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C. Sreekuttan Unnithan[a]; A. Penlidis[b]; S. Nanjundan[c]
[a] Department of Chemistry, Dr. M.G.R. Deemed University, Chennai, India [b] Department of Chemical Engineering, University of Waterloo, Ontario, Canada [c] Department of Chemistry, Anna University, Chennai, India

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Copolymerization of 4-Propanoylphenyl Acrylate with Methyl Methacrylate: Synthesis, Characterization and Reactivity Ratios

C. SREEKUTTAN UNNITHAN,[1] A. PENLIDIS,[2]
AND S. NANJUNDAN[3]

[1]Department of Chemistry, Dr. M.G.R. Deemed University, Chennai, India
[2]Department of Chemical Engineering, University of Waterloo, Ontario, Canada
[3]Department of Chemistry, Anna University, Chennai, India

The new acrylic monomer 4-propanoylphenyl acrylate (PPA) was synthesized and copolymerized with methyl methacrylate (MMA) in methyl ethyl ketone at 70 ± 1°C using benzoyl peroxide as a free radical initiator. The copolymers were characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. The compositions of the copolymers were determined by ^{1}H-NMR analysis. The reactivity ratios of the monomers were determined using Fineman-Ross ($r_1 = 0.5535$ and $r_2 = 1.5428$), Kelen-Tüdös ($r_1 = 0.5307$ and $r_2 = 1.4482$), and Ext. Kelen-Tüdös ($r_1 = 0.5044$ and $r_2 = 1.4614$), as well as by a nonlinear error-in-variables model (EVM) method using a computer program, RREVM ($r_1 = 0.5314$ and $r_2 = 1.4530$). The solubility of the polymers was tested in various polar and non-polar solvents. The elemental analysis was determined by a Perkin-Elmer C-H analyzer. The molecular weights (M_w and M_n) of the copolymers were determined by gel permeation chromatography. Thermogravimetric analysis of the polymers reveals that the thermal stability of the copolymers increases with an increase in the mole fraction of MMA in the copolymers. Glass transition temperatures of the copolymers were found to increase with an increase in the mole fraction of MMA in the copolymers.

Keywords 4-propanoylphenyl acrylate, copolymerization, reactivity ratios, methyl methacrylate, ^{1}H- and ^{13}C-NMR spectra, thermal studies

Introduction

In recent years, the synthesis of polymers containing functional groups has been an active field of research in polymer science, because it provides an approach to a subsequent modification of the polymer for the required application. Incorporation of activated acrylates or methacrylates into polymers provides a versatile route for the preparation of reactive polymers (1, 2). Acrylic polymers have acquired prime importance in various avenues of industrial applications in leather, textile and building materials. In particular, phenyl acrylate polymers, by the incorporation of an active group in the phenyl ring, show not only enhanced thermal stability, but also have several potential

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Address correspondence to S. Nanjundan, Department of Chemistry, Anna University, Chennai-25, India. E-mail: snanjundan@yahoo.com

applications. Copolymers of activated monomers have been employed to study kinetic aspects of macromolecular drug carriers, immobilized enzymes and polymer reagents for peptide synthesis (3, 4). Copolymers of acrylic monomers with methyl methacrylate have been used as primers for automotive finishes, clean lacquers for polishing metals and enamels for household appliances (5), formulations of base and top coats for leather (6, 7), binders in protective coatings because of their durability and transparency (8), drug binding materials (9), optical telecommunication materials and photo resist materials (10, 11).

Determinations of copolymer composition and monomer reactivity ratios are very important for understanding the kinetic and mechanistic aspects of copolymerization and also in evaluating the specific application of the copolymer (12). ^{1}H-NMR spectroscopic analysis has been established as a powerful tool for the estimation of copolymer composition (13–16). The accurate estimation of copolymer composition and determination of monomer reactivity ratios are significant for producing tailor-made copolymers. The present article reports the synthesis, characterization and thermal properties of copolymer of 4-propanoylphenyl acrylate with methyl methacrylate. The monomer reactivity ratios of the comonomers are also reported.

