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COPOLYMERS OF 3,5-DIMETHYLPHENYL METHACRYLATE AND METHYLMETHACRYLATE: SYNTHESIS, CHARACTERIZATION, AND DETERMINATION OF REACTIVITY RATIOS

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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. Taking six different feed compositions of 3,5-dimethylphenyl methacrylate and methyl methacrylate, the copolymers were synthesized in EMK solution at $70 \pm 1^{\circ}C$ using benzoyl peroxide as initiator. The copolymers were characterized by FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopic techniques. The solubilities of the polymers were tested in various polar and nonpolar solvents. The elemental analysis was determined by Perkin-Elmer C-H analyzer. The glass transition temperatures of the polymers were determined by differential scanning calorimeter. Thermogravimetric analysis of the polymers were performed in air. Copolymer compositions were determined using ^{1}H-NMR spectra. The monomer reactivity ratios

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were determined by the application of conventional linearization methods such as Fineman-Ross, Kelen-Tüdös, and extended Kelen-Tüdös, as well as by a nonlinear "error-in-variables" method using a computer program, RREVM.

Key Words: 3,5-Dimethylphenyl methacrylate; Copolymerization; Reactivity ratios; ^{1}H-NMR spectra; ^{13}C-NMR spectra; Methyl methacrylate; Thermal studies

INTRODUCTION

Methacrylic copolymers have achieved prime importance in various avenues of industrial application.[1–4] Copolymerization of functional (meth)acrylates with some other monomers provides a simple route for synthesizing biologically active materials and application for coatings.[5–6] Copolymers formed from methyl methacrylate are used in the production of biological active films and optical telecommunication materials.[7–8] The use of alkyl and phenyl(meth) acrylates as binders in protective coatings because of their excellent durability, water white color, and transparency has been reported.[9–10] Poly(phenyl methacrylates) are harder polymers of high tensile strength, and their glass transation temperature is higher than their acrylate counterparts, because substitution of the methyl group for the α-H on the main chain restricts the freedom of rotation and motion of the polymer backbone. They also find application in laser photoresist materials.[11]

The accurate estimation of copolymer composition and determination of monomer reactivity ratio is significant for tailor-made copolymers. In the past few decades, ^{1}H-NMR spectroscopic analysis has been established as a powerful tool for the estimation of copolymer composition.[12–16] The present paper reports the synthesis, characterization of copolymers of 3,5-dimethylphenyl methacrylate (DMPMA) and methyl methacrylate (MMA), and the determination of monomer reactivity ratios.

EXPERIMENTAL

Materials

3,5-Dimethyl phenol (Lancaster) was used as such without purification. Methyl methacrylate (MMA) (EMERK) was purified by distillation under reduced pressure. Benzoyl peroxide(BPO) was recrystallized from a chloroform–methanol (1:1) mixture. All the solvents were purified by distillation prior to their use. Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride using the procedure of Stampel et al.[17]

3,5-Dimethylphenyl methacrylate was prepared from methacryloyl chloride and 3,5-dimethylphenol according to the reported method.[18]

Homopolymerization

One gm of the monomer DMPMA and 50 mg of benzoyl peroxide were dissolved in 10 mL of ethyl methyl ketone (EMK) in a polymerization tube and oxygen-free nitrogen gas was purged through the solution for 20 minutes. Then the solution was thermostated at $70 \pm 1°C$. After 9 hours, the polymer was precipitated by adding the reaction mixture to methanol. The polymer was purified by repeated reprecipitation by methanol from a solution of the polymer in DMF. The polymer was then dried in vacuum at 50°C. Yield was 75%.

Copolymerization

Predetermined quantities of DMPMA, MMA, EMK, and benzoyl peroxide were placed in a standard reaction tube (100 mL), and the mixture was flushed with oxygen free nitrogen for 20 minutes. The tube was tightly sealed and immersed in a thermostated water bath maintained at $70 \pm 1°C$. The polymer was precipitated by pouring the solution into excess methanol. The precipitated polymer was filtered and purified by repeated reprecipitation from chloroform solution using methanol and finally dried in a vacuum oven at 50°C for 24 hours. The copolymer conversions were restricted to less than 10%.

Measurements

Elemental analysis was carried out by Perkin-Elmer C-H analyzer. Infrared spectra were recorded with a Nicolet 360 FT-IR ESP spectrophotometer as KBR pellets. ^{1}H-NMR spectra of all the monomer and polymer samples were run on a Bruker 270 MHz FT-NMR spectrometer at room temperature using $CDCl_3$ and TMS as a solvent and an internal standard, respectively. The proton decoupled ^{13}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. Thermogravimetric analysis was performed with Mettler TA 3000 thermal analyzer in air atmosphere 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.

RESULTS AND DISCUSSION

Poly(3,5-dimethyphenyl methacrylate) was obtained by the free radical solution polymerization of the monomer at $70 \pm 1°C$ in EMK solvent using benzoyl peroxide as the initiator. The copolymerization of DMPMA with MMA in EMK solution was studied in a wide composition interval with mole fractions of DMPMA ranging from 0.15 to 0.9 in the feed. The reaction time was selected in 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.

