

Solution Polymerization of Acrylonitrile with Vinyl Acids in Dimethylformamide

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SYNOPSIS

Solution copolymerization of acrylonitrile (AN) with various vinyl acids, i.e., acrylic acid (AA), methacrylic acid (MAA), and itaconic acid (IA), was carried out in DMF at 70°C using α,α' -azobisisobutyronitrile (AIBN) as an initiator with an acidic monomer of 0.012–0.092 mol %. Copolymers were characterized by FTIR, CHN analysis, ^1H - and ^{13}C -NMR, and viscometry. The reactivity ratios were calculated using Fineman–Ross and Kelen–Tüdös methods. In all three systems, the value of r_1 (AN) is much less than the value of r_2 . However, the r_2 (MAA) is higher than r_2 of (AA) and (IA). The reactivity ratios were calculated using Q and e schemes also. The results are in good agreement with experimentally calculated data. The tacticity and sequence length distribution of these copolymers were calculated using ^{13}C -NMR from $\text{C}\equiv\text{N}$ and CH signals. It was observed that the isotacticity of acrylonitrile–itaconic acid copolymer P(AN–IA) with 8.2 mol % of a comonomer is lower than that of P(AN–MAA) with 10.3 mol % and P(AN–AA) with 7.61 mol %. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Acrylonitrile-based copolymers are widely used in the production of acrylic fibers. Polyacrylonitrile fibers suffer from poor hygroscopicity and low dye uptake. Suitable comonomers are, therefore, incorporated into the polymer to overcome these shortcomings. Acidic comonomers not only improve the hygroscopicity but also help in the cyclization of the nitrile group to form a ladder structure during thermoxidation of acrylic fibers for producing panox and carbon fibers.¹ Among the various polymerization techniques used in the production of acrylonitrile polymers, solution polymerization is one of the most popular ones.² The advantage of solution polymerization over the other techniques is that the polymer solution can be converted directly to the spinning dope in the process of fiber production.³ Polymers prepared by solution-polymerization techniques have lower molecular weight and perhaps fewer molecular defects in the form of branching as reported

by Minagawa⁴ for aqueous suspension polymerization.

Radical copolymerization of acrylonitrile with 2-hydroxy alkyl methacrylate in DMF and DMSO has been investigated.⁵ The polymers prepared in DMSO were reported to be richer in hydroxy alkyl acrylate than those prepared in DMF. The influence of reaction medium on the rate of copolymerization and reactivity of the monomers of acrylonitrile with haloalkyl acrylates and methacrylate in acetone and water has also been investigated.⁶ Tsai and Lin,^{7–10} Mamazhanov et al.^{11,12} and Tur'yanskaya and Geller¹³ used a solution-polymerization technique to copolymerize acrylonitrile with different copolymers including acidic comonomers to produce hygroscopic fibers.

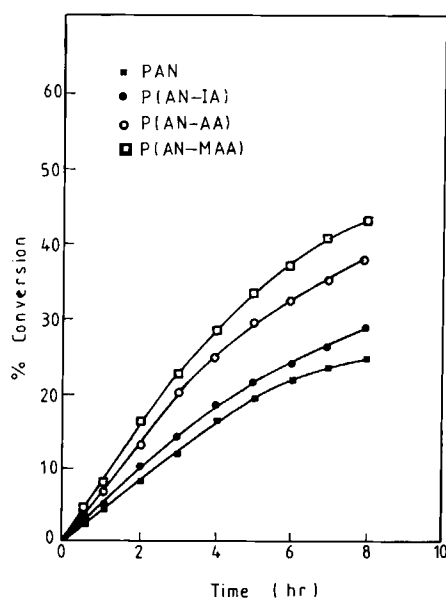
In addition to solution polymerization, suspension polymerization is another popular method which has been widely used to produce acrylonitrile copolymers.¹⁴ Acrylonitrile was copolymerized with acrylic acid, methacrylic acid, and itaconic acid using aqueous suspension polymerization technique at 40°C using ammonium persulfate and sodium metabisulfite as the redox initiator.¹⁵ Recently, Ebdon et al.¹⁶ reported the free-radical aqueous slurry polymerization of acrylonitrile using the redox initiator

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Table I Polymerization of AN with Vinyl Acids

Polymer	Code	Monomer Feed (Mol Fraction)	Conversion (%)	Nitrogen Content (Wt %)	Comonomer Content (Mol Fraction)			$[\eta]$ (dL g ⁻¹)
					CHN	IR	¹ H-NMR	
PAN	PO	—	29.0	24.03	—	—	—	0.72
P(AN-AA)	PA1	0.0226	43.9	22.28	0.0551	0.0497	—	1.1
P(AN-AA)	PA2	0.0459	43.2	21.78	0.0712	0.0761	—	1.2
P(AN-AA)	PA3	0.0685	41.8	21.33	0.0852	0.0821	—	1.24
P(AN-AA)	PA4	0.0922	39.6	18.65	0.1751	0.1692	—	1.25
P(AN-MAA)	PM1	0.0121	42.5	22.84	0.0312	0.0312	0.0314	1.13
P(AN-MAA)	PM2	0.0190	43.1	22.28	0.0461	0.0448	0.0481	1.17
P(AN-MAA)	PM3	0.0395	44.6	20.95	0.0830	0.0839	0.0842	1.19
P(AN-MAA)	PM4	0.0519	46.2	20.27	0.1025	0.1031	0.1016	1.21
P(AN-MAA)	PM5	0.0784	48.5	18.76	0.1479	0.1582	0.1312	1.19
P(AN-IA)	PI1	0.0128	35.9	22.02	0.0358	0.0326	—	1.05
P(AN-IA)	PI2	0.0265	29.6	21.62	0.0435	0.0448	—	1.07
P(AN-IA)	PI3	0.0300	26.2	20.84	0.0587	0.0572	—	1.0
P(AN-IA)	PI4	0.0392	25.6	20.74	0.0607	0.0621	—	1.1
P(AN-IA)	PI5	0.0530	26.4	19.42	0.0881	0.0862	—	0.95

at 40°C. They used an NMR technique to analyze the end groups and other minor structures derived from transfer to the bisulfite ion of the redox initiator during the polymerization. They showed that polyacrylonitrile possesses predominantly sulfonate and nonsulfonate end groups. However, it contains small quantities of acrylic acid and acrylamide units; these units, being polar in nature, may improve the hydrophilicity of the acrylic fibers.