Experimental

Materials

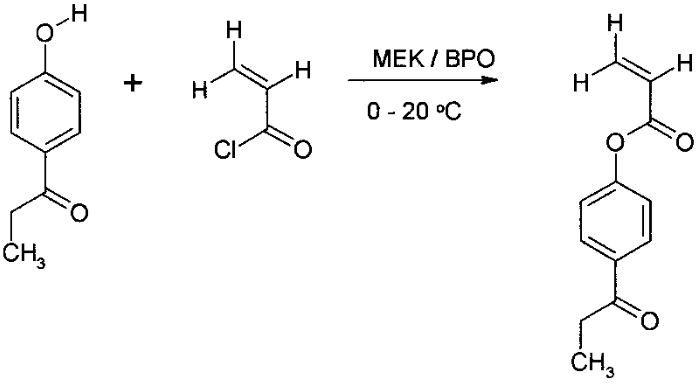
4-Hydroxy propiophenone (Lancaster) was used as is without purification. Methyl methacrylate (EMERK) was purified by distillation under reduced pressure. Benzoyl peroxide (BPO) was recrystallized from a chloroform methanol (1:1) mixture. All solvents were purified by distillation prior to their use.

Synthesis of 4-Propanoylphenyl Acrylate (PPA)

Acryloyl chloride was prepared from acrylic acid and benzoyl chloride using the procedure of Stampel et al. (17). For the synthesis of 4-propanoylphenyl acrylate (PPA), 4-hydroxy propiophenone (15 g, 0.10 mol) and triethylamine (14.7 mL, 0.11 mol) were dissolved in methyl ethyl ketone (MEK) (300 mL) in a three-necked flask fitted with a mechanical stirrer and a dropping funnel and placed in an ice bath. Acryloyl chloride (8.9 mL, 0.11 mol) dissolved in MEK (25 mL) and taken in a 100 mL dropping funnel was added dropwise into the flask in such a way that the temperature was maintained around 0–5°C. The reaction was allowed to proceed for 1 h at 0°C with constant stirring. Then, the ice bath was removed and the reaction mixture was stirred at room temperature for a further period of 1 h. The precipitated triethylammonium chloride was filtered off and the solvent in the filtrate was removed using a rotary evaporator. The residue obtained was dissolved in ether and washed with 0.1% NaOH and distilled water. The ether solution was dried with anhydrous sodium sulphate and the residue obtained was recrystallized from ethanol to get white flakes of pure 4-propanoylphenyl acrylate. M.P.45°C. Yield: 15.1 g (74%). Scheme 1 shows the reaction for the synthesis of PPA.

The structure of the monomer was confirmed by elemental analysis, FT-IR, ^{1}H-NMR and ^{13}C-NMR analysis.

Elemental analysis (%): Carbon 70.42 (Found), 70.58 (Calcd), Hydrogen 5.84 (Found), 5.92 (Calcd).



Scheme 1. Synthesis of PPA.

IR (KBr, cm^{-1}): 3109 and 3076 (=C–H stretching); 2984, 2936, 2907 and 2878 (–C–H stretching); 1744 (ester >C=O); 1682 (>C=O ketone); 1633 (C=C olefinic); 1600, 1504 and 1407 (C=C aromatic); $1457_{(as)}$ and $1377_{(s)}$ (CH_3 bending); 1297 and 1149 (C–O stretching); 854 and 797 (C–H out of plane bending); 565 and 484 (C=C out of plane bending).

^{1}H-NMR ($CDCl_3$, ppm): 7.33 (d, 2H) and 8.04 (d, 2H aromatic); 6.31 (q, 1H) and 6.61 (q, 1H, H_2C=); 6.03 (q, 1H, =CH–); 3.01 (q, 2H, CH_2); 1.24 (t, 3H, CH_3).

^{13}C-NMR ($CDCl_3$, ppm): 199.38 (>C=O, ketone); 163.79 (ester >C=O); 153.94, 133.09, 129.44 and 121.74 (aromatic carbons); 127.40 (=CH–); 134.39 (=CH_2); 31.61 (CH_2); 8.05 (CH_3).

Copolymerization

Copolymers of PPA and MMA having different compositions were synthesized in MEK solution using BPO as a free radical initiator. Predetermined quantities of PPA, MMA, BPO (0.25% w/v) and MEK were mixed in a polymerization tube, and the reaction was carried out under N_2 atmosphere at 70 ± 1°C. After the desired time (<10% conversion), the copolymer was precipitated by pouring the contents into excess methanol. The precipitated polymer was filtered, washed with methanol, and purified by repeated precipitation from the solution of the polymer in MEK by methanol. The polymer was finally dried in vacuum at 45°C for 24 h.

