

Effect of Reaction Medium on Radical Copolymerization of Acrylonitrile with Vinyl Acids

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ABSTRACT: Radical polymerization of acrylonitrile (AN) with methacrylic acid (MAA) and itaconic acid (IA) was carried out in a mixture of dimethylformamide (DMF) and water at 70°C using α , α' -azobisisobutyronitrile (AIBN) as an initiator. Monomer feed in the polymerization vessel was 98:2 (AN:MAA/IA) in the molar ratio, and the DMF:H₂O ratio was varied between 20:80 and 80:20 (w/w). Copolymers were characterized by FTIR, carbon, hydrogen, nitrogen elemental CHN analysis, ¹H- and ¹³C-NMR, and viscometry. The rate of polymerization (R_p) was found to decrease with an increase in DMF concentration in the reaction medium, that is, in 20% DMF for AN-MAA system, the R_p is 1.23% min⁻¹ in 1 h of polymerization, while in 80% DMF, R_p is reduced to 0.37% min⁻¹. The nature of the vinyl acid also affects the R_p . It has been shown that the rate of polymerization is higher for an AN-MAA system as compared to an AN-IA system ($R_p = 1.0\%$ min⁻¹) and the methacrylic or itaconic acid content in the copolymer increases with an increase in the DMF concentration. The MAA content in the poly-(AN-MAA) polymer produced in 20% DMF is 3.2 mol %, which increases to 6.1 mol % (calculated through FTIR spectra) when DMF is increased to 80% in the reaction medium. The intrinsic viscosity [η] of the poly(AN-IA) and poly(AN-MAA) copolymers in DMF was found to be in the range of 0.67–2.90 dLg⁻¹ depending on the reaction medium. In determining the intrinsic viscosity, a definite deviation from rectilinearity of the concentration dependence in the high-dilution region is observed, thereby demonstrating the polyelectrolyte behavior of these polymers. Through FTIR and NMR spectral studies, PAN homopolymer and other copolymers have shown the formation of a small quantity of acrylamide units. In addition copolymer P₁₀, which contains 10.1 mol % IA, has shown anhydride formation. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1640–1652, 2001

INTRODUCTION

Copolymerization of acrylonitrile (AN) with some acidic comonomers, such as acrylic, methacrylic, and itaconic acids, along with a third comonomer has been reported in the literature^{1–5} as improving the hydrophilicity and dyeability of acrylic fibers made from this process. Incorporation of

acidic comonomers is also prevalent in the manufacture of acrylic precursors for carbon fibers.^{6–9} Acrylonitrile may be polymerized by various methods such as solution, emulsion, aqueous suspension, and solvent–water suspension polymerization.⁷ For aqueous suspension polymerization, three loci of polymerization have been reported by Peebles.¹⁰ Since AN is partly soluble in water, a two-phase liquid system can exist in which one phase would be a monomer-rich phase, while the other would be a monomer-poor phase. The distribution of comonomers between these two liquid phases would influence the rate of polymeriza-

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tion. It has been demonstrated that initiation and some propagation occur in the aqueous phase prior to the precipitation of the growing radicals. The second locus of polymerization would take place at the particle-solution interface, while the third locus of polymerization would be interior polymerization through buried free radicals, which is controlled by the diffusion of monomer to the active site. In another study Vijayendran¹¹ showed the distribution of carboxylic comonomers, such as acrylic acid (AA), methacrylic acid (MAA), and itaconic acid (IA), in the aqueous phase to that buried in the carboxylated polystyrene lattices produced by emulsion polymerization. Because IA is more hydrophilic, it remains in the aqueous phase, while MAA, which is more hydrophobic, is buried in the particle core.

The effect of hydrogen bonding on the reactivity of unsaturated carboxylic acid toward styrene and acrylonitrile has been very well documented by Herma and Ulbricht¹² and Plochocka.¹³ The effect of the solvent on reactivity ratios for AA (or MAA)-styrene (or AN) systems follows the trend as follows: r_1 increases and r_2 decreases in the following order—DMF \leq DMSO $<$ β -butyrolactone $<$ ethylene carbonate $<$ dioxane \sim acetone. They suggested that the lower reactivity of unsaturated carboxylic acids in proton-acceptor solvents, as compared to copolymerizations in bulk or in water at pH 2.5, results in hydrogen bonding of the COOH group to the solvent. This affects the electron density of the adjacent double bond of a monomer and mesomeric stabilization of its radical.

Radical copolymerization of acrylonitrile with vinyl acids in DMF¹⁴ and suspension polymerization⁵ have also been investigated. Higher values of r_2 (AA) for the AN-AA system in comparison to r_2 (IA) for the AN-IA system indicate greater reactivity of AA toward the propagating species.⁵ However, with all three acids in DMF solution polymerization, the r_2 of MAA is higher than the r_2 of AA and IA.¹⁴ The influence of reaction medium on the rate of copolymerization and reactivity of acrylonitrile with haloalkyl acrylates and methacrylate in acetone and water has also been investigated.¹⁵ Tsai and Lin,¹⁶⁻¹⁷ used a solution-polymerization technique to copolymerize acrylonitrile with different monomers including acidic comonomers.