**Figure 1** Time vs. conversion of PAN and AN-vinyl acid comonomers.

The bulk copolymerization of acrylonitrile and methacrylic acid at 60°C was studied in detail by Borbely et al.¹⁷ The copolymer composition and diad, triad, and tetrad fractions in the comonomer sequence distribution were calculated from the NMR data.

Bajaj et al.¹⁸ demonstrated the potential of ¹³C-NMR spectroscopy for measuring the acrylonitrile units in polyacrylonitrile and acrylonitrile-haloalkyl acrylate/methacrylate copolymers synthesized in various reaction media. Brar et al.¹⁹⁻²³ also determined

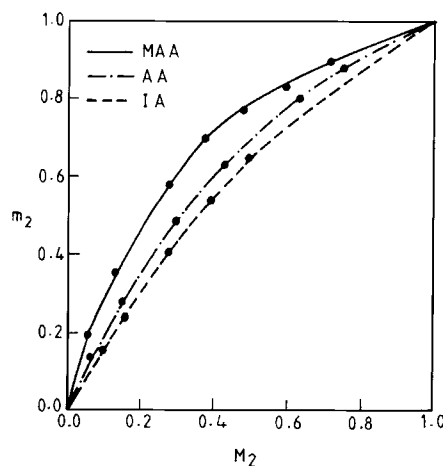
**Figure 2** Monomer-copolymer composition curves of AN-IA, AN-AA, and AN-MAA copolymer systems. M_2 = mol fraction of vinyl acid in the feed; m_2 = mol fraction of vinyl acid in the copolymer.

Table II Data for Reactivity Ratios Calculation

Sample Code	Monomer Content in Feed (Mol Fraction)		Copolymer Composition (Mol Fraction)		Nitrogen Content
	M_1 (AN)	M_2 (Acid)	m_1 (AN)	m_2 (Acid)	
P(AN-AA)	0.932	0.068	0.867	0.133	19.88
	0.851	0.149	0.728	0.272	15.94
	0.707	0.293	0.513	0.487	10.42
	0.676	0.324	0.473	0.527	9.55
	0.581	0.419	0.369	0.631	7.24
	0.479	0.521	0.289	0.711	5.53
	0.341	0.629	0.195	0.805	3.63
	0.256	0.744	0.117	0.883	2.13
P(AN-MAA)	0.943	0.057	0.810	0.190	17.35
	0.874	0.126	0.646	0.354	12.65
	0.798	0.202	0.543	0.457	10.09
	0.716	0.284	0.421	0.579	7.38
	0.626	0.374	0.302	0.698	5.01
	0.527	0.473	0.241	0.759	3.89
	0.416	0.584	0.169	0.831	2.65
P(AN-IA)	0.294	0.706	0.108	0.892	1.65
	0.983	0.017	0.970	0.030	22.39
	0.957	0.043	0.928	0.072	20.19
	0.912	0.088	0.861	0.139	17.21
	0.856	0.144	0.773	0.227	13.97
	0.791	0.209	0.672	0.328	10.91
	0.715	0.285	0.578	0.422	8.61
	0.516	0.484	0.355	0.645	4.41

the reactivity ratios, number-average sequence length, and monomer sequence distribution using ^{13}C -NMR for a number of copolymer systems like poly(acrylic acid)-methyl methacrylate, polyacrylonitrile-ethyl acrylate, and poly(methyl methacrylate)-ethyl methacrylate. Balard et al.²⁴ reported that ^{13}C -NMR spectra of nitrile carbons in polyacrylonitrile can be interpreted in terms of steric triads and pentads. Pichot et al.²⁵ employed ^{13}C -NMR to elucidate the sequence distribution of poly(acrylonitrile-methacrylic acid).

In the present study, copolymerization of acrylonitrile (AN) with three vinyl acids, i.e., methacrylic acid (MAA), acrylic acid (AA), and itaconic acid (IA), with the objective of improving the hygroscopicity of fibers is reported. Solution polymerization was carried out in DMF to compare their reactivity ratios and also using the polymer solution directly for spinning after stripping the unreacted monomers and adjusting the dope viscosity. The composition of these copolymers was determined by CHN analysis and FTIR. Tacticity and sequence

length distribution of the copolymers were calculated using ^{13}C -NMR spectroscopy.

EXPERIMENTAL

Materials

Acrylonitrile (AN) was freed from the inhibitor by washing with a sodium hydroxide solution, then with distilled water to remove traces of alkali. This was kept over fused calcium chloride overnight and distilled before use under a nitrogen atmosphere at 77°C. Acrylic acid (AA) was distilled under vacuum at 60°C/15 mmHg. Methacrylic acid (MAA) was purified by distillation under vacuum at 77°C/12 mmHg. Itaconic acid (IA) was recrystallized twice from water. α,α' -Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Dimethylformamide (DMF) was dried over calcium oxide and distilled at 153°C.