Spectral Measurements

Elemental analysis was carried out with a Perkin-Elmer C-H analyzer. IR spectra were recorded with a Nicolet 360, FT-IR, ESP spectrophotometer as KBr pellets. ^{1}H-NMR spectra of the monomer and all the polymer samples were run on a Bruker 270 MHz FT-NMR spectrometer at room temperature using $CDCl_3$ as the solvent and TMS as an internal standard. The proton decoupled ^{13}C-NMR spectra were run on the same instrument operating at 22.63 MHz and the chemical shifts were recorded under similar conditions. The molecular weights (M_w and M_n) were determined using a Waters 501 gel permeation chromatograph. Tetrahydrofuran was used as an eluent and polystyrene standards were employed for calibration. Thermogravimetric analysis was performed with a Mettler TA 3000 thermal analyzer in air atmosphere at a heating rate of

15°C/min. The glass transition temperature was determined with a NETZSCH- Geratebau Gmbh DSC 204 thermal analyzer at a heating rate of 10°C/min in N_2 atmosphere.

Results and Discussion

Copolymerizations of PPA with MMA from different feed compositions were carried out in MEK solvent by free radical solution polymerization. The reaction time was selected between 12 min and 2 h to give low conversion (<10%) in order to make use of the instantaneous copolymer composition equation and to obtain polymer samples having homogeneous composition to the extent possible. Scheme 2 shows the synthesis of poly (propanoylphenyl acrylate-*co*-methyl methacrylate).

Characterization

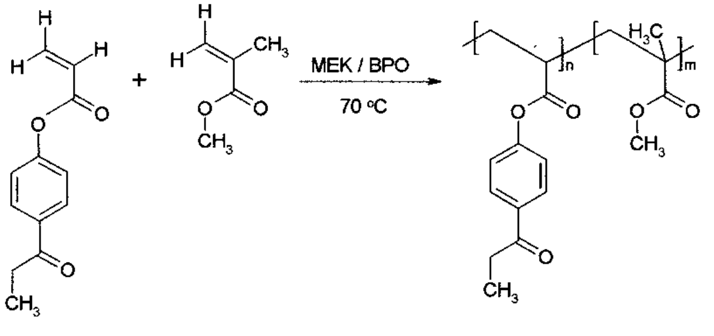
Solubility. The copolymers were soluble in chloroform, dimethyl formamide, dimethyl acetamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene, xylene and insoluble in n-hexane and hydroxyl group containing solvents such as methanol and ethanol.

IR Spectrum

The IR spectrum of the copolymer, poly(PPA-*co*-MMA) (0.3932:0.6068) is shown in Figure 1. It shows peaks at 3051 cm^{-1}, corresponding to the aromatic C–H stretching. The asymmetrical and symmetrical stretching due to the methyl and methylene groups are observed at 2984, 2950, and 2867 cm^{-1}. The shoulder at 1760 and peak at 1731 are attributed to the ester carbonyl stretching of MMA units. The keto carbonyl stretching of PPA unit occurs at 1687 cm^{-1}. The aromatic C=C stretching is observed at 1600, 1503 and 1412 cm^{-1}. The asymmetrical and symmetrical bending vibrations of methyl group are seen at 1451 and 1384 cm^{-1}, respectively. The C-O stretching due to the ester groups in MMA and PPA units give rise to signals at 1204, 1165, and 1123 cm^{-1}. The C–H out of plane bending vibrations of the aromatic nuclei is observed at 794 cm^{-1}. The C=C out of plane bending vibration of aromatic nuclei is seen at 565 cm^{-1}.

^{1}H-NMR Spectrum

^{1}H-NMR spectrum of the copolymer, poly(PPA-*co*-MMA) (0.3932:0.6068) is shown in Figure 2. The aromatic protons show resonance signals at 8.13–7.01 ppm. The resonance



Scheme 2. Synthesis of poly(PPA-*co*-MMA).