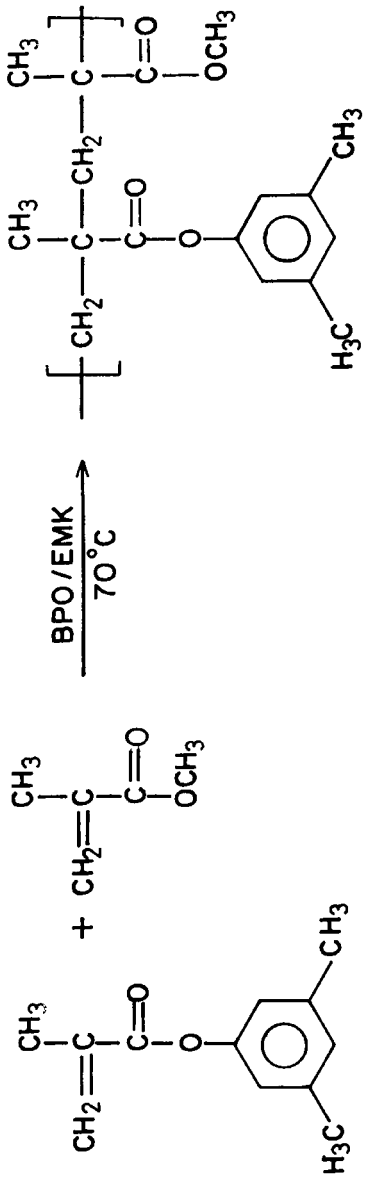
The homopolymer and the copolymers were soluble in chloroform, acetone, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene, xylene, and insoluble in n-hexane and hydroxyl-group containing solvents such as methanol and ethanol.

Characterization of Polymers

The IR spectrum of the homopolymer shows a peak at 3025 cm^{-1} due to the =C-H stretching of the aromatic ring. The peaks at 2960, 2926, 2872 cm^{-1} are attributed to the asymmetrical and symmetrical C-H stretching of methylene and methyl groups. The ester carbonyl stretching is observed at 1750 cm^{-1}. The ring stretching vibration of the aromatic nuclei were observed at 1605, 1585, and 1474 cm^{-1}. The symmetrical bending vibrations of methyl group is seen at 1375 cm^{-1}. The peak at 1146 cm^{-1} is due to the C-O stretching. The C-H out-of-plane bending vibration of the 1,3,5-trisubsituted aromatic nuclei are observed at 870 and 762 cm^{-1}. The out-of-plane bending vibration of the aromatic C=C is seen at 683 cm^{-1}.

The ^{1}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 signal at 2.19 ppm. The broad resonance signal shown at 1.97−1.07 ppm are due to the backbone methylene group and the α-methyl group.

The proton decoupled ^{13}C-NMR spectrum of the homopolymer shows signal at 175.76 ppm due to the ester carbonyl carbon. The aromatic carbon attached to the oxygen atom gave signal at 151.02 ppm. The aromatic carbon atoms to which methyl groups are attached gave resonance signals at 139.57 ppm. The other aromatic carbons gave signal at 119.16, 118.9, and 127.90 ppm. The backbone methylene and tertiary carbons give 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 α-methyl group.



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

Table 1. Composition Data for Free Radical Polymerization of DMPMA(1) with MMA (2) in EMK Solution at 70°C

Copolymer	M_1[a]	Conversion (%)	Intensities of Protons		C	m_1[a]
			I_{Ar}	I_{Ali}		
1	0.1518	9.31	6.561	93.440	0.0702	0.2013
2	0.3560	9.84	10.511	73.913	0.1422	0.4420
3	0.5058	8.72	15.402	84.549	0.1820	0.5933
4	0.6540	8.96	17.598	82.402	0.2135	0.7238
5	0.7968	7.85	19.354	80.646	0.2399	0.8416
6	0.9051	9.18	20.273	78.242	0.2591	0.9325

[a] M_1 and m_1 are the mole fraction of DMPMA in the feed and in the copolymers, respectively.

The IR spectrum of the copolymer poly(DMPMA-co-MMA) (0.5933:0.4067) is shown in Fig. 1. It shows a peak at 3030 cm^{-1} corresponding to the C-H stretching of the aromatic system. The symmetrical and asymmetrical stretching due to the methyl and methylene groups are observed at 2965 and 2875 cm^{-1}. The peak at 1745 cm^{-1} is attributed to the ester carbonyl stretching of both DMPMA and MMA units. The aromatic C=C stretching are observed at