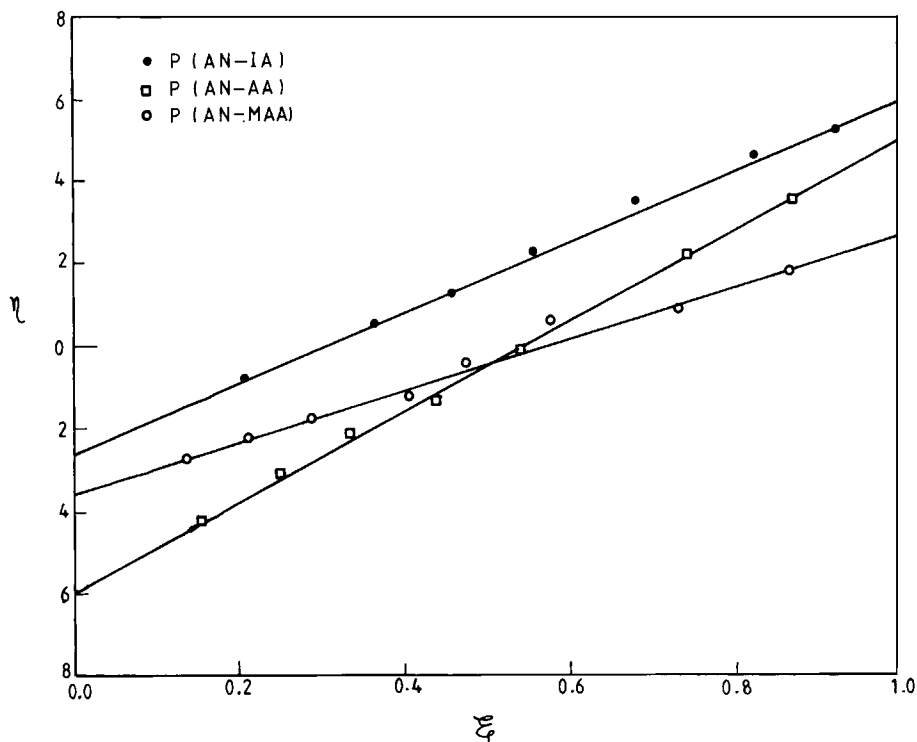


Figure 3 Kelen-Tüdös plot of AN-vinyl acid copolymers.

Polymerization

Copolymerization of AN with these vinyl acids (AA, MAA, IA) were carried out in a four-necked reactor at 70°C under nitrogen atmosphere. The reactor was fitted with a condenser and a stirrer and the third neck was used for nitrogen purging. The mol fraction of the acid comonomers was varied from 0.012 to 0.092 and the solvent to monomer ratio was kept at 2. AIBN (0.075 wt % on the basis of monomers) was used to initiate the reaction. Maleic acid (0.046 wt %) was used to prevent discoloration of copolymers. The reaction was stopped after 8 h.

Similar polymerization conditions were used to prepare the copolymers for determining the reactivity ratios. The mol fraction of the acid comonomers were varied between 0.017 to 0.744 and the copolymerization was stopped at low conversion of $\leq 15\%$.

Intrinsic Viscosity Measurements

Intrinsic viscosity $[\eta]$ of the copolymers was measured in DMF solution using a Ubbelohde viscometer in a constant temperature water bath at $25 \pm 0.1^\circ\text{C}$.

FTIR

IR spectra of copolymers of AN/vinyl acids was recorded on JASCO Micro FTIR 200 spectrophotometer using KBr pellets.

Elemental Analysis

Elemental analysis of the copolymers was carried out using a Carlo Erba 1106 elemental analyzer to determine the carbon, hydrogen, and nitrogen content of these copolymers.

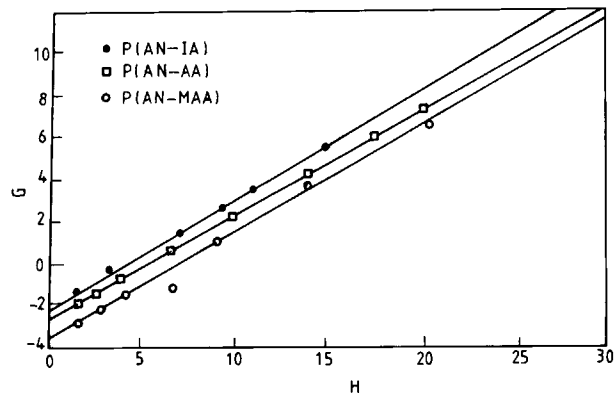


Figure 4 Fineman-Ross plot of AN-vinyl acid copolymers.

Table III Reactivity Ratios of AN and Vinyl Acids

	P(AN-IA)		P(AN-MAA)		P(AN-AA)	
	r_1 (AN)	r_2 (IA)	r_1 (AN)	r_2 (MAA)	r_1 (AN)	r_2 (AA)
K-T ^a method	0.575	2.05	0.265	3.452	0.495	2.502
F-R ^a method	0.624	2.3	0.582	3.48	0.531	2.6

^a K-T, Kelen-Tüdös; F-R, Fineman-Ross.

NMR Spectroscopy

¹H- and ¹³C-NMR spectra of these copolymers were recorded on a JEOL FX 100 NMR spectrophotometer with ¹H nuclei resonating at 99.55 MHz and ¹³C nuclei resonating at 25 MHz and tetramethylsilane (TMS) as an internal standard. The 8–10% (w/v) solution of the polymers in DMSO-*d*₆ at 90°C was used.

RESULTS AND DISCUSSION

The results of copolymerization and the comonomer content in the feed (M_2) and in the copolymers (m_2) are given in Table I. With increasing the mol fraction in the feed, there is an increase in the comonomer content in the copolymers. From the time vs. conversion curves (Fig. 1), it is clear that the addition of the acid comonomer increases the percentage conversion of copolymers. Further, the conversion of P(AN-MAA) is higher than that for P(AN-AA) and P(AN-IA) systems (P = poly). This is probably because the polymer radical with an acid unit at the chain end is considerably more active than is the polyacrylonitrile (PAN) growing radical, which means that the addition of either of the monomers will be more rapid than in the case of a radical terminating in an AN unit. The concave shape of the curve (Fig. 2) representing the feed ratio (M_2) vs. copolymer composition (m_2) indicates that the distribution of monomeric units is random and in no case is the homopolymer formation expected.