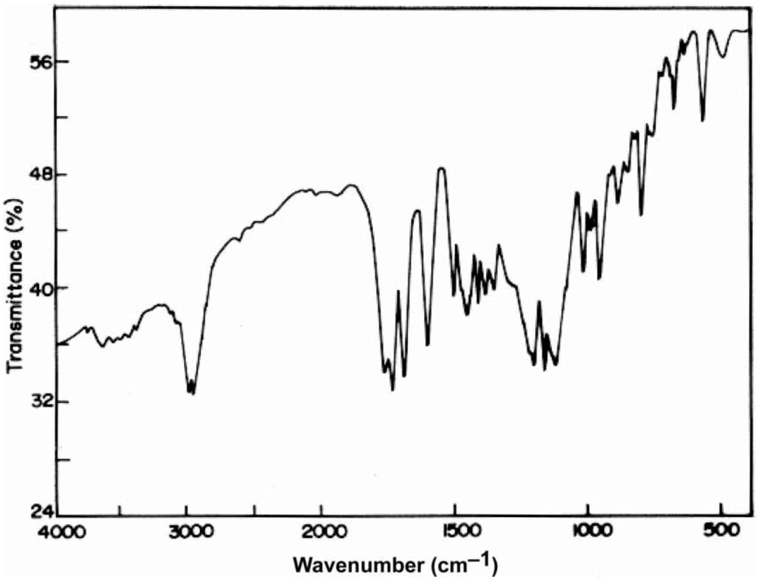


Figure 1. IR spectrum of poly(PPA-*co*-MMA) (0.3932:0.6068).

signals at 3.83–3.44 ppm are due to the methoxy protons of MMA unit. The methylene protons of the propanoyl group of PPA unit show a signal at 2.96 ppm. The methyne protons of the backbone show signals between 2.82 and 2.22 ppm. Due to the existence of tacticity, the resonance signals corresponding to the methylene group of the backbone are observed between 2.22–1.58 ppm. The methyl protons of the pendant group of PPA and α-methyl protons of the MMA unit show resonance signals at 1.58–0.77 ppm.

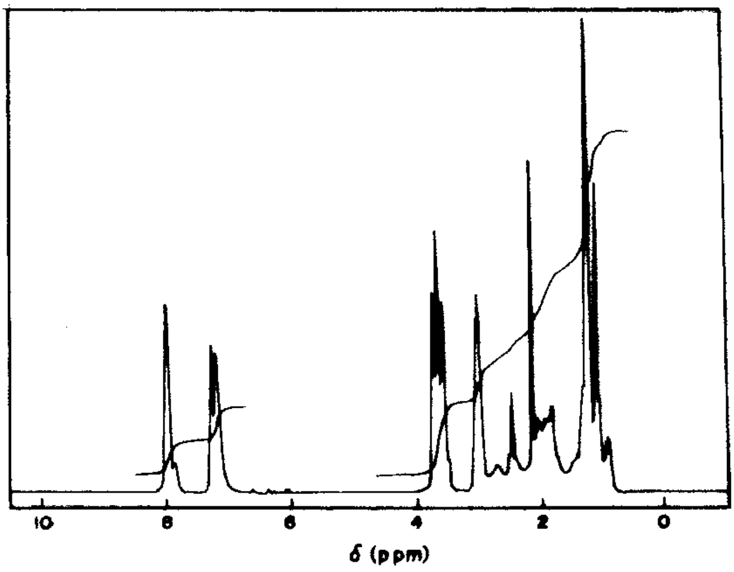


Figure 2. ^{1}H-NMR spectrum of poly(PPA-*co*-MMA) (0.3932:0.6068).

^{13}C-NMR Spectrum

The proton decoupled ^{13}C-NMR spectrum of poly(PPA-*co*-MMA) (0.3932: 0.6068) is shown in Figure 3. The resonance signal at 199.30 ppm (C_8) is due to the keto carbonyl carbon of PPA unit. The signals at 176.66 (C_3) and 174.41 ppm (C_{14}) are due to the ester carbonyl carbon groups of the PPA and MMA units, respectively. The resonance signals at 153.84 ppm (C_4) and 134.55 ppm (C_7) are due to the aromatic carbons attached to the oxygen and keto groups, respectively. The other aromatic carbon signals are observed at 129.43 (C_6) and 121.40 ppm (C_5). The backbone tertiary carbons show a signal at 36.25 (C_{12}) ppm and methylene carbons at 44.65–44.36 ppm (C_1 and C_{11}). The methylene and methyl carbons in the pendant group of PPA unit show signals at 31.61 and 8.34 ppm, respectively. The α-methyl group of the MMA unit shows a resonance signal at 18.61 ppm.

Molecular Weights

The number and weight average molecular weights (M_w and M_n) and polydispersity indices of homopolymers, as well as copolymers determined by gel permeation chromatography, are given in Table 1. The polydispersity indices of poly(PPA) and poly (MMA) are 1.58 and 1.84, respectively. The theoretical value of (M_w/M_n) for polymers produced through radical combination and disproportionation are 1.5 and 2.0, respectively (18). In the homopolymerization of MMA, chain termination by disproportionation dominates coupling (19). The value of (M_w/M_n) for poly(PPA) suggests that chain termination by dimerization dominates disproportionation. The polydispersity indices of the copolymers suggest that chain termination by disproportionation was predominant when the mole fraction of MMA in the feed was very high and radical combination was predominant when the mole fraction of PPA was high in the feed.

