

4-Acetamidophenyl Acrylate Copolymers with Acrylonitrile and *N*-Vinyl-2-pyrrolidone: Synthesis, Characterization, and Reactivity Ratios

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Received 29 June 2004; accepted 19 May 2005

DOI 10.1002/app.22671

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: 4-Acetamidophenyl acrylate (APA) was synthesized and characterized by IR, ^1H and ^{13}C NMR spectroscopies. Homo- and copolymers of APA with acrylonitrile (AN) and *N*-vinyl-2-pyrrolidone (NVP) were prepared by a free radical polymerization. All the copolymer compositions have been determined by ^1H NMR technique, and the reactivity ratios of the monomer pairs have been evaluated using the linearization methods Fineman–Ross, Kelen–Tudos, and extended Kelen–Tudos. Nonlinear error-in-variable model (EVM) method was used to compare the reactivity ratios.

The reactivity ratios for copoly(APA–AN) system were $\text{APA}(r_1) = 0.70$ and $\text{AN}(r_2) = 0.333$, and for copoly(APA–NVP) system the values were $\text{APA}(r_1) = 4.99$ and $\text{NVP}(r_2) = 0.019$. Thermal stability and molecular weights of the copolymers are reported. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1919–1927, 2006

Key words: 4-acetamidophenyl acrylate; acrylonitrile; *N*-vinyl-2-pyrrolidone; reactivity ratios; ^1H and ^{13}C NMR

INTRODUCTION

Copolymerization is one of the important techniques adopted in effecting systematic changes in the polymer properties and is especially employed in the production of commercial polymers. The advantage of durability and versatility, and the possibility to tailor make molecules relatively easily to specific applications have made activated acrylate polymers prime candidates for numerous and diverse applications.^{1,2}

In this connection, importance has been given to the synthesis of polymeric systems with pharmacologically active compounds that can be easily degraded in the physiological environment.³ Macromolecular drug derivatives can be prepared by the chemical transformation of the drugs into a reactive monomer suitable for polymerization or by binding the drug to an existing natural or synthetic polymer.^{4,5} Polymeric derivatives of some common drugs such as salicylic acid, acetamidophen, sulfadiazene, and lactic acid have been prepared with methacryloyl chloride as the acrylating agent.⁶

Estimations have been made of the reactivity ratios of the copolymerization of 2-carboxyphenyl acrylate with styrene and *N*-vinyl-2-pyrrolidone (NVP).⁷ Methacrylate monomers of 2-carboxyphenol and 4-ac-

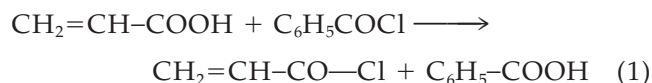
etamidophenol and their homopolymers were found to possess antipyretic activity.⁸

The present report describes the free radical solution copolymerization of 4-acetamidophenyl acrylate (APA) with acrylonitrile (AN) and NVP. Copolymer composition was determined by ^1H NMR and the reactivity ratios were evaluated using not only linearization methods (Fineman–Ross,⁹ Kelen–Tudos,^{10,11} and extended Kelen–Tudos¹³ methods) but also nonlinear error-in-variable (EVM) method.¹⁴ Thermal properties (TGA and DSC) and molecular weights by GPC were evaluated.

EXPERIMENTAL

Synthesis of acryloyl chloride

Aliphatic acid chlorides are the ones first reported¹⁵ to be synthesized with good yield using benzoyl chloride, in contrast to the methods for synthesizing acryloyl chloride using the conventional phosphorus trichloride¹⁶ or thionyl chloride, resulting in poor yield. 70% yield of acryloyl chloride is reported to have resulted by the reaction of acrylic acid with benzoyl chloride¹⁷ using a vigreux column. In the current investigation, replacement of the 25-cm distilling vigreux column by a splash head reduced the overall time of the reaction by one third without any decrease in the yield.



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TABLE I
Low Conversion Copolymerization Data of Copoly(APA/AN)

Polymer no.	Mole fraction				Amount of solvent (mL)	M_1/M_2 (x)	m_1/m_2 (y)	Yield (%)
	APA in feed (M_1)	AN in feed (M_2)	APA in copolymer (m_1)	AN in copolymer (m_2)				
1	0.10	0.90(2.770) ^a	0.1538	0.8462	29.0	0.1111	0.1818	6.5
2	0.25	0.75(1.160)	0.4179	0.5821	14.6	0.3333	0.7179	9.8
3	0.40	0.60(0.970)	0.5625	0.4375	15.3	0.6667	1.2857	11.3
4	0.55	0.45(0.590)	0.6000	0.4000	12.4	1.2222	1.5000	7.4
5	0.70	0.30(0.330)	0.6818	0.3182	10.4	2.3333	2.1427	12.9
6	0.85	0.15(0.160)	0.8182	0.1818	10.1	5.6667	4.5006	10.1

Solvent: *N,N*-dimethyl formamide; BPO, 1% (w/w) of monomer 1 and 2; [Monomer 1 + Monomer 2] = 2.0 mol/L.

^a Values in parentheses are in grams.

Synthesis of 4-acetamidophenyl acrylate

p-Hydroxyacetanilide (54.5 g, 0.36 mol) dissolved in dichloromethane (250 mL) was placed, along with triethylamine (53 mL, 0.38 mol), in a two-necked 500-mL flask. Freshly distilled acryloyl chloride (31 mL, 0.38 mol) in dichloromethane (50 mL) was added dropwise to the reaction mixture at 0°C, with continuous stirring. An hour after the completion of addition, the contents were washed with water to remove the quaternary ammonium salt formed, and the unreacted *p*-hydroxyacetanilide was then removed by washing with 5% sodium hydroxide solution. The organic layer was then dried with anhydrous Na₂SO₄, and the monomer APA was recovered after solvent evaporation [mp = 121.3°C; yield = 62 g (84%)].