Reactivity Ratios

The composition of AN/vinyl acids copolymers was determined from the nitrogen content and IR spectra of the copolymers (Table II). The reactivity ratios were calculated using Fineman-Ross²⁶ and Kelen-Tüdös²⁷ methods. Advantage of the Kelen-Tüdös method over the conventional and Fineman-Ross method have already been emphasized.^{28,29}

The graphical evaluated linear equation proposed by Kelen and Tüdös is

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha}$$

$$\frac{G}{\alpha + F} = \left(r_1 + \frac{r_2}{\alpha} \right) \frac{F}{\alpha + F} - \frac{r_2}{\alpha}$$

where G and F are represented by

$$G = \frac{X(Y-1)}{Y} \quad \text{and} \quad F = \frac{X^2}{Y}$$

where X and Y are the ratios of the mol fractions of the monomers in the feed and in the copolymer formed:

$$\eta = \frac{G}{\alpha + F} \quad \text{and} \quad \xi = \frac{F}{\alpha + F}$$

where α is an arbitrary constant ($\alpha > 0$) given by

$$\alpha = (F_m F_M)^{-1/2}$$

Table IV r_1 and r_2 Calculated from Standard Q and e Scheme

AN	Q	e	r_1	r_2	$1/r_1$	r_1/r_2	r_2/r_1
AN	0.48	1.23	—	—	—	—	—
AA	0.83	0.88	0.376	2.353	2.66	0.160	6.26
MAA	0.234	0.65	0.419	3.343	2.387	0.125	7.978
IA	0.75	0.107	0.505	1.928	1.980	0.262	3.817

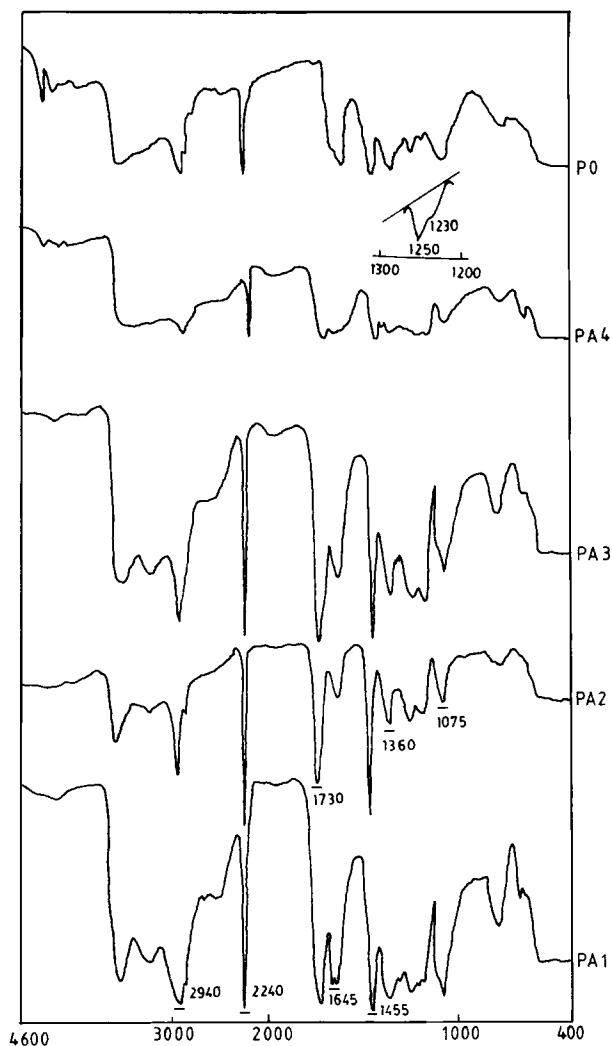


Figure 5 IR spectra of PAN and AN-AA copolymers. P0 = (PAN), PA1 = (5.51 mol %) of acid; PA2 = (7.12 mol %), PA3 = (8.52 mol %), PA4 = (17.51 mol %).

where F_M and F_m represent the lowest and highest values calculated from the series of measurements made during copolymerization.

The plot of η vs. ξ gives a straight line. Extrapolation of the line to $\xi = 1$ gives r_1 and $\xi = 0$ gives r_2/α . Kelen-Tüdös plots for calculating reactivity ratios of the monomers are shown in Figure 3.

Reactivity ratios calculated by the Fineman-Ross method used the equation

$$G = r_1 H - r_2$$

where

$$G = \frac{f_1}{f_2} \left(1 - \frac{F_2}{F_1} \right)$$

$$H = (f_1/f_2)^2 \frac{F_2}{F_1}$$

where f_1 and F_1 are the mol fractions of AN in the feed and the copolymer and f_2 and F_2 represent the mol fraction of acid comonomer in the feed and in the copolymer, respectively.

The plot of G vs. H gives a straight line with the slope as r_1 and an intercept as r_2 (Fig. 4). The values of r_1 (AN) and r_2 (acid comonomers) calculated from both methods are given in Table III.

In AN-AA copolymers $[P(\text{AN-AA})]$, $r_1(\text{AN}) = k_{11}/k_{12}$ and $r_2(\text{AA}) = k_{22}/k_{21}$, where k_{11} and k_{12} are the rate constants for the addition of AN and AA monomers, respectively, to the PAN radical. The values of $r_1 < 1$ and $r_2 > 1$. In this case, the propagation reaction $\sim M_2 M_2$ and $\sim M_1 M_2$ will be preferred over $\sim M_2 M_1$ and $\sim M_1 M_1$; hence, the probability of $M_2(\text{AA})$ entering the copolymer chain is higher as compared to $M_1(\text{AN})$. The copolymer formed will therefore be richer in $M_2(\text{AA})$. In other

