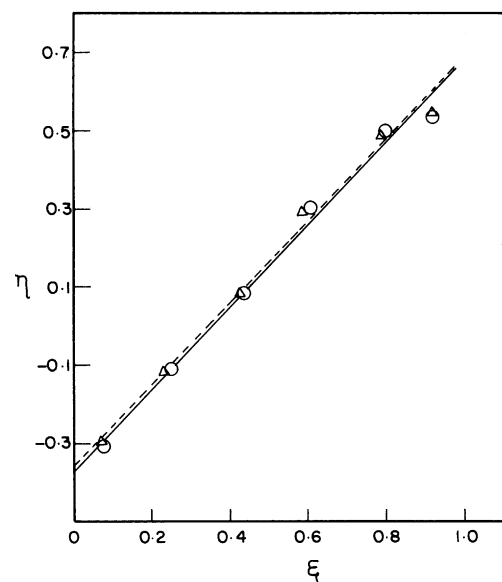


Fig. 7. K–T(○) and Ext K–T(Δ) plot for poly(DMPMA-co-GMA) system.

#### 4. Conclusions

Poly(DMPMA) and the copolymers of DMPMA with GMA were synthesised by free radical solution polymerization. Characterization of poly(DMPMA) and poly(DMPMA-co-GMA) were performed by IR,  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR techniques. Thermogravimetric analysis indicated that the thermal stability of the copolymers increases with the increase of DMPMA content. Values of the polydispersity index for poly(DMPMA), poly(DMPMA-co-GMA) and poly(GMA), suggest a strong tendency for chain termination by disproportionation in all cases and that the tendency increases with increasing GMA content in the feed. The copolymer compositions were found by  $^1\text{H}$ -NMR analysis of the polymers. The reactivity ratios were determined by F–R, K–T and Ext K–T methods giving values in good agreement. The values of  $r_1$  and  $r_2$  are less than unity indicating that the system gives rise to an azeotropic polymerization. The value of the product  $r_1 r_2$  indicates a strong tendency to alternation.

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