Homopolymerization of 4-acetamidophenyl acrylate

This was carried out using solution polymerization technique. About 100 mg of BPO was added to 2 g of APA dissolved in 10 mL of methyl ethyl ketone taken in a polymerization tube. The content was degassed with nitrogen and kept at (70 ± 1)°C in a water bath for 24 h. After this, the polymer was precipitated by

pouring the contents of the polymerization tube into excess methanol. The resultant precipitate was filtered and dried in vacuum at 40°C for 12 h.

Copolymerization

Copolymerization was carried out by solution polymerization technique using EMK as a solvent and BPO as a free radical initiator at (70 ± 1)°C under nitrogen atmosphere. Appropriate amounts of APA, AN or NVP, BPO, and solvent were mixed in a polymerization tube, degassed with nitrogen, and kept in a thermostat for a definite period of time so as to maintain the conversion below 15% (Tables I and II). Then, the contents were precipitated by pouring into excess methanol and were filtered. The precipitate was purified by dissolving in dimethyl formamide and reprecipitated using methanol, filtered, and dried in a vacuum oven at 40°C for 12 h.

Measurements

IR spectra of the monomer and polymers were recorded on Hitachi 270–50 spectrometer using KBr pellets. ¹H and ¹³C NMR spectra of the samples were

TABLE II
Low Conversion Copolymerization Data of Copoly(APA/NVP) System

Polymer No.	Mole fraction of APA in feed (M_1)	Mole fraction of NVP in feed (M_2)	Mole fraction of APA in copolymer (m_1)	Mole fraction of NVP in copolymer (m_2)	Amount of solvent (mL)	M_1/M_2 (x)	m_1/m_2 (y)	Yield (%)
1	0.10	0.90(5.802) ^a	0.5134	0.4866	29.0	0.1111	1.0551	8.8
2	0.25	0.75(2.434)	0.6879	0.3121	14.6	0.3333	2.2041	10.3
3	0.40	0.60(2.034)	0.8495	0.1505	15.3	0.6667	5.6465	3.3
4	0.55	0.45(1.234)	0.8684	0.1316	12.4	1.2222	6.5988	9.0
5	0.70	0.30(0.689)	0.9179	0.0821	10.4	2.3333	11.1803	10.5

Solvent: 1,4-dioxane.

^a Values in parentheses are in grams.

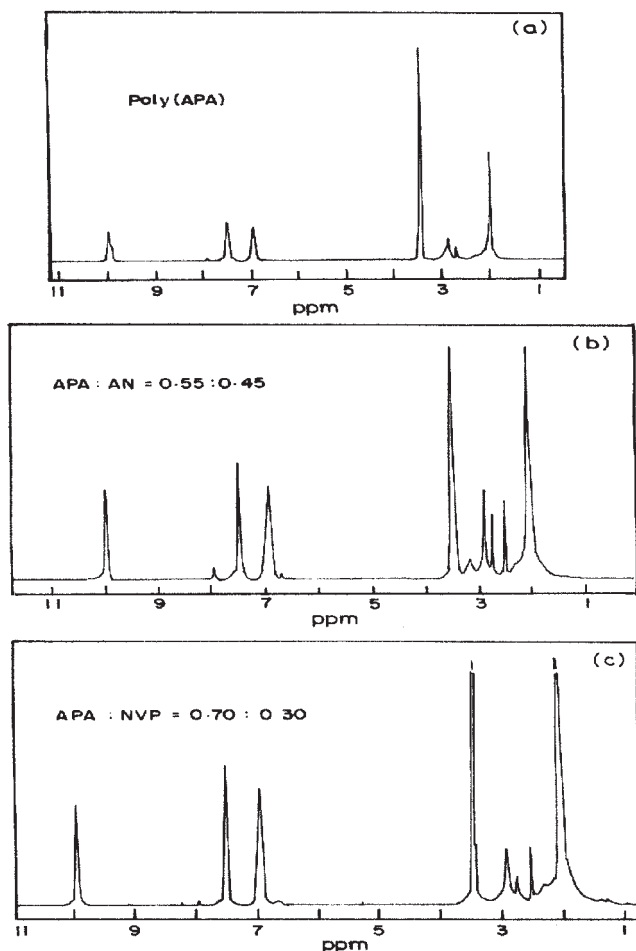


Figure 1 ¹H NMR spectra of (a) APA homopolymer, (b) APA-AN copolymer (0.55:0.45), and (c) APA-NVP copolymer (0.70:0.30).

obtained using a Bruker 320-MHz spectrophotometer. The spectra were recorded at room temperature with 15–20% (w/v) solution of the sample in CDCl₃ or DMSO-*d*₆, with TMS as an internal standard. TGA and DTA curves of the homo- and co-polymers were recorded on Mettler TA 3000 thermogravimetric analyzer in nitrogen atmosphere, at a heating rate of 20°C/min with a time constant of 1 s. The number-average and weight-average molecular weight of the polymers were determined by gel permeation chromatography using polystyrene standard and THF as eluent.

RESULTS AND DISCUSSION

The monomer (APA) formed was characterized by IR, ¹H, and ¹³C NMR spectroscopies.