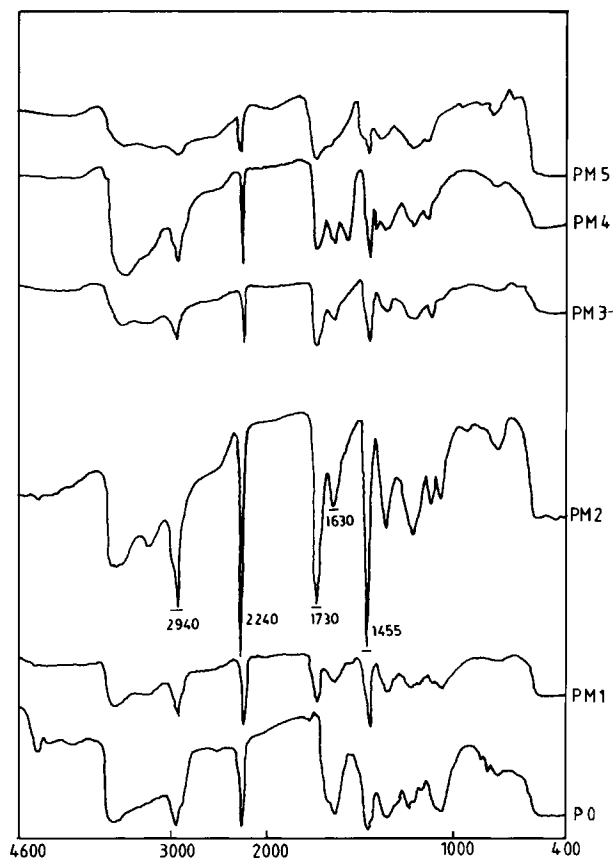


Figure 6 IR spectra of PAN and AN-MAA copolymers: P0 = PAN; PM1 = (3.12 mol %) of acid; PM2 = (4.61 mol %); PM3 = (8.30 mol %); PM4 = (10.25 mol %); PM5 (14.79 mol %).

systems, P(AN-MAA) and P(AN-IA), the trend is also similar, indicating that the growing acidic comonomer radicals $\sim\text{MAA}^*$ or $\sim\text{IA}^*$ have a greater tendency toward its own monomer unit.

The value of $1/r_1$ is higher for the P(AN-MAA) system, viz., 3.77 compared to 2.02 of P(AN-AA) and 1.74 for P(AN-IA) systems, indicating the cross-propagation of the $\sim\text{AN}^*$ radical toward acids in the following order:



The reactivity ratios were also calculated using Q and e scheme (Table IV). The results are in good agreement, as shown in Table III.

Reactivity ratios of AN and these vinyl acids copolymers synthesized by different methods have also been reported. Bajaj et al.¹⁵ reported the reactivity ratios of r_1 (AN) and r_2 (IA or AA) for copolymers prepared by aqueous suspension polymerization using a redox initiator at 40°C, while Pichot et al.²⁵ reported the reactivity ratios of the AN-MAA system by emulsion polymerization:

Method of Polymerization	Comonomer	Kelen-Tüdös method	
		r_1 (AN)	r_2 (Acid)
Aqueous suspension ¹⁵	IA	0.84	6.73
	AA	0.34	3.25
Emulsion ²⁵	MAA	0.128	2.40
Solution in DMF	AA	0.495	2.502
	MAA	0.265	3.452
	IA	0.575	2.05

The reactivity of monomers in a system depends on the method of polymerization and the medium and temperature of the polymers. However, irrespective of the method of polymerization, the acidic comonomers are found to be more reactive than is AN.

Intrinsic Viscosity

The intrinsic viscosity (IV) of the copolymers increases with increase in the acidic comonomer content (Table I). For similar mol fractions (0.083–0.088) of the acid comonomers, the IV shows the following trend:

$$\text{PA3} > \text{PM3} > \text{PI5}$$

Mol fraction	0.085	0.083	0.088
$[\eta]$	(1.24)	(1.17)	(0.95)

The change in the IV of copolymers is probably due to the change in hydrodynamic volume and the molecular weight of copolymers. However, the hydrodynamic volume depends on the size, tacticity, and density of the polymer coils in the solution.³⁰

FTIR Spectra

A comparison of IR bands in AN copolymers with PAN homopolymer help in the assignment of the peaks (Figs. 5–7). In the case of PAN, the absorption band at 530 cm^{-1} is assigned to $\text{C}-\text{C}\equiv\text{N}$. Although there is some confusion in the assignment of this band, the band at 1075 cm^{-1} is assigned to the CH mode. However, the band at 1075 cm^{-1} is mixed with some other mode and the vibrational energy is not localized in the CH bending motion. The band at 1230 cm^{-1} is due to the twisting mode of the methylene (CH_2) group coupled with the methine group. The 1250 cm^{-1} band is assigned to the bending mode of the methine ($-\text{CH}$) group coupled with the rocking mode of the methylene (CH_2) groups. These two peaks have been considered by Minagawa et

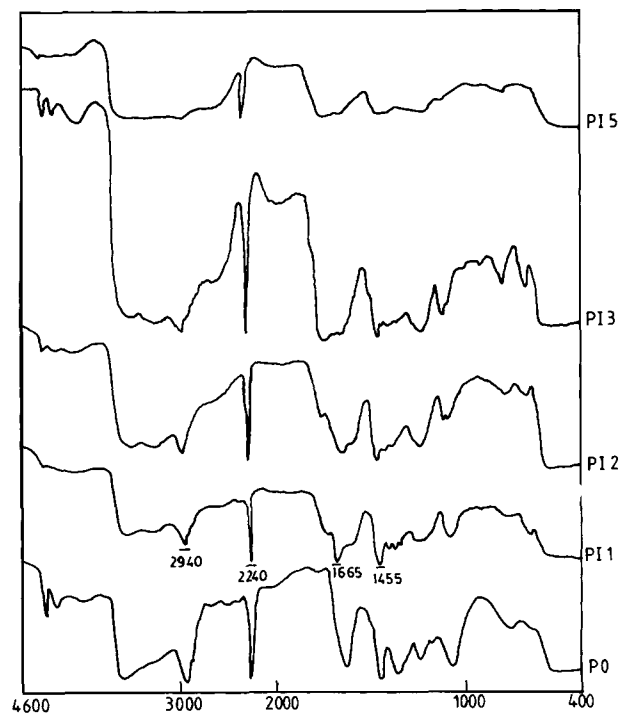


Figure 7 IR spectra of PAN and AN-IA copolymers: P0 = PAN; P1 = (3.58 mol %) of acid; P2 = (4.35 mol %); P3 = (5.87 mol %); P4 = (6.07 mol %); P5 = (8.81 mol %).