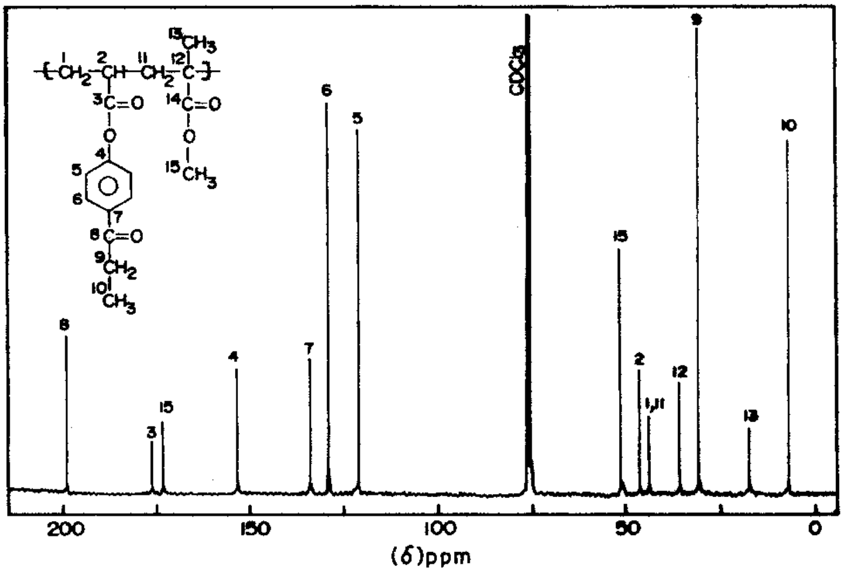


Figure 3. ^{13}C-NMR spectrum of poly(PPA-*co*-MMA) (0.3932:0.6068).

Table 1

Molecular weight data for homo and copolymers of PPA and MMA

Polymer	m_1[a]	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n
Poly(PPA)	1.0000	3.15	1.99	1.58
Poly(PPA-*co*-MMA)	0.1038	4.87	2.59	1.88
	0.2436	4.79	2.65	1.81
	0.3932	4.64	2.52	1.84
	0.5022	4.63	2.63	1.76
	0.6728	4.89	2.84	1.72
	0.8414	4.53	2.76	1.64
Poly(MMA)	0.0000	2.43	2.32	1.84

[a] m_1 is the mole fraction of PPA in the copolymer.

Thermal Analysis

Glass Transition Temperature. Glass transition temperatures (T_g) of the copolymers were determined by differential scanning calorimetry and the T_g data are presented in Table 2. The T_g value of poly(PPA) is 43°C, and that of poly(MMA) is 105°C. All prepared copolymers show a single T_g, showing the absence of formation of a mixture of photopolymers or the formation of a block copolymer. As expected, T_g values of the copolymers are found to depend on comonomer composition and the values increase with increase in MMA content in the copolymer.

Thermogravimetric Analysis

The TGA data for the homopolymers and copolymers of PPA and MMA are given in Table 2. TGA traces of poly(PPA), poly(MMA) and poly(PPA-*co*-MMA) (0.3932:0.6068) are shown in Figure 4. The thermograms clearly indicate that poly(MMA) undergoes single stage decomposition, whereas poly(PPA) and poly(PPA-*co*-MMA) undergo two stage decomposition in air atmosphere. The initial decomposition temperatures of

Table 2

TGA and DSC data for PPA-MMA copolymer system

			Temperature (°C) at weight loss (%)					
Polymers	M_1	*IDT*[a] (°C)	10%	30%	50%	70%	90%	T_g[b] (°C)
Poly(MMA)	0.0000	235	383	391	397	407	414	105
Poly(PPA-*co*-MMA)	0.2436	205	270	274	300	317	335	67
	0.5022	214	332	341	350	358	365	58
	0.6725	223	367	369	373	380	389	53
Poly(PPA)	1.0000	195	244	255	265	279	298	43

[a] *IDT*—Initial decomposition temperature.

[b] T_g—Glass transition temperature.