IR spectra

The secondary amide “associated” NH group absorption (stretching) appears as two bands at 3305 and

3068 cm⁻¹. Aromatic C—H stretching and methyl C—H stretching appear at 3005 and 2926 cm⁻¹ respectively. Amide carbonyl absorbs at 1669 cm⁻¹, and the ester group shows absorption at 1745 cm⁻¹. The CH₂=CH— stretching occurs at 1640 cm⁻¹. The C—O—C stretching appears at 1199 cm⁻¹.

¹H NMR

The ¹H NMR spectrum of APA monomer (Fig. 1(a)) gives rise to peaks at 2.1 ppm (methyl protons), 6.0–6.5 (vinyl protons), 7.0–7.5 ppm (aromatic protons), and 8.2 ppm (NH proton).

¹³C NMR

The ¹³C NMR spectra of APA is shown in Figure 2(a). The off-resonance proton decoupled carbon-13 spectrum obtained additionally confirms the structure of the monomer. Carbon 11 appears as quartet (CH₃); signals due to carbons 7 and 8 as well as carbons 5 and

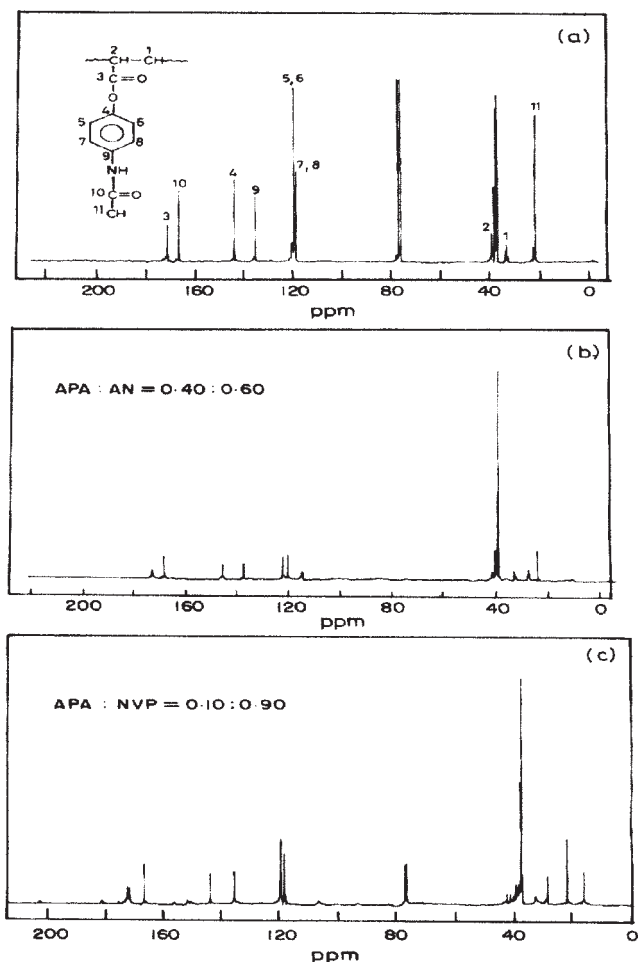
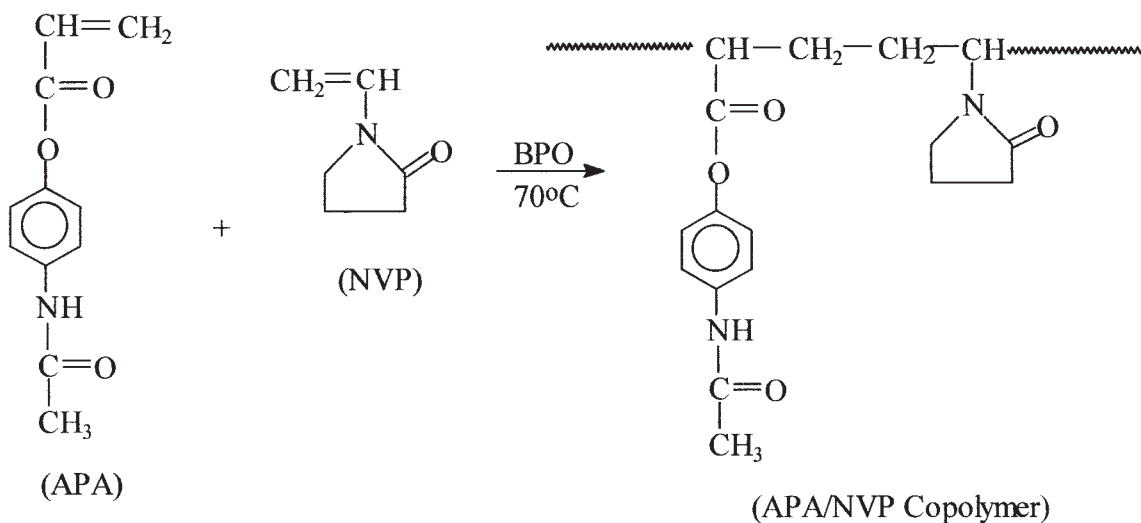
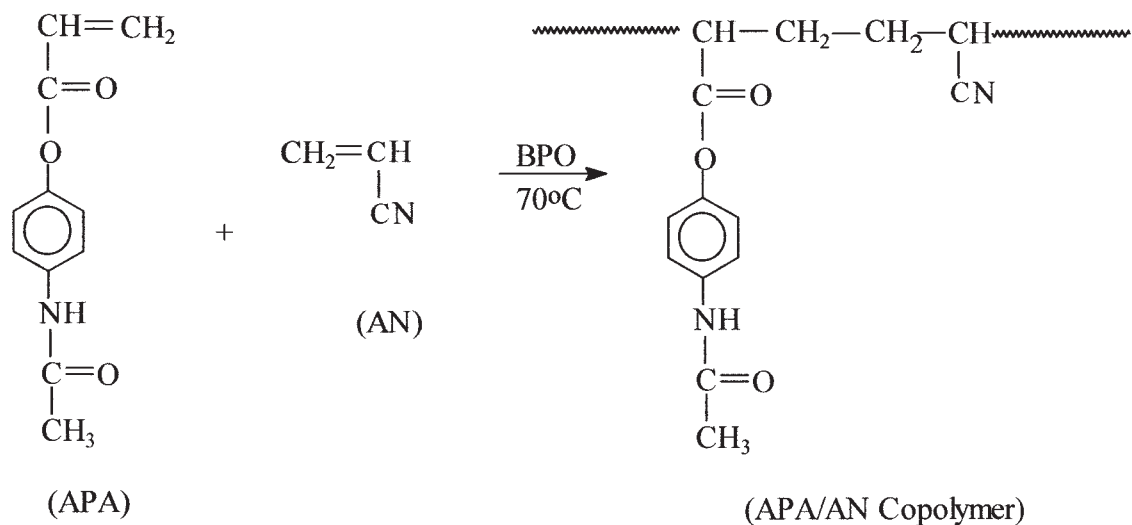