Table V $^1\text{H-NMR}$ Assignment in P0 (PAN) and AN Copolymers PA4, PM5, and PI5

	Chemical Shifts (δ)	Nature of the Resonance	Assignment
P0	2.071	Enveloped	CH_2
	1.86–2.48		
	3.122	Quintet unresolved split	CH
	3.09–3.24		
PA4	2.056	Enveloped	CH_2
	1.82–2.42		
	3.120	Unsymmetric multiplet	CH
	2.72–3.85		
PM5	2.017	Enveloped	CH_2
	1.823–2.65		
	3.098	Unsymmetric multiplet	CH
	2.847–3.527		
	1.279	Strong	CH_3
	1.05–1.49		
PI5	2.063	Enveloped	CH_2
	1.81–2.55		
	3.176	Quartet	CH
	2.73–3.24		

al.³¹ for calculating the tacticity of PAN. The bands appearing at 1220–1270, 1345–1375, and 1440–1465 cm^{-1} were assigned to C—H vibrations of different modes. Bands at 1640 and 1735 cm^{-1} were assigned to the hydrolysis of AN units during the polymerization process. A strong band appearing at 2240 cm^{-1} is assigned to $\text{C}\equiv\text{N}$.

In the IR spectra of the copolymer, the strong band at 1730 cm^{-1} is due to the carboxyl stretching vibration of the carboxylic acid of different acids. Pandey³² determined the composition of acrylic fiber from measuring optical density, i.e., the ratio of the absorbance peak at 1730 cm^{-1} ($\text{C}=\text{O}$) and 2240 cm^{-1} ($\text{C}\equiv\text{N}$). The position of the band due to the $\text{C}=\text{O}$ stretching vibration becomes changed in the copolymers. This peak appears at 1645 and 1635 cm^{-1} for P(AN-AA) and P(AN-MAA), respectively. However, it further shifts to 1665 cm^{-1} in P(AN-IA). The broad band extending from 3420 to 3520 cm^{-1} is due to the —OH stretching vibration.

The composition of copolymers was calculated by considering bands at 2240 cm^{-1} due to $\text{C}\equiv\text{N}$ and 1730 cm^{-1} due to $\text{C}=\text{O}$. The intensities of absorption of $\text{C}=\text{O}$ and $\text{C}\equiv\text{N}$ have been used to estimate

the acid content in the copolymers using a calibration curve.

NMR Studies

$^1\text{H-NMR}$

The $^1\text{H-NMR}$ spectra of P0 (PAN) displayed a strong envelope between $\delta 1.86$ to $\delta 2.48$ with its peak at $\delta 2.071$ to methylene protons and a quintet between $\delta 3.012$ to $\delta 3.882$ with its peak at $\delta 3.122$ due to backbone methine protons. A strong absorption at 2.531 was observed which is probably due to hydrogen atoms remaining in dimethyl sulfoxide- d_6 (Table V)

In the $^1\text{H-NMR}$ spectra of PA4 [P(AN-AA)], the methylene signal has shifted to downfield $\delta 2.056$ and it became narrow compared with that of P0. An unsymmetric quartet appeared between $\delta 2.72$ and $\delta 3.951$ with its peak at $\delta 3.120$ which was due to —CH protons. The presence of the methine proton of the AA comonomer in addition to that of AN increased the intensity of the signal and these chemical shifts are broader compared with P0.

The CH_2 absorption of PI5 [P(AN-IA)] was shifted to downfield at $\delta 2.063$ with a sharper nature

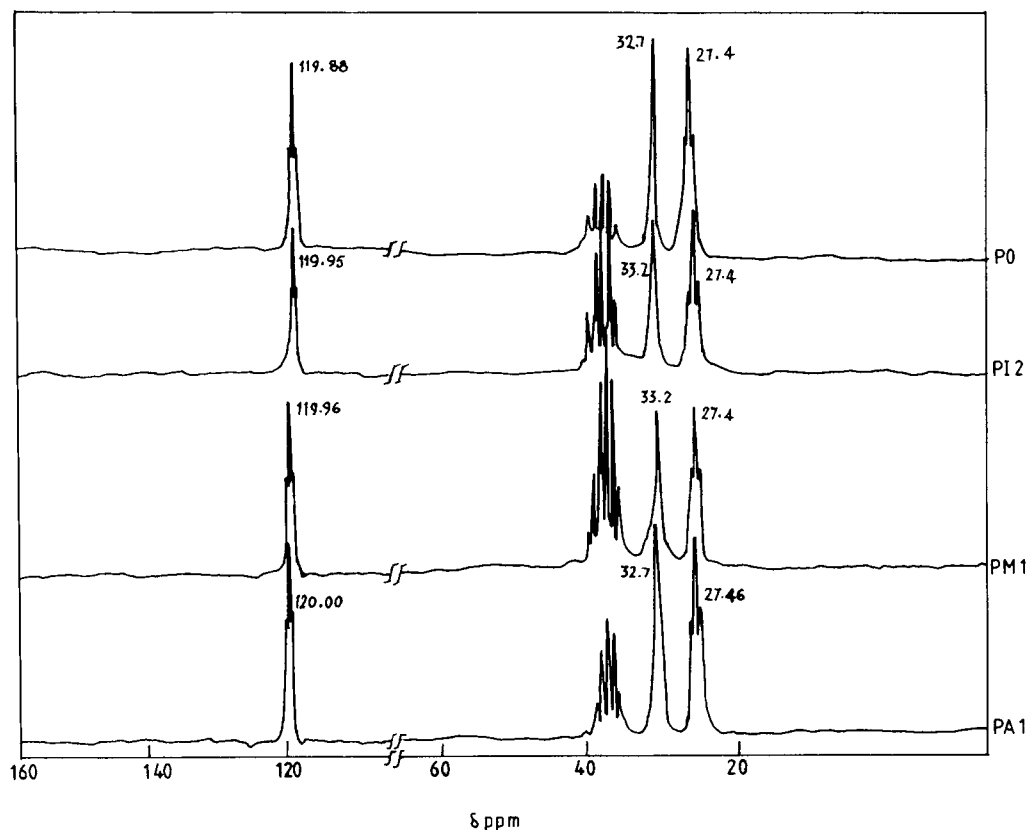
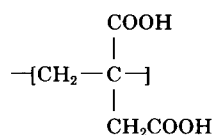