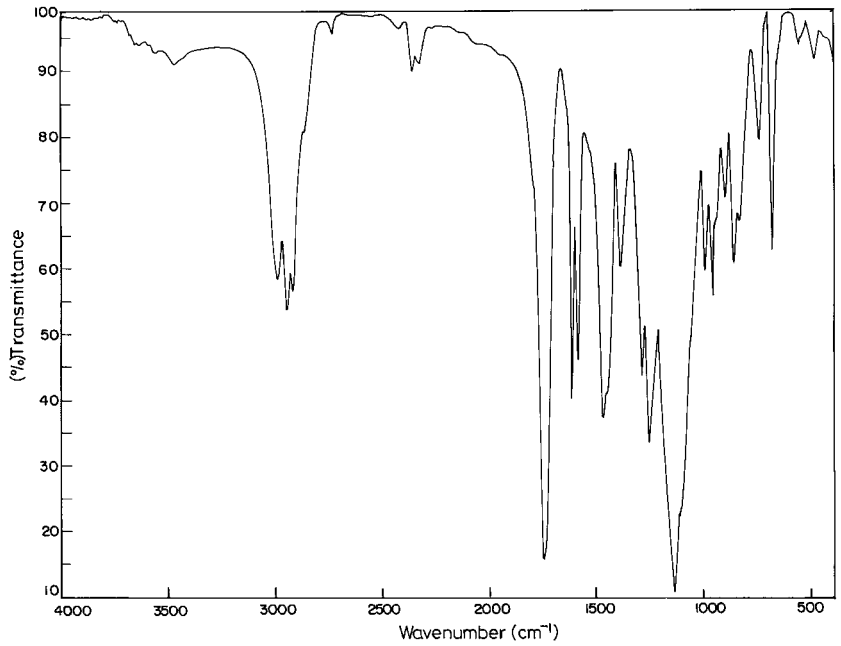


Figure 1. IR Spectrum of poly(DMPMA-co-MMA) (0.5933:0.4067).

1617, 1583, and 1466 cm^{-1}. The symmetrical bending vibrations of methyl groups is seen at 1375 cm^{-1}. The ether link due to OMe group and C-O link in the ester of DMPMA units and C-O link in the ester of MMA units showed signals at 1148, 1265, and 1300 cm^{-1}, respectively. The C-H out-of-plane bending vibrations of the aromatic nuclei are observed at 874 and 766 cm^{-1}. The out-of-plane bending vibration of aromatic C=C is seen at 692 cm^{-1}.

The ^{1}H-NMR spectrum of the copolymer poly(DMPMA-co-MMA) (0.5993:0.4067) is shown in Fig. 2. The chemical shifts assignments for the copolymers were based on the chemical shifts observed for the respective homopolymers. The aromatic protons show signals between 6.68−7.12 ppm. Signals at 3.64 ppm were due to the methoxy protons of the MMA unit. Due to the existence of tacticity, the resonance signals corresponding to the methylene group of the backbone are observed between 2.73−1.21 ppm. The methyl protons attached to the aromatic nuclei give a signal centered at 2.31 ppm. The α-methyl group of the DMPMA and MMA units show a signal between 1.2−0.92 ppm.

The proton decoupled ^{13}C-NMR spectrum of poly (DMPMA-co-MMA) (0.5933:0.4067) is shown in Fig. 3. It shows resonance signals at

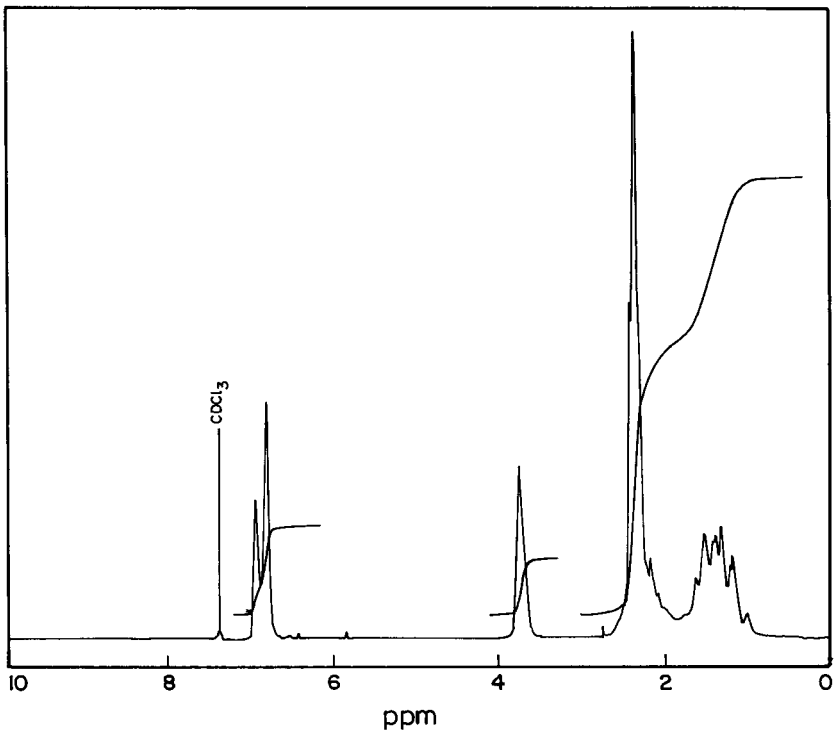


Figure 2. ^{1}H-NMR Spectrum of poly(DMPMA-co-MMA) (0.5933:0.4067).