Figure 2 ¹³C NMR spectra of (a) APA homopolymer, (b) APA-AN copolymer (0.40:0.60), and (c) APA-NVP copolymer (0.10:0.90).



Scheme 1

6 appear as doublets (aromatic C—H); carbon 1 appears as a triplet ($\text{CH}_2=$), carbon 2 appears as a doublet ($=\text{CH}$), and all other carbons appear as singlets.

Copolymerization of 4-acetamidophenyl acrylate with acrylonitrile and *N*-vinyl-2-pyrrolidone

APA is copolymerized with AN in *N,N*-dimethyl formamide and *N*-vinyl-2-pyrrolidone in dioxane solvent

at 70°C using BPO as the initiator with different initial compositions of APA, AN, or NVP (Tables I and II).

Scheme 1 represents the constituent monomeric units of APA and AN in copoly(APA/AN). The number of aromatic protons from APA unit is taken into account as five (x), including the downfield NH proton. The aliphatic protons from APA unit are six (y) in number. The aliphatic protons from AN unit are three (z) in number, and there are no aromatic protons (w) in AN unit.

TABLE III
¹H NMR Analysis Data of Copoly(APA/AN) System

Sample no.	Mole fraction of APA in feed (M_1)	Chemical shift of protons (ppm)								Mole fraction of APA in copolymer (m_1)
		I_{aro}	I_{ali}	X			Y		Z	
				2H (ring)	2H (ring)	1H (NH)	3H (CH ₂ CH)	3H (COCH ₃)	3H (CHCH ₂)	
1	0.10	3.0	13.5	7.09	7.57	10.04	1.2–3.3	2.0	1.2–3.3	0.1538
2	0.25	5.6	11.4	7.10	7.57	10.04	1.2–3.3	2.0	1.2–3.3	0.4179
3	0.40	0.3	0.5	6.90	7.45	9.95	1.2–3.3	2.0	1.2–3.3	0.5625
4	0.55	0.5	0.8	6.91	7.46	9.95	1.2–3.3	2.0	1.2–3.3	0.6000
5	0.70	2.5	3.7	7.09	7.56	10.02	1.2–3.3	2.0	1.2–3.3	0.6818
6	0.85	0.6	0.8	6.90	7.46	9.95	1.2–3.3	2.0	1.2–3.3	0.8182

TABLE IV
¹H NMR Analyses Data of Copoly(APA/NVP) System

Sample no.	Mole fraction of APA in feed (M_1)	Chemical shift of protons (ppm)										Mole fraction of APA in co-polymer (m_1)		
		I_{Aro}	I_{Ali}	X			Y		Z					
				2H (ring)	2H (ring)	1H (NH)	3H (—CH ₂ CH—)	3H (COCH ₃)	2H (—CHCH ₂)	1H (—CHCH—)	2H (α-CH ₂)		2H (β-CH ₂)	2H (γ-CH ₂)
1	0.10	0.145	0.419	6.91	7.47	9.93	1.2–3.1	2.03	1.2–1.7	2.6–2.8	1.7–2.0	1.2–1.7	2.8–3.1	0.5134
2	0.25	0.161	0.325	6.91	7.47	9.94	1.2–3.1	2.03	1.2–1.7	2.6–2.8	1.7–2.0	1.2–1.7	2.8–3.1	0.6879
3	0.40	0.209	0.317	6.91	7.47	9.93	1.2–3.1	2.03	1.2–1.7	2.6–2.8	1.7–2.0	1.2–1.7	2.8–3.1	0.8495
4	0.55	0.235	0.346	6.91	7.47	9.93	1.2–3.1	2.03	1.2–1.7	2.6–2.8	1.7–2.0	1.2–1.7	2.8–3.1	0.8684
5	0.70	0.256	0.349	6.91	7.47	9.92	1.2–3.1	2.03	1.2–1.7	2.6–2.8	1.7–2.0	1.2–1.7	2.8–3.1	0.9179

TABLE V
Parameters of Fineman–Ross and Kelen–Tudos Plot of Copoly (APA/AN) System