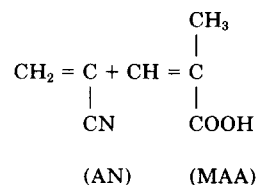
Figure 8 ^{13}C -NMR spectra of (P0) PAN, PA1 (5.51 mol %) AN-AA, PM1 (3.12 mol %) AN-MAA, and PI2 (4.35 mol %) AN-IA copolymers.

because of environmental effect on this signal. However, in PI5, the CH_2 methylene proton present in the vicinity of COOH group in the IA component

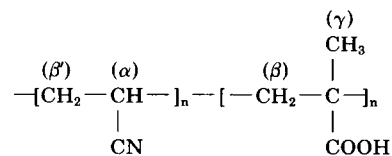


appears to be overlapped with $-\text{CH}_2$ protons of the backbone. The methine (CH) signal in PI5 appeared at upfield $\delta 3.176$ as compared to P0, due to the presence of an electron-rich OH group of IA.

A strong signal between $\delta 1.05$ and $\delta 1.49$ with its peak at $\delta 1.279$ was observed in PM5 [P(AN-MAA)]. This signal was assigned to the methyl (CH_3) group of the MAA. In this copolymer, an envelope signal at $\delta 2.063$ was due to CH_2 protons and chemical shifts between $\delta 2.73$ and $\delta 3.23$ were due to CH protons. Although the number of methine protons in PM5 and P0 has not changed, but because of an environmental change in PM5, the chemical shifts become broader compared with P0:



↓



By using methyl proton signals in the P(AN-MAA) copolymer, the composition of P(AN-MAA) was calculated from measuring the intensity of the signal due to CH_3 (γ) of MAA and the CH_2 signal of both acid and AN (β, β') components and subtracting the contribution of AN (β') from the CH_2 protons. The AN content was calculated using the following equation for P(AN-MAA) copolymers³³:

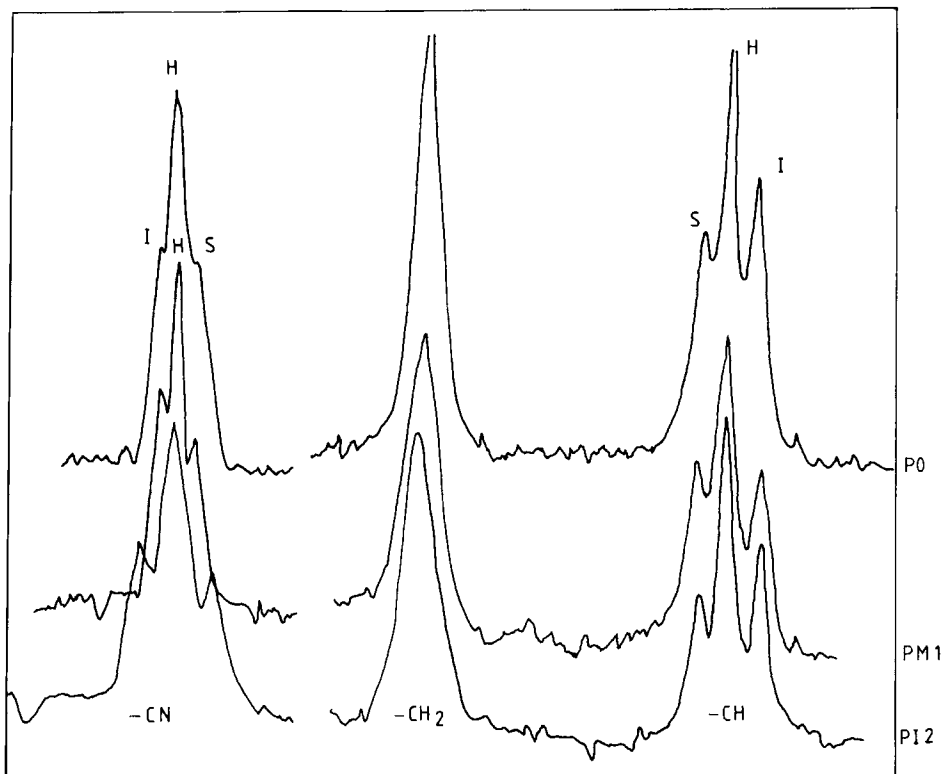


Figure 9 25 MHz ^{13}C -NMR spectra of CH and CN signals of P(AN), AN-MAA, AN-IA copolymers in $\text{DMSO-}d_6$ at 90°C : P0 = PAN; PM1 = (3.12 mol %); PI2 = (4.35 mol %).

Table VI Triad Tacticity of PAN and AN Copolymers (on the Basis of $-\text{CH}$ Signals)

Code	Peak Position			Tacticity			Stereoregularity Index $4 \text{ IS}/\text{H}^2$
	iso (mm)	H (mr/rm)	S (rr)	I (mm)	H (mr/rm)	S (rr)	
P0	26.752	27.411	27.851	30.66	44.44	24.88	1.540
PA1	26.830	27.464	27.860	30.87	45.62	23.50	1.394
PA2	26.733	27.318	27.757	23.63	48.18	28.18	1.147
PA3	26.831	27.464	27.910	30.06	44.23	25.71	1.572
PA4	26.685	27.318	27.757	30.73	46.78	22.47	1.262
PM1	26.685	27.269	27.708	27.04	48.46	24.49	1.127
PM2	26.831	27.415	27.952	29.76	44.44	25.80	1.555
PM3	26.790	27.464	27.903	26.92	46.15	26.92	1.36
PM4	26.685	27.318	27.752	30.76	45.25	25.22	1.516
PM5	26.830	27.411	27.990	30.34	45.72	23.93	1.389
PI1	26.928	27.464	27.952	30.86	44.44	24.69	1.540
PI2	26.831	27.415	27.952	26.91	46.32	26.76	1.342
PI3	26.782	27.415	27.854	27.71	46.74	25.54	1.296
PI5	26.782	27.367	27.805	29.64	44.66	25.69	1.527