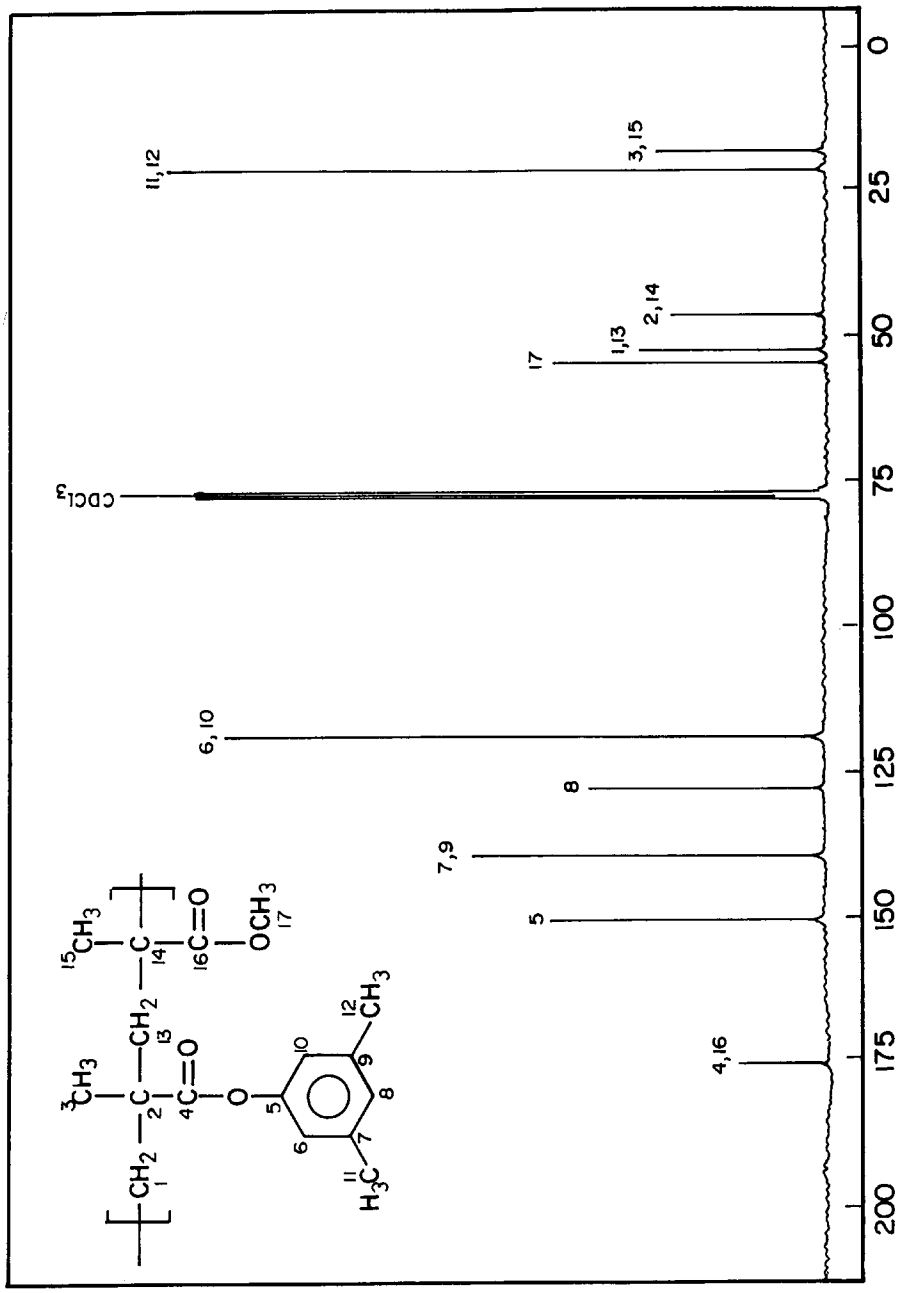


Figure 3. ^{13}C-NMR Spectrum of poly(DMPMA-co-MMA) (0.5933:0.4067).

175.06 ppm due to the ester carbonyl carbon of DMPMA and MMA units. The aromatic carbon attached to the oxygen atom shows resonance signal at 151.01 ppm. The other aromatic carbon signals are observed at 139.56 (C_7 and C_9), 127.89 ppm (C_8), 119.12, and 118.88 ppm (C_6 and C_{10}). The methoxy carbon signal of MMA unit is observed at 58.51 ppm. The signal due to the backbone methylene and tertiary carbon atoms are observed at 52.31 and 44.21 ppm, respectively. The methyl group attached to the aromatic nuclei shows signal at 21.66 ppm. The α-methyl group of both the monomer units show resonance at 18.35 ppm.

Glass Transition Temperature

The glass transition temperature (T_g) of copolymers were determined by differential scanning calorimetry and the data are presented in Table 2. The T_g of poly(DMPMA) is 85°C, and that of poly(MMA) is 105°C. The results clearly indicate that the T_g values of copolymers depend on the composition of comonomers, and the value increases with increases in the mole fraction of MMA in the copolymer. The variation of T_g of copolymers with the mole fraction of the DMPMA unit in the copolymer is shown in Fig. 4.