Polymer no.	$x(y-1)$ $y(G)$	$x^2 y$ (F)	$y-1 z$ (G')	$Y z^2$ (P')	$G \alpha +$ $F(\eta)$	$F \alpha +$ $F(\xi)$	$G' \alpha' +$ $F'(\eta)$	$F' \alpha' +$ $F'(\xi)$
1	-0.5000	0.0679	-0.4909	0.0654	-0.6545	0.0889	-0.6473	0.0862
2	-0.1310	0.1547	-0.1262	0.1436	-0.1540	0.1819	-0.1508	0.1716
3	0.1481	0.3457	0.1432	0.3228	0.1422	0.3319	0.1410	0.3178
4	0.4074	0.9958	0.4043	0.9809	0.2408	0.5886	0.2415	0.5860
5	1.2443	2.5409	1.2524	2.5739	0.3844	0.7850	0.3834	0.7879
6	4.4076	7.1349	4.4713	7.3427	0.5628	0.9111	0.5564	0.9138

α , 0.6960; α' , 0.6930.

TABLE VI
Parameters of Finemenn–Ross and Kelen–Tudos Plot of Copoly(APA/NVP) System

Polymer no.	$x(y-1) y G$	$x^2 y F$	$y-1 z G'$	$Y z^2 F'$	$G \alpha + F \bar{\eta}$	$F \alpha + F \bar{\xi}$	$G' \alpha' + F' \bar{\eta}$	$F \alpha' + F' \bar{\xi}$
1	0.0058	0.0117	0.0048	0.0081	0.0665	0.1342	0.0709	0.1196
2	0.1821	0.0504	0.1642	0.0410	1.4464	0.4003	1.6322	0.4076
3	0.5486	0.0787	0.5352	0.0749	3.5577	0.5104	3.9792	0.5569
4	1.0370	0.2264	0.9844	0.2040	3.4349	0.7499	3.7344	0.7739
5	2.1246	0.4870	2.0167	0.4388	3.7771	0.8658	4.0463	0.8804

$\bar{\alpha}$, 0.0755; α' , 0.0596.

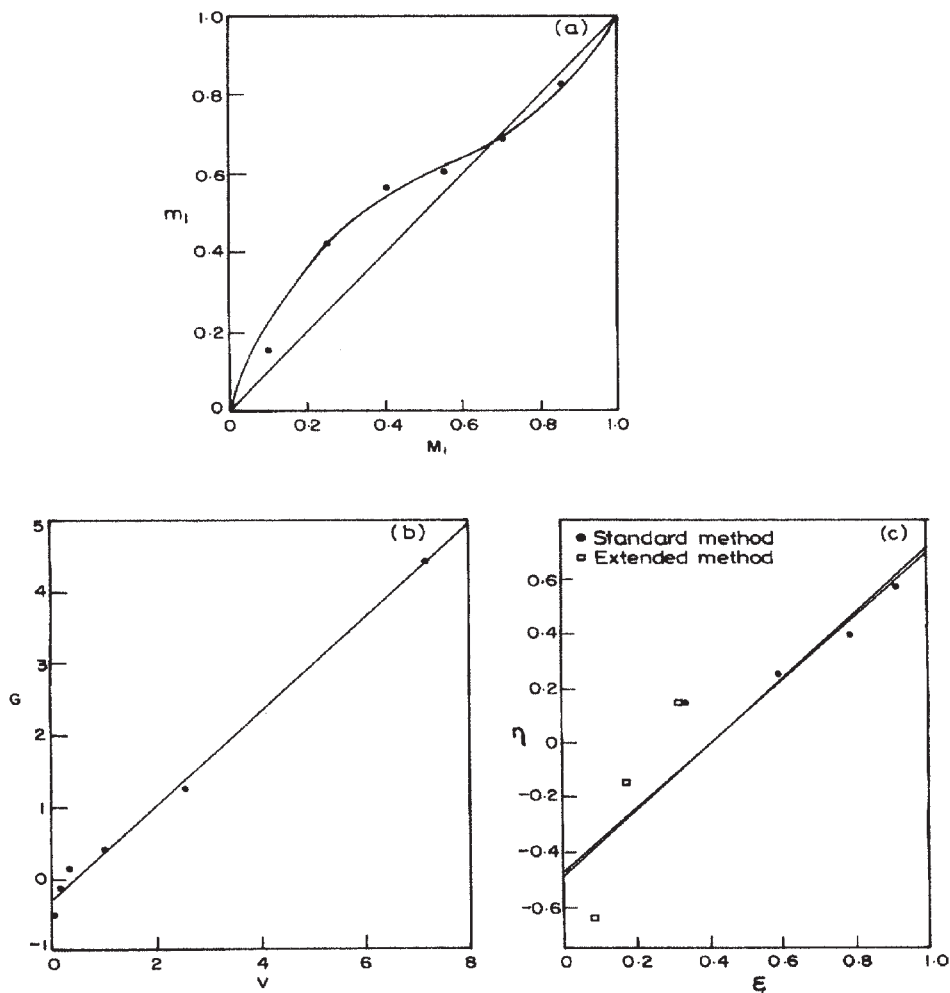


Figure 3 APA-AN copolymer system: (a) Copolymer composition plot, (b) Fineman-Ross plot, and (c) Kelen-Tudos plots (standard and extended methods).