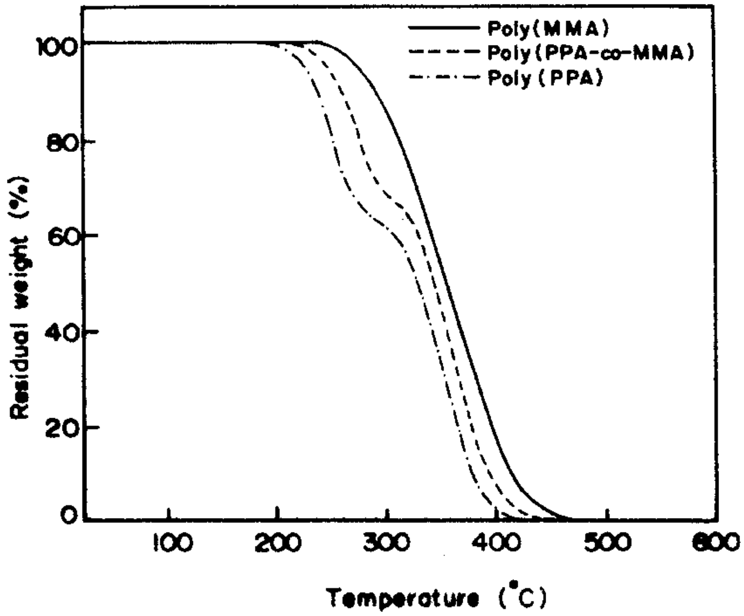


Figure 4. TGA curves for poly(MMA), poly(PPA-*co*-MMA) and poly(PPA).

poly(MMA), poly(PPA-*co*-MMA), and poly(PPA) are 236, 214 and 195°C, respectively. TGA results indicate that the thermal stability of the copolymer increases with increase in the MMA content of the copolymer.

Copolymer Composition

The copolymer composition was determined by ^{1}H-NMR spectral analysis of the copolymer. The assignment of the resonance peaks in the ^{1}H-NMR spectrum allows the accurate evaluation of the content of each kind of monomer incorporated into the copolymer chain. Hence, in the present investigation, the copolymer compositions were determined by measuring the ratios of integrated peak areas of aromatic protons to those of total aliphatic protons in the copolymer.

The following formula was derived, to determine the composition of the copolymers. If m_1 is the mole fraction of PPA and $(1 - m_1)$ is that of MMA, then

$$C = \frac{\text{Integrated peak areas of aromatic protons } (I_{Ar})}{\text{Integrated peak areas of total aliphatic protons } (I_{Ali})}$$

$$C = \frac{4m_1}{8m_1 + 8(1 - m_1)} \tag{1}$$

On further simplification it gives,

$$m_1 = 2C \tag{2}$$

Based on Equation (2), the mole fraction of PPA in all the copolymers was calculated by measuring the integrated peak areas of aromatic protons and aliphatic protons from the spectra of all the copolymers. Table 3 gives the values of C and the corresponding mole

Table 3
Composition data for free radical copolymerization of PPA (1) with MMA (2) in MEK solution at 70°C

Copolymer	Feed composition M_1[a]	Conversion (%)	Integrated peak areas I_{Ar}	Integrated peak areas I_{Ali}	C	Copolymer composition m_1[a]
1	0.1465	7.90	6.524	99.740	0.0654	0.1038
2	0.3397	7.65	10.694	87.799	0.1218	0.2436
3	0.4882	8.32	16.432	83.568	0.1966	0.3932
4	0.6357	8.56	20.075	79.925	0.2511	0.5022
5	0.7915	9.45	25.176	74.824	0.3364	0.6728
6	0.9019	8.15	29.507	70.125	0.4207	0.8414

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

fraction in the copolymers. The kinetic behavior of the copolymerization was determined by plotting the mole fraction of PPA in the feed against that in the copolymer (Figure 5). The copolymer composition curve indicates that the composition of PPA in the copolymer is always lower than that in the feed.