Thermogravimetric Analysis

The TGA data for the homopolymers and copolymers of DMPMA and MMA are given in Table 2. TGA curves for poly(DMPMA), poly(MMA), and a sample of poly (DMPMA-co-MMA) (0.5933:0.4067) are shown in Fig. 5. The thermograms clearly indicate that poly(DMPMA) and poly-(DMPMA-co-MMA) undergo two-stage decomposition, while poly(MMA) undergoes a single-stage decomposition. The initial decomposition temperature of poly(DMPMA), poly(DMPMA-co-MMA), and poly(MMA) are

Table 2. DSC and TGA Data for DMPMA-MMA Copolymer System

				Temperature at Weight Loss (°C)				
Polymers	m_1	T_g (°C)	*IDT*[a]	10%	30%	50%	70%	90%
Poly (MMA)	0.0000	105	244	270	284	300	334	380
	0.4420	92	247	273	298	310	358	414
Poly (DMPMA-co-MMA)	0.5933	90	250	275	305	330	370	431
	0.7238	88	253	278	312	340	382	448
Poly (DMPMA)	1.0000	85	260	319	343	375	406	475

[a]*IDT* is initial decomposition temperature.

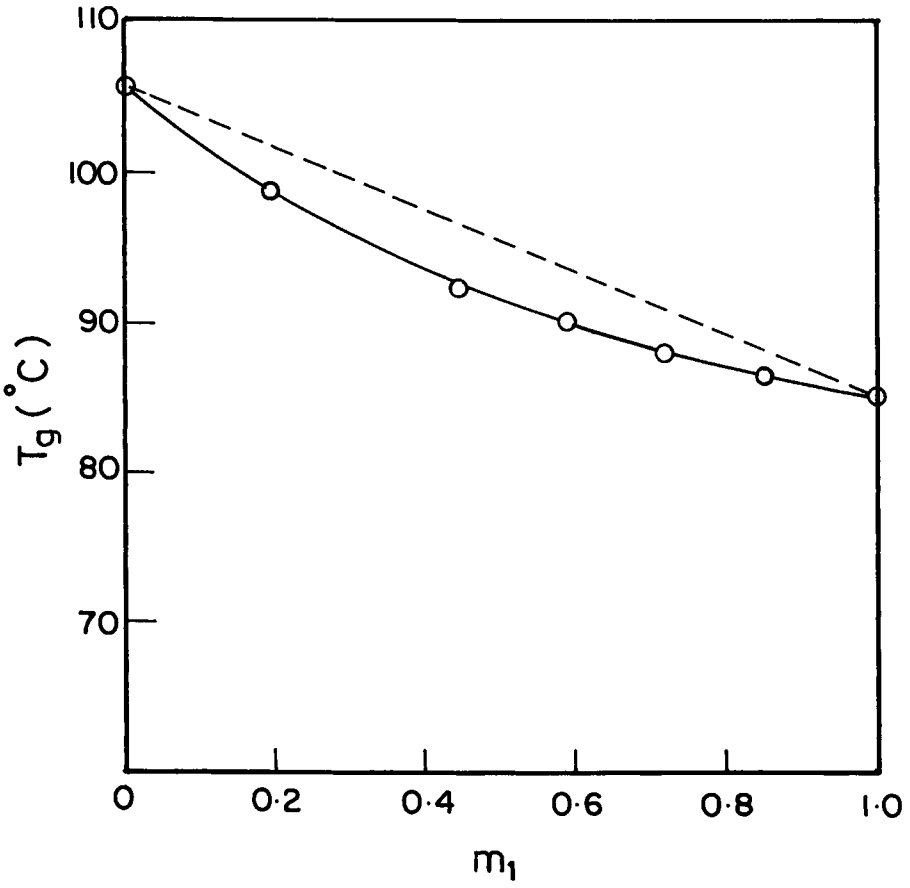


Figure 4. Variation of Tg with composition of poly(DMPMA-co-MMA) system.

260°, 250°, and 244°C. TGA results indicate that the thermal stability of the copolymer increases with increase in DMPMA content in the copolymer.

Copolymer Composition

The chemical structure of copolymers may be represented as in Sch. 1. The average composition of the copolymer samples were determined from the corresponding ^{1}H-NMR spectra. The assignment of the resonance peaks in the ^{1}H-NMR spectrum leads to the accurate evaluation of the content of each kind of monomeric unit incorporated into the copolymer chains.

The following expression is used to determine the composition of the copolymers. Let m_1 be the mole fraction of DMPMA and 1-m_1 be that of MMA. DMPMA contains three aromatic protons and eleven aliphatic protons, and MMA contains eight aliphatic protons.