The mole fraction " m_1 " of APA in the copolymer (APA/AN) is determined by substituting x , y , w , and z by the appropriate values in the mole fraction equation

$$m_1 = \frac{zI_{\text{aro}} - wI_{\text{ali}}}{(x - w)I_{\text{ali}} - (z - y)I_{\text{aro}}} \quad (2)$$

$$m_1 = \frac{3I_{\text{aro}}}{5I_{\text{ali}} - 3I_{\text{aro}}} \quad (3)$$

For copoly(APA/NVP) system, the number of aliphatic protons from NVP unit is 9 (z), and there are no aromatic protons (w) from NVP unit, that is,

$$m_1 = \frac{9I_{\text{aro}}}{5I_{\text{ali}} + 3I_{\text{aro}}} \quad (4)$$

APA-AN copolymer system

The ^1H NMR of the copolymer (0.55 APA-0.45 AN) is represented in Figure 2(b), and the results from the ^1H NMR analyses are represented in Table III.

In ^1H NMR, the aromatic protons of APA unit (Fig. 1(a)) appear at 6.9-7.1 and at 7.45-7.57 ppm, and the NH protons appear at 9.95-10.05 ppm. The methyl protons appear around 2.03 ppm, and the backbone protons of the polymeric chain due to both APA unit and AN unit appear at 1.2-3.3 ppm (Fig. 1(b)).

In the ^{13}C NMR spectrum (Fig. 2(a)), the acrylate carbonyl and acetanilide carbonyl of the APA unit appear at 173 and 168 ppm respectively. The C_4 of APA unit appears at 145 ppm, para carbon at 137 ppm, ortho carbons at 121 ppm, and meta carbons at 120 ppm, while the methyl group appears at 24 ppm. The backbone carbons appear at 35 and 44 ppm. In addition to the chemical shifts representing the APA unit, the nitrile carbon of AN appears at 115 ppm, and the backbone carbons of AN unit appear at 27 and 33 ppm for copoly(APA-AN) (Fig. 2(b)).

APA-NVP copolymer system

Figure 1(c) represents the ^1H NMR of copoly(APA-NVP) (0.70:0.30), and Table IV represents the results

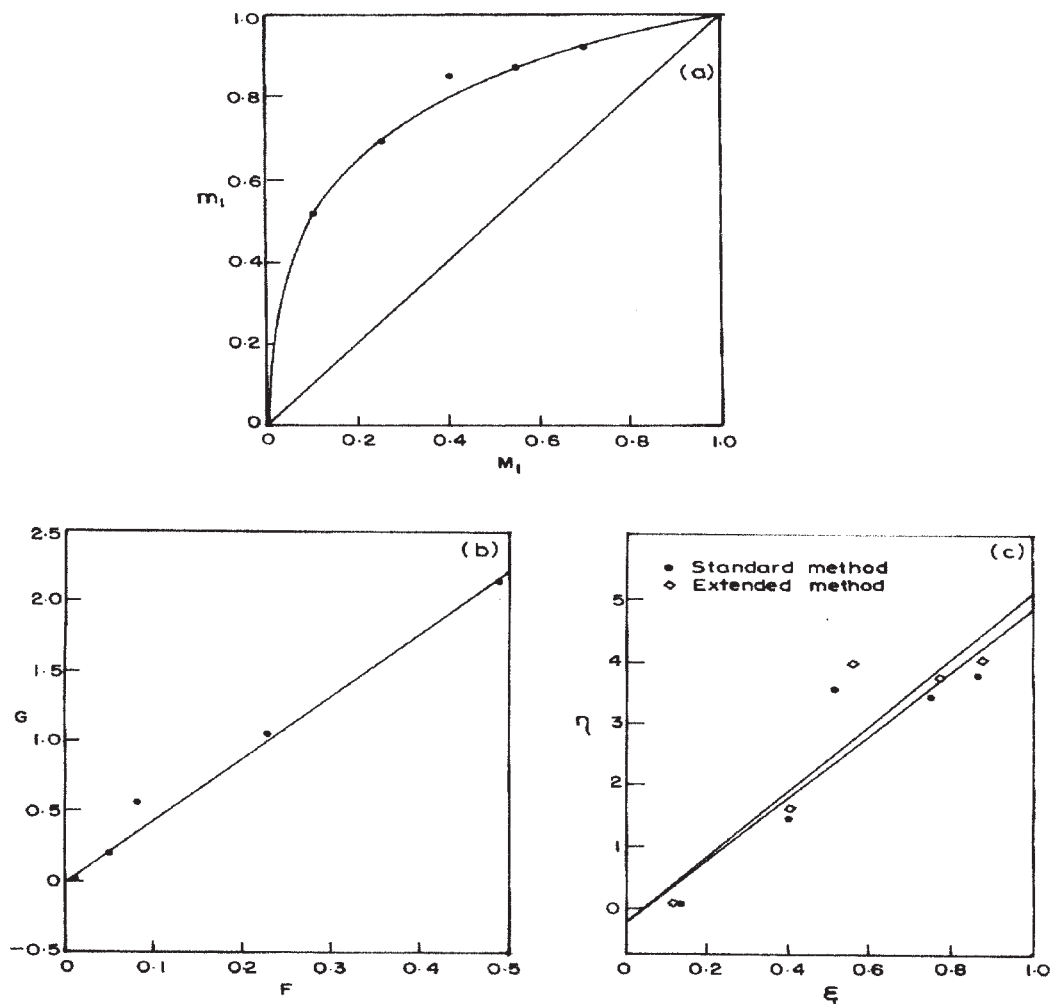


Figure 4 APA-NVP copolymer system: (a) Copolymer composition plot, (b) Fineman-Ross plot, and (c) Kelen-Tudos plots (standard and extended methods).

from ^1H NMR analyses. In ^1H NMR, the aromatic protons of APA unit appear at 6.91 and 7.47 ppm and the NH proton appears at 9.93 ppm. The methyl protons appear around 2.03 ppm, and the backbone protons of the polymeric chain appear at 1.2–3.3 ppm. In NVP unit, the methylenes at α , β , and γ to the carbonyl group appear at 1.7–2.0, 1.2–1.7, and at 2.8–3.1 ppm respectively. The methylene of the polymeric backbone of the NVP unit appears at 1.2–1.7 ppm, and the methine appears at 2.6–2.8 ppm in addition to the characteristic chemical shifts due to APA unit.