Table VII Triad Tacticity of PAN and AN Copolymers (on the Basis of C≡N Signals)

	Chemical Shifts			Tacticity (%)			Stereoregularity Index 4IS/H ²
	I (mm)	H (mr/rm)	S (rr)	I (mm)	H (mr/rm)	S (rr)	
P0	120.171	119.878	119.58	27.77	46.97	25.25	1.274
PA1	120.290	120.007	119.710	27.02	45.04	27.92	1.487
PA2	120.049	119.757	119.410	30.37	48.14	21.48	1.125
PA3	120.29	120.049	119.710	25.74	50.49	23.76	0.959
PA4	121.007	119.757	119.463	32.02	44.44	23.52	1.525
PM1	120.102	119.710	119.418	27.91	47.28	24.80	1.238
PM2	120.244	119.957	119.650	29.79	46.81	23.40	1.272
PM3	120.292	119.952	119.659	26.14	47.41	26.44	1.229
PM4	120.049	119.757	119.464	28.22	51.33	20.45	0.876
PM5	120.301	120.024	119.650	29.70	45.54	24.75	1.417
PI1	120.295	120.002	119.659	27.85	47.37	25.15	1.248
PI2	120.244	119.952	119.612	28.38	48.65	22.97	1.075
PI3	120.247	119.945	119.610	29.30	50.32	20.39	0.944
PI5	121.024	120.100	119.807	27.27	52.27	20.45	0.8164

$$\% \text{ AN} = \frac{I[\text{CH}_{2(\text{AN})}(\beta') + \text{CH}_{2(\text{MAA})}(\beta)] - I[\text{CH}_3(\gamma)/3 \times 2]}{I[\text{CH}_{2(\text{AN})}(\beta') + \text{CH}_{2(\text{MAA})}(\beta)]} \times 100$$

The results obtained were found to be quite close to the results obtained by CHN analysis (Table I).

¹³C-NMR

¹³C-NMR spectra of PAN and a copolymer of AN with vinyl acids are shown in Figure 8. In the PAN homopolymer, —CH₂ carbon appeared at δ 32.7 ppm. The methine (—CH) carbon gives rise to three well-resolved peaks centered at δ ~ 27 ppm due to triad chemical shift sensitivity.^{34,35} Similarly, nitrile (CN) carbon resonance is mostly downfield from δ119.5 to δ120.2 ppm. These peaks may therefore be used for determining the triad tacticity.³⁶ Coleman et al.,³⁷ based on computer modeling, suggested that tacticity determines the degree of intramolecular nitrile group cyclization. It is easier to cyclize the isotactic sequence than the syndiotactic configurations.

Different peaks in the nitrile carbon (C≡N) signal are due to isohetero- and syndiotactic triads with iso appearing at a higher magnetic fields. However, in methine —CH signals, the iso appears at a lower magnetic field followed by hetero- and syndiotactic signals at lower magnetic fields, respectively³⁸ (Fig. 9).

Using Randall's method,³⁹ tacticity was calculated from relative intensities of the respective peaks of nitrile and methine splitting as obtained from computer data (Tables VI and VII). The number-average

sequence length of like (*no*), meso (*nm*), and racemic (*nr*) configuration were calculated using the following relations⁴⁰ (Table VIII):

$$no = [(rr) + \frac{1}{2}(mr)]^{-1}$$

$$nm = \frac{[(mm) + \frac{1}{2}(mr)]}{\frac{1}{2}(mr)}$$

$$nr = \frac{rr + \frac{1}{2}(mr)}{\frac{1}{2}(mr)}$$

The isotacticity for PAN calculated on the basis of methine and nitrile signals is 30.66 and 27.77, respectively. However, this value reduces with the incorporation of vinyl acid comonomers. The value of isotacticity calculated from CH signals for the PA1 sample (5.51 mol %) was 30.87 and this value was reduced to 29.76 for sample PM2 (4.61 mol %). However, the isotacticity content of sample PI2 containing 4.35 mol % of IA was only 26.06%. The change in tacticity values are due to the steric hindrance of the vinyl acids, and since IA with two bulkier side groups gives higher steric hindrance, the tacticity values of P(AN-IA) samples are found to be low. However, in the polymerization process, the kinetics of polymerization is strongly influenced by the presence of a comonomer which has a strong effect on the stereoregularity of the polymer chain.

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Table VIII Sequence Lengths Distribution of PAN and AN-Vinyl Acid Copolymers Calculated from CH and C≡N Signals

Code	Sequence Lengths from CH Signals			Sequence Lengths from C≡N Signal		
	<i>nm</i>	<i>no</i>	<i>nr</i>	<i>nm</i>	<i>no</i>	<i>nr</i>
PO	2.379	2.123	2.119	2.18	2.052	2.075
PM1	2.112	1.271	2.011	2.180	2.069	2.049
PM2	2.161	2.082	2.339	2.272	2.136	1.999
PM3	2.166	2.00	2.166	2.102	1.994	2.115
PM4	2.339	2.090	2.115	2.099	2.168	1.797
PM5	2.327	2.137	2.046	2.304	2.104	2.086
PA1	2.353	2.137	2.036	2.199	1.982	2.239
PA2	1.980	1.913	2.169	2.261	2.195	1.892
PA3	2.355	2.089	2.161	2.019	2.040	1.941
PA4	2.313	2.180	1.960	2.441	2.186	2.058
PI1	2.388	2.132	2.113	2.176	2.047	2.060
PI2	2.162	2.003	2.155	2.167	2.114	1.940
PI3	2.186	2.045	2.093	2.164	2.195	1.810
PI4	2.327	2.082	2.150	2.043	2.146	1.782

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