Monomer Reactivity Ratios

The type of copolymer formed will be understood from the values of reactivity ratios of the comonomers. The monomer reactivity ratios of PPA and MMA were first evaluated from the monomer feed ratios and the resultant copolymer compositions by the application of linear methods such as Fineman-Ross (20), Kelen-Tüdös (21) and Extended Kelen-Tüdös (22) methods. The significant parameters of F-R, K-T and ext. K-T equations

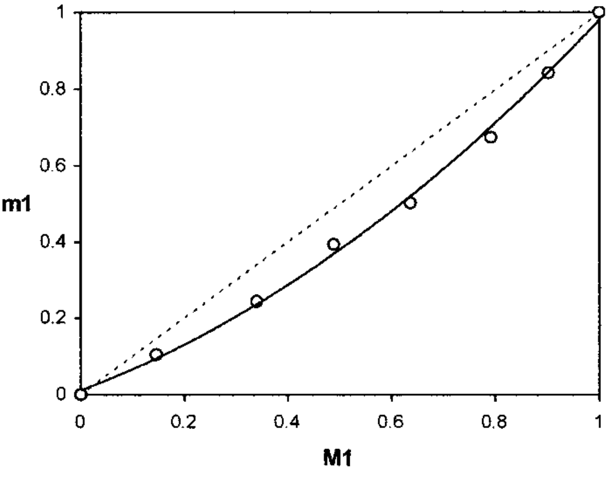


Figure 5. Copolymer composition diagram of poly(PPA-*co*-MMA) system.

Table 4
F-R and K-T parameters for the copolymerization of PPA with MMA

Copolymer	$F = M_1/M_2$	$F = m_1/m_2$	$H = F^2/f$	$G = F(f-1)/f$	$\eta = g/(\alpha + H)^a$	$\xi = H/(\alpha + H)^a$
1	0.1718	0.1158	0.2548	−1.3117	−0.5779	0.1122
2	0.5144	0.3220	0.8217	−1.0831	−0.3818	0.2896
3	0.9557	0.6479	1.4097	−0.5193	−0.1516	0.4116
4	1.7449	1.0088	2.0181	0.0152	0.0030	0.5996
5	3.7961	2.0562	7.0082	2.9499	0.2161	0.7767
6	9.1936	5.3051	15.9322	7.4606	0.4157	0.8877

[a] $\alpha = \sqrt{H_{max}} \times \sqrt{H_{min}} = 2.0148$.

are presented in Tables 4 and 5. The reactivity ratios for PPA (r_1) and MMA (r_2) from the F-R plot (Figure 6), and K-T and Ext. K-T plots (Figure 7) are given in Table 6. The monomer reactivity ratios determined by conventional linearisation methods are only approximate and are usually employed as good starting values for non-linear parameter estimation schemes.

Several non-linear methods have been attempted to determine the monomer reactivity ratios (23–27). To determine more reliable values of monomer reactivity ratios, a non-linear error-in-variables model (EVM) method is used utilizing the computer program, RREVM (24). The determined values of r_1 and r_2 are found to be 0.5314 and 1.4530, respectively. The 95% joint confidence region for the determined r_1 and r_2 values using RREVM is shown in Figure 8. The value of r_1 is less than 1 and that of r_2 is greater than 1, which indicates the presence of a higher amount of MMA units in the copolymer than that in the feed. However, the product of r_1 and r_2 is less than 1, which indicates that the system leads to a random distribution of the monomer units with a longer sequence of MMA units in the copolymer chain.

Table 5
Extended K-T parameters for the PPA-MMA copolymer system

	Copolymer system					
Parameters	1	2	3	4	5	6
ζ_2	0.0863	0.0946	0.1057	0.1276	0.1591	0.1362
ζ_1	0.0582	0.0592	0.0717	0.0738	0.0862	0.0786
Z	0.6644	0.6141	0.6660	0.5616	0.5202	0.5591
$\bar{F}$	0.1743	0.5243	0.9728	1.7963	3.9527	9.4886
H	0.2623	0.8538	1.4607	3.1985	7.5984	16.9713
G	−1.3308	−1.1041	−0.5287	0.0157	2.0304	7.7000
η	−0.8595	−0.5160	−0.1925	0.0035	0.2285	0.4217
ξ	0.1694	0.3990	0.5318	0.7132	0.8553	0.9296

$\alpha = (\bar{F}_{min} \times \bar{F}_{max})^{1/2} = 1.2860$; $\mu = 0.4901$.

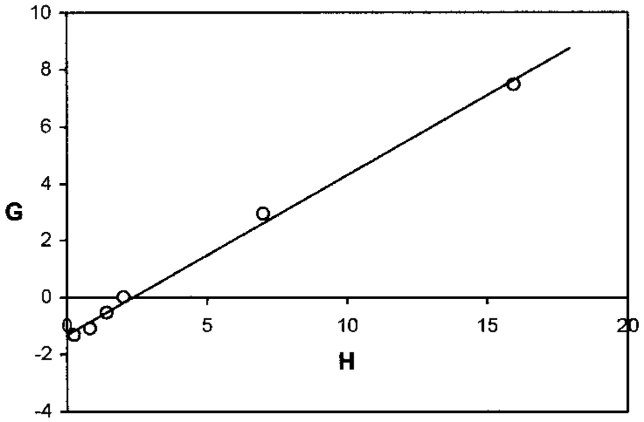


Figure 6. F-R plot for poly(PPA-*co*-MMA) system.