In ^{13}C NMR spectrum (Fig. 2(c)), the carbonyl group from both APA and NVP units appear at 170–173 ppm and the acetanilide carbonyl of the APA unit appears at 167 ppm. The C_4 of APA unit appears at 143 ppm, para carbon at 135 ppm, ortho carbons at 120 ppm, and meta carbons at 118 ppm, whereas the CH_3 group appears at 22 ppm. In NVP unit, the methylenes at α , β , and γ to the carbonyl group appear at 44, 43, and 16 ppm. The methine of the NVP unit appears at 30 ppm and the rest of the backbone carbons of the copolymer

appear at 31–44 ppm (solvent DMSO appears at 39 ppm).

The reactivity ratios, r_1 and r_2 , of APA with AN or NVP, respectively, are computed by Fineman-Ross and Kelen-Tudos (both standard and extended) methods, and the corresponding parameters are listed in Tables V and VI.

In Fineman-Ross method, the plot of G versus F gives a straight line with a slope equal to r_1 and intercept equal to r_2 (Figs. 3(b) and 4(b)).

In the Kelen-Tudos method, the plot of η versus ξ gives a straight line (Figs. 3(c) and 4(c)). From the α -value and the intercept at $\xi = 0$, r_2 is calculated, while the intercept at $\xi = 1$ gives r_1 .

The nonlinear error-in-variable model (EVM) method using a computer programming (PREVM) was used to calculate the reactivity ratio (Fig. 5)

The comparative values of r_1 and r_2 calculated by the three methods, the product of reactivity ratios (r_1r_2) and the nature of the copolymer sequence, which is inferred from r_1r_2 values, are presented in Table VII.

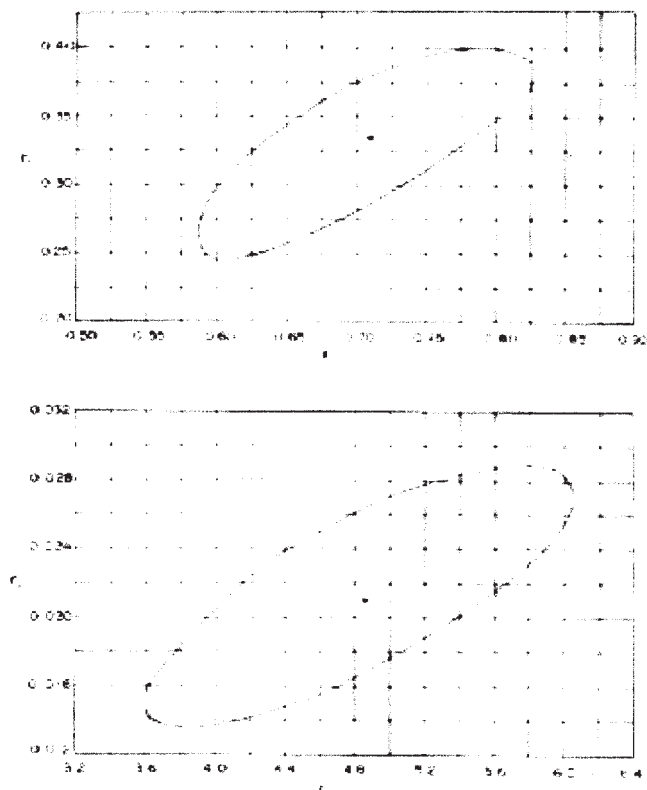


Figure 5 EVM method: (a) APA-AN copolymer system and (b) APA-NVP copolymer system.

The Fineman-Ross plot and Kelen-Tudos plots for copoly(APA-AN) system are represented by Figures 3(b) and 3(c) respectively. The copoly(APA/AN) system is lying in the range $0 < r_1 r_2 < 1$, and the product of reactivity ratios is closer to zero than to unity. Hence, there is a greater tendency for the monomeric units to alternate in the copolymer chain. The plot of copolymer composition versus initial monomer composition (Fig. 3(a)) is sigmoidal, and it crosses the ideal line at $M_1 = m_1 = 0.67$, indicating the azeotropic composition. Since the azeotropic composition is greater than 0.5, APA is inferred to be more reactive than AN.

The Fineman-Ross plot and Kelen-Tudos plots for copoly(APA-NVP) system are represented by Figures 4(b) and 4(c) respectively. Table VII represents the comparative values of r_1 and r_2 (along with their product) determined by the aforementioned methods and the nature of the copolymer sequence. The product of reactivity ratios is closer to zero than to unity; but the copoly(APA/NVP) system is not alternating in sequence. This is because $r_2 \ll r_1$ and the corresponding plot (M_1 versus m_1) (Fig. 4(a)) is not sigmoidal. APA is found to be much reactive than NVP.