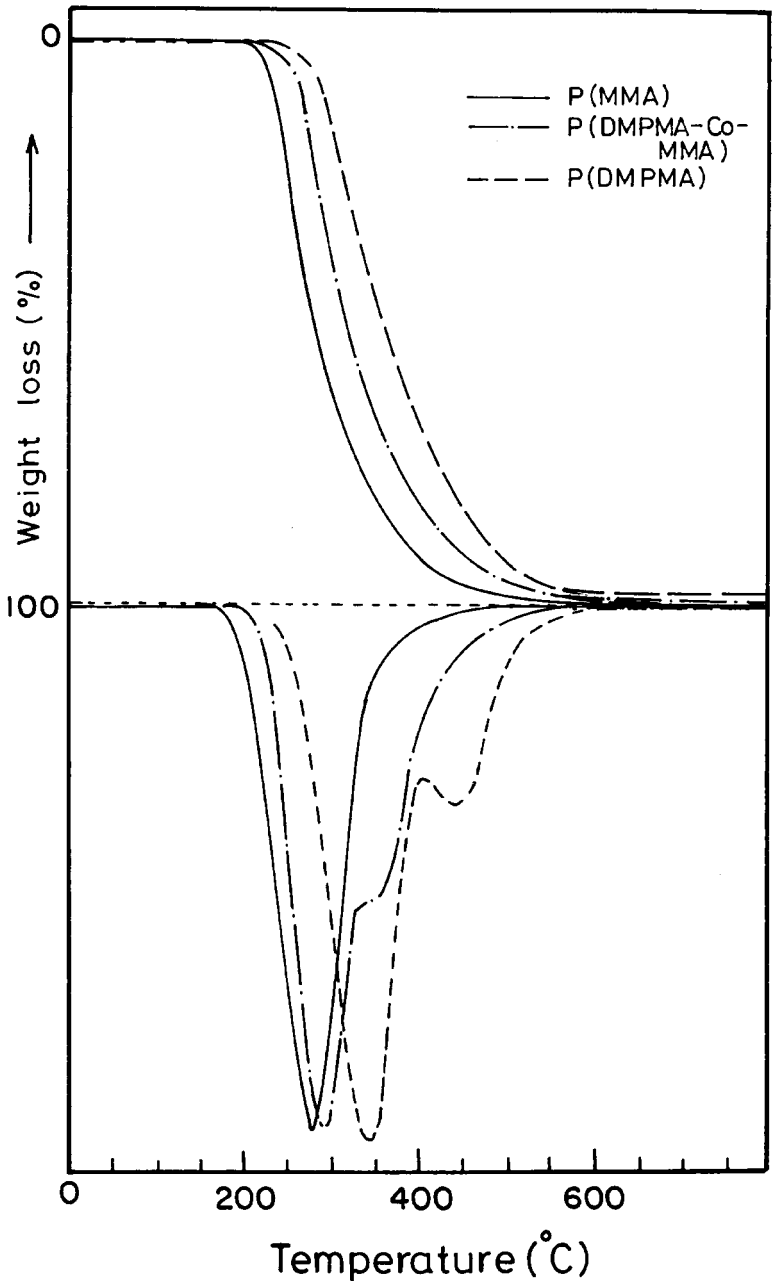


Figure 5. TGA curves for poly(MMA), poly(DMPMA-co-MMA), poly(DMPMA).

$$C = \frac{\text{Intensities of aromatic protons } (I_{Ar})}{\text{Intensities of aliphatic protons } (I_{Ali})} = \frac{3m_1}{11m_1 + 8(1 - m_1)} \cdots \quad (1)$$

which on simplification gives:

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

From Equation 2, the mole fraction of DMPMA in the copolymers were determined by measuring the intensity of aromatic proton signals and aliphatic proton signals. Table 1 gives the values of C and the corresponding mole fractions of DMPMA (M_1). The plot of the mole fraction of DMPMA (M_1) in the feed vs. that in the copolymer (m_1) is shown in Fig. 6. It indicates that the composition of DMPMA in the copolymer is always higher than that in the feed.