Conclusion

The new acrylic monomer, PPA was synthesized. Copolymers of PPA and MMA having different composition were synthesized in solution by free radical polymerization. The structure of the monomer and the copolymers was confirmed by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. 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. Thermogravimetric analysis indicated that the thermal stability of the copolymers increases with increase in MMA units in the copolymer. The T_g of the copolymers were found to increase with increase in MMA units in the copolymer. The polydispersity indices of poly(PPA), poly(PPA-*co*-MMA)

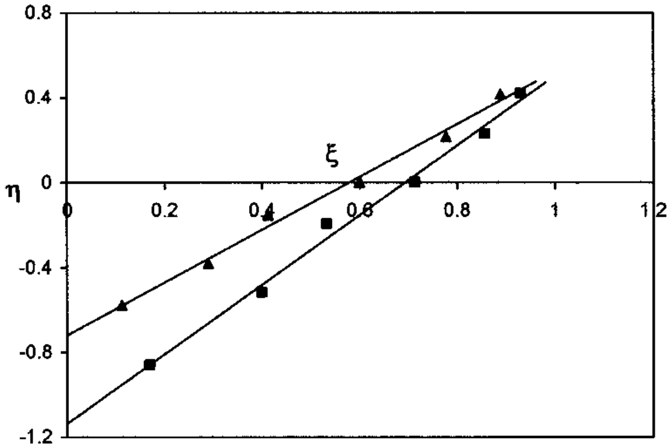


Figure 7. K-T (O) and Ext. K-T (Δ) plot for poly(PPA-*co*-MMA) system.

Table 6
Copolymerization parameter for the free radical copolymerization of PPA with MMA

Methods	r_1^a	r_2^b	r_1r_2
Fineman–Ross	0.5535	1.5428	
Kelen–Tüdös	0.5307	1.4482	
Ext. Kelen-Tüdös	0.5044	1.4614	
RREVM	0.5314	1.4530	0.7712

[a] r_1 is the reactivity ratio for PPA.
[b] r_1 is the reactivity ratio for MMA.

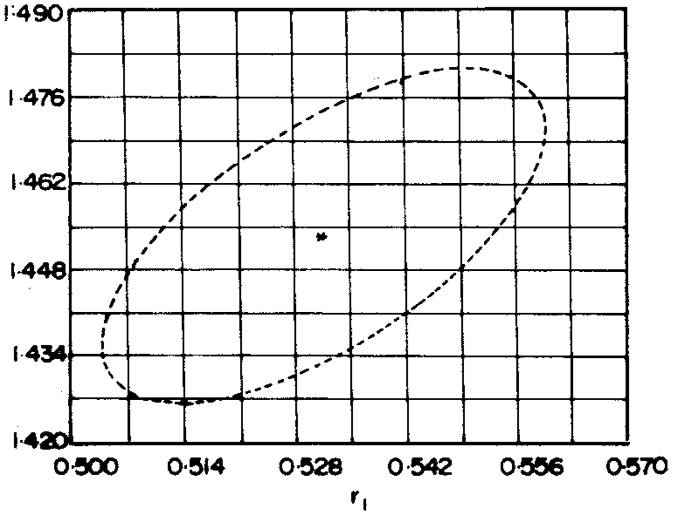


Figure 8. 95% Joint confidence region of r_1 and r_2 values by RREVM for PPA-MMA copolymer

and poly(MMA) obtained from GPC suggest a tendency for chain termination by disproportionation at very high mole fraction of MMA and recombination at high mole fraction of PPA in the feed. The copolymer composition was calculated by ^{1}H-NMR spectroscopy. The reactivity ratios of the comonomers were determined by F-R, K-T and Ext. K-T method, as well as by a non-linear error-in-variables model method (EVM) using the computer program RREVM. The value of r_1 (PPA) is less than 1, and r_2 is greater than 1 indicating that MMA is more reactive than PPA. The value of the product r_1r_2 is less than 1, which indicates the random distribution of the monomer units with a longer sequence of MMA units in the copolymer chain.

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