Study of thermal properties and molecular weights

Thermal properties of poly(APA), copoly(APA-AN) (0.56:0.44), and copoly(APA-NVP) (0.51:0.49) were studied by TGA and DSC. The corresponding thermal data are given in Table VIII. The IDT value shows that copoly(APA-NVP) has higher thermal stability than copoly(APA) and copoly(APA-AN). T_g values of poly(APA) and copolymers of APA-AN and APA-NVP were not much different from each other.

The polydispersity index (M_w/M_n) (Table VIII) of poly(APA) was found to be 2.1, which means that termination takes place via disproportionation mechanism. But, the polydispersity index of the copolymers were found to be higher than 2 (4.6 and 11.9). This may be due to M_w which is sensitive to the presence of high molecular weight species and partly may be due to the peak broadening of the GPC curves.

CONCLUSIONS

Several copolymers of different feed ratios of APA with AN or NVP were prepared by free radical polymerization at 70°C. The copolymer composition was estimated using ^1H NMR spectroscopy. Reactivity ratios of APA with AN and NVP were evaluated by Fineman-Ross, Kelen-Tudos, and extended Kelen-Tudos methods. The average of three linearization methods were taken. The values obtained in the linearization methods were compared and were in com-

TABLE VII
Reactivity Ratios of Copoly(APA/AN) and Copoly(APA/NVP) Systems

Method	APA/AN system				APA/NVP system			
	r_1 (APA)	r_2 (AN)	r_1/r_2	Nature of copolymer sequence	r_1 (APA)	r_2 (NVP)	r_1/r_2	Nature of copolymer sequence
Fineman-Ross	0.655 ± 0.120	0.310 ± 0.031	0.203	Alternating	4.427 ± 0.479	0.018 ± 0.061	0.080	Random
Kelen-Tudos								
standard	0.709 ± 0.029	0.342 ± 0.019	0.242	Alternating	4.852 ± 0.227	0.021 ± 0.019	0.102	Random
extended	0.691 ± 0.034	0.324 ± 0.022	0.224	Alternating	5.128 ± 0.278	0.016 ± 0.019	0.082	Random
Average	0.700 ± 0.0315	0.333 ± 0.0205			4.990 ± 0.2525	0.0185 ± 0.019		
EVM	0.71	0.33	0.234	Alternating	4.86	0.021	0.102	Random

TABLE VIII
Thermal and Molecular Weight Data of Homo- and Copolymers

Polymer	IDT (°C)	50% DT (°C)	90% DT (°C)	IPDT (°C)	T_s (°C)	$M_w \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n
Poly(APA)	280	345	550	343	100	14.61	6.96	2.1
Copoly(APA/AN) ($m_r = 0.56$)	305	365	510	—	96	65.21	14.07	4.63
Copoly(APA/NVP) ($m_r = 0.51$)	350	380	525	—	98	173.60	14.57	11.90

IDT, initial decomposition temperature; IPDT, integral procedural decomposition temperature.

plete agreement with those of the nonlinear method (EVM).

$$r_1(\text{APA}) = 0.70 \pm 0.03 \quad \text{and}$$

$$r_2(\text{AN}) = 0.333 \pm 0.021$$

$$r_1(\text{APA}) = 4.99 \pm 0.25 \quad \text{and}$$

$$r_2(\text{NVP}) = 0.019 \pm 0.02$$

The initial decomposition temperature of the copolymers were higher than that of the APA homopolymer.

References

- Arshady, R.; Reddy, B. S. R.; George, M. H. *Polymer* 1986, 27, 769.
- Reddy, B. S. R. *J Polym Mater* 1999, 16, 271.
- Ferruti, P. *Makromol Chem Suppl* 1981, 5, 1.
- Hastings, G. W. *Polymer* 1985, 26, 1331.
- Thamizharasi, S.; Janardhan, V.; Reddy, B. S. R. *Eur Polym J* 2002, 38, 551.
- San Roman, J.; Madruga, E. L. *Polymer* 1989, 30, 949.
- Desai, M. D. B.; Reddy, B. S. R.; Arshady, R.; George, M. H. *Polymer* 1986, 27, 96.
- San Roman, J.; Darias, V.; Bravo, L.; Mateo, C. S.; Del, C.; Lusua, T. M.; Abdullah, S. S.; Vrivias, J. M. *Pharmazie* 1992, 47, 867.
- Finemann, M.; Ross, S. D. *J Polym Sci* 1950, 5, 259.
- Kelen, T.; Tudos, F. *J Macromol Sci Chem* 1975, 9, 1.
- Tudos, F.; Kelen, T.; Foldes-Berezhnykh, T.; Turcsanyi, B. *React Kinet Catal Lett* 1975, 2, 439.
- Kelen, T.; Tudos, F.; Turcsanyi, B.; Kennedy, J. P. *J Polym Sci Polym Chem Ed* 1977, 15, 3041.
- Kelen, T.; Tudos, F.; Turcsanyi, B.; Kennedy, J. P. *J Polym Sci Polym Chem Ed* 1981, 19, 1119.
- Dube, M.; Amin Sanayei, R.; Penlidis, A.; O'Driscoll, R.; Reilly, P.M. *J Polym Sci Part A: Polym Chem* 1991, 29, 703.
- Brown, C. *J Am Chem Soc* 1938, 60, 1325.
- Rehberg, C. E.; Dixon, M. B.; Fisher, C. H. *J Am Chem Soc* 1945, 67, 209.
- Stempel, G. H.; Cross, R. P.; Mariella, R. P. *J Am Chem Soc* 1950, 72, 2299.