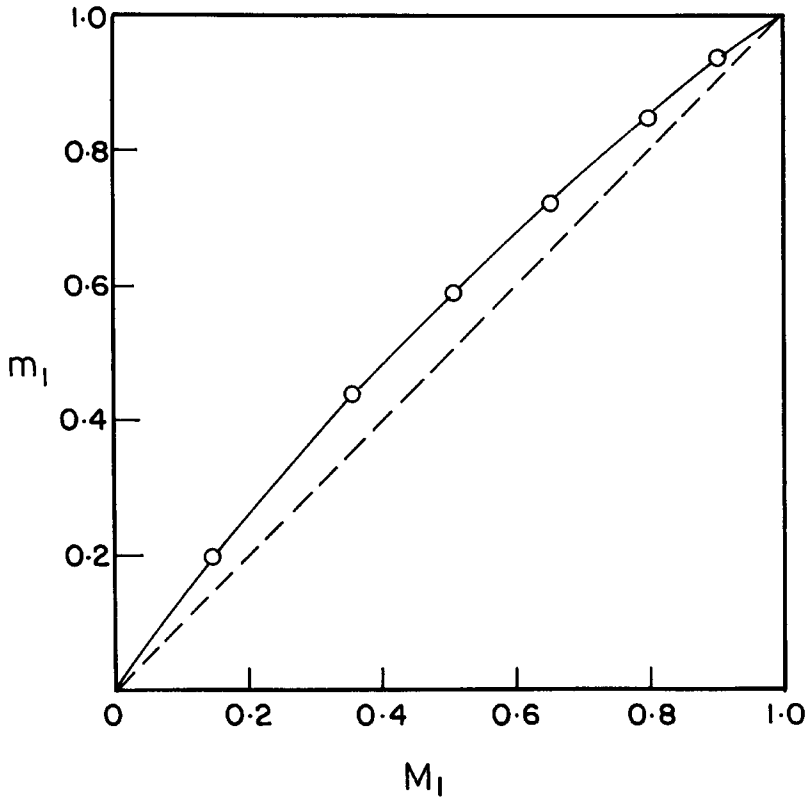


Figure 6. Copolymer composition diagram of poly(DMPMA-co-MMA) system.

Table 3. F-R and K-T Parameters for DMPMA-MMA Copolymer System

$F = M_1/M_2$	$f = m_1/m_2$	$H = F^2/f$	$G = F(f-1)/f$	$\eta = G/(\alpha + H)^a$	$\xi = H/(\alpha + H)^a$
0.1789	0.2520	0.1270	−0.5310	−0.5098	0.1219
0.5527	0.7921	0.3856	−0.1450	−0.1115	0.2966
1.0234	1.4588	0.7179	0.3218	0.1971	0.4392
1.8901	2.6205	1.3632	1.1688	0.5131	0.5985
3.9212	5.3131	2.8939	3.1831	0.8358	0.7598
9.5374	13.8148	6.5843	8.8470	1.1798	0.8780

[a] α is equal to 0.9144.

Reactivity Ratios

From the monomer feed ratios and the copolymer composition, the reactivity ratio of DMPMA and MMA were determined by the application of conventional linearization methods, such as Fineman-Ross (F-R),[19] Kelen-Tüdös (K-T),[20] and Extended Kelen-Tüdös (Ext.K-T).[21] The F-R and K-T parameters for the copolymers are presented in Table 3 and those for Ext-K-T are shown in Table 4. The values from the F-R plot [Fig. 7], K-T, and Ext K-T plots (Fig. 8) are presented in Table 5. The determination of reactivity ratios by conventional linearization methods is nowadays considered not correct, and hence a nonlinear error-in-variable method using the computer program, RREVM was also attempted.[22−23] The resulting values are presented in Table 5. The 95% posterior probability contour for the estimated r_1 and r_2 values using the nonlinear procedure is shown in Fig. 9.

Table 4. Extended K-T Parameters for DMPMA-MMA Copolymer System

	Copolymer System					
Parameters	1	2	3	4	5	6
ζ_2	0.0844	0.08061	0.0681	0.0688	0.0598	0.0644
ζ_1	0.1189	0.1155	0.0971	0.0954	0.0810	0.0932
Z	1.4356	1.4603	1.4476	1.4066	1.3699	1.4710
$\bar{F}$	0.1755	0.5424	1.0077	1.8630	3.8785	9.3914
H	0.1223	0.3714	0.6961	1.3245	2.8312	6.3844
G	−0.5210	−0.1424	0.3169	1.1521	3.1485	8.7116
η	−0.3705	−0.0860	0.1600	0.4417	0.7651	1.1361
ξ	0.08697	0.2244	0.3516	0.5078	0.6880	0.8326

$\alpha = 1.2838$, $\mu = 0.5319$.

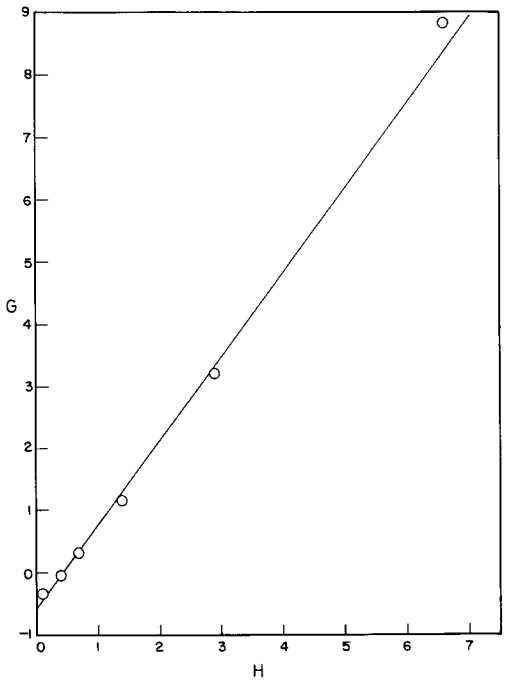


Figure 7. F-R plot for poly(DMPMA-co-MMA) system.

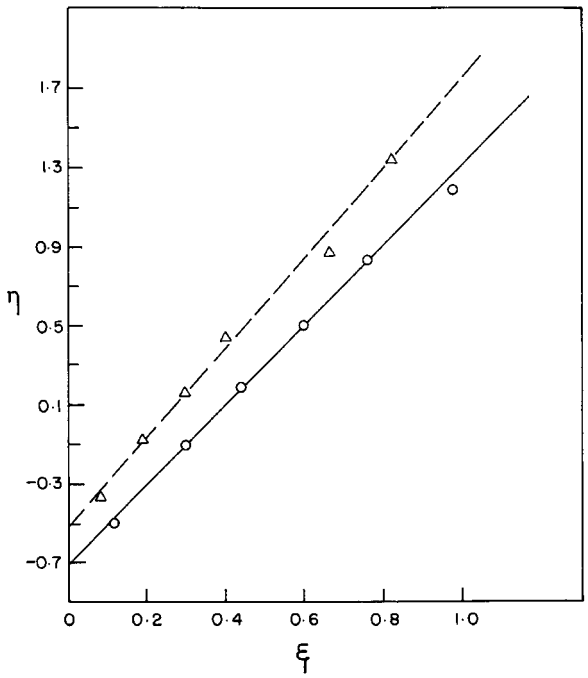


Figure 8. K-T(O) and Ext. K-T(Δ) plot for poly(DMPMA-co-MMA) system.

Table 5. Copolymerization Parameters for the Free Radical Copolymerization of DMPMA with MMA

Methods	r_1[a]	r_2[a]	$r_1 \times r_2$	$1/r_1$	$1/r_2$
Fineman-Ross	1.4014	0.7031	0.98	0.714	1.422
Kelen-Tüdös	1.4038	0.7044	0.98	0.712	1.420
Ext. Kelen-Tüdös	1.4245	0.6935	0.98	0.702	1.442
RREVM	1.4880	0.7216	1.07	0.672	1.386

[a] r_1 and r_2 are the reactivity ratios for DMPMA and MMA, respectively.

The value of r_1 is larger than 1, and that of r_2 is less than 1; this suggests the presence of a higher amount of DMPMA units in the copolymer than in the feed. The value of the product of r_1 and r_2 suggests that there is random distribution of the monomer units in the copolymer.

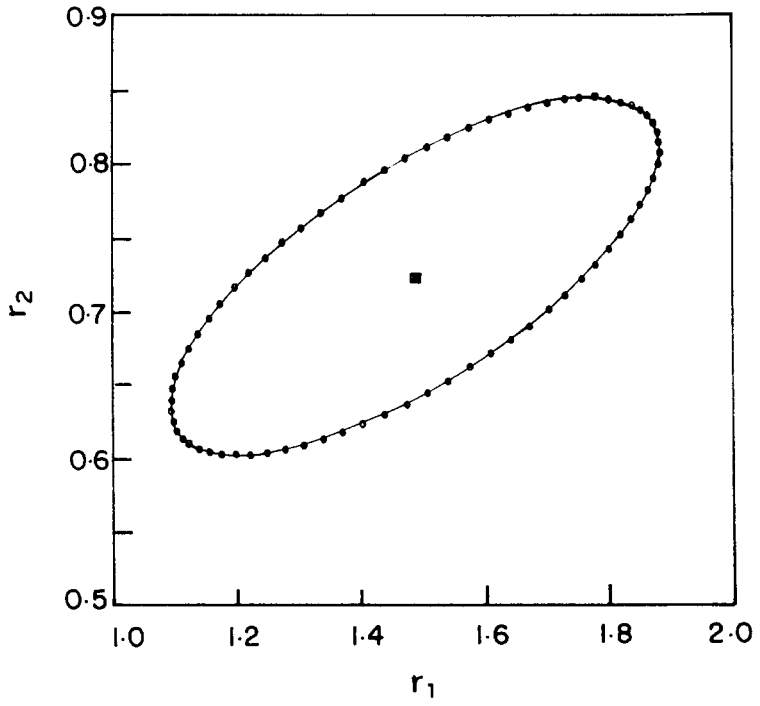


Figure 9. 95% joint confidence region of r_1 and r_2 values by RREVM for DMPMA-MMA copolymer system.

CONCLUSION

Poly(DMPMA) and the copolymers of DMPMA with MMA were synthesized by free-radical solution polymerization. Characterization of poly(DMPMA) and poly(DMPMA-co-MMA) were performed with IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopic techniques. The homopolymer and the copolymers are soluble in chloroform, acetone, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran benzene, toluene, xylene and insoluble in n-hexane and hydroxyl-group containing solvents such as methanol and ethanol. Thermogravimetric analysis indicated that the thermal stability of the copolymer increases with the increase of DMPMA units in the copolymer. The copolymer composition was calculated by ^{1}H-NMR analysis of the polymers. The reactivity ratios were determined by conventional linearization methods such F-R, K-T, and Ext K-T methods, as well as by the nonlinear error-in-variables method using a computer program, RREVM. The r_1 values from these methods are greater than 1, and r_2 values are less than 1. This indicates that DMPMA is more reactive than MMA. The value of the product of r_1 and r_2 is close to 1, resulting in the random distribution of the monomeric units in the copolymer.

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