Gromov et al.¹⁸ used a DMSO-water mixture to study the effect of solvent on chain propagation and termination reaction rates in the radical polymerization of acrylamide, methacrylamide, and

acrylic, methacrylic, and fluoroacrylic acids. Mitsubishi¹⁹⁻²⁰ also used a DMF-water mixture for getting a poly(AN-MAA) copolymer of \bar{M}_w 240,000 with $\bar{M}_w/\bar{M}_n = 3.2$. In another patent,²¹ a DMF-water (80:20) mixture was used for producing a poly(AN-IA) copolymer of a high molecular weight suitable for producing acrylic precursors for carbon fibers.

In this article the effect of the DMF-water ratio in the reaction medium on the rate of copolymerization of acrylonitrile with methacrylic or itaconic acid is discussed along with the influence of DMF concentration on polymer composition, tacticity, and comonomer sequence-length distribution.

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. It was then kept over fused calcium chloride overnight and distilled before use under a nitrogen atmosphere at 77°C. Methacrylic acid (MAA) was purified by distillation under a vacuum of 12 mmHg at 77°C. Itaconic acid (IA) and α, α' -azobisisobutyronitrile (AIBN) were purified by recrystallization from methanol. Dimethylformamide (DMF) was dried over calcium oxide and distilled at 153°C.

Polymerization

Copolymerization of AN with vinyl acids (MAA and IA) was carried out in a four-necked reactor at 70°C under a nitrogen atmosphere. The reactor was fitted with a condenser and a stirrer, and the third neck was used for nitrogen purging. The mole fraction of the acid comonomers was kept at 0.02. In some experiments the mole fraction of the acid comonomer was increased to 0.10 to accommodate FTIR and NMR studies. The reaction medium used was a mixture of DMF and water. In a batch containing 20 g of monomer and 100 g of reaction medium, the DMF-water ratio was varied from 80:20 to 20:80. AIBN (2.5 wt % on the basis of the monomer) was used to initiate the polymerization. For rate studies the polymerization was continued for 3 h. A large quantity of distilled water was added in the reactor, and the precipitated polymer was filtered, washed succes-

sively with distilled water and acetone, and dried under vacuum at 60°C till a constant weight was obtained.

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 $25 \pm 0.1^\circ\text{C}$.

Acidimetric Titration

The acid content in the copolymers was determined by titration of a 0.6–1% polymer solution in DMF against 0.01N aqueous NaOH using a phenolphthalein indicator.

FTIR

The FTIR spectra of AN–vinyl acid copolymers were recorded on a JASCO Micro FTIR 200 spectrophotometer using KBr pellets.

Elemental Analysis

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

NMR Spectroscopy

The ^1H - and ^{13}C -NMR spectra of these copolymers were recorded under the standard conditions at 25°C in DMSO- d_6 on a Bruker 300-MHz spectrometer, operating at 300 and 75 MHz, respectively.

X-ray Diffractometry

The wide-angle X-ray diffraction (WAXD) pattern of the finely powdered samples was recorded on a Philips X-ray diffractometer operated at a voltage of 40 kV and a current of 30 mA, using nickel-filtered Cu $K\alpha$ radiation (wavelength of 0.154 nm). The continuous scan method had a scanning range of 10° – 35° , involving a scanning speed of $1^\circ/\text{min}$ and yielded diffraction profiles for each sample. The Bragg equation was used to calculate the interlayer spacing, d . To acquire the average size, L_c , of the laterally ordered phase, or alternatively the crystal size, the Scherrer equation [eq. (2)] was used.

$$n\lambda = 2d \sin \theta \quad (\text{i})$$

$$L_c = K\lambda/\beta \cos \theta \quad (\text{ii})$$

Where $\lambda = 0.154$ nm, n and θ are the order and angle of reflection, respectively, K is the apparatus constant taken as 0.89, and β is the half-value width in radian of the X-ray intensity versus the 2θ curve. Hinrichsen's method²² was used for calculating the crystallinity index. The ratio of the crystalline area to the total area was taken as the index of crystallinity.

The percentage crystallinity was calculated by the relation

$$\chi_c = \frac{A_c}{A_c + A_a} \times 100$$

where A_c and A_a are the area under the crystalline and amorphous portion of the X-ray diffractographs.

RESULTS AND DISCUSSION

Rate and Conversion

The rate of copolymerization (R_p) of AN with vinyl acids decreases with an increase in the DMF concentration in the reaction medium (Table I). The increase of the polymerization rate in the DMF–water (20:80) mixture is not caused by an increase in the rate of initiation but is due to the effect of DMF (high chain transfer coefficient) on the propagation and termination reactions.

As suggested by Gromov,¹⁸ polymer radicals can form donor-acceptor complexes with solvent molecules. In the present system DMF, being a stronger donor, will form a donor-acceptor complex with the growing polymer radical, leading to a reduction in the rate of polymerization with an increase in DMF concentration in the reaction medium. This effect will lead to slower propagation in a DMF-rich reaction medium. Thus, polymer conversion is reduced from 73.5% with DMF:H₂O = 20:80 to 22% with DMF:H₂O = 80:20 for the AN–MAA system and from 60% to 18% for the AN–IA system. The intrinsic viscosity of poly(AN–MAA) or poly(AN–IA) polymers also decreases with increase in DMF content (Table I) in the polymerization reaction medium; for example, the $[\eta]$ of the P₁ sample [poly(AN–MAA)] is 2.8 dLg⁻¹, and for P₄ it is reduced to 0.69 dLg⁻¹. The drop in intrinsic viscosity values in DMF-rich polymerization may be attributed to the high termination rate, which results from the high chain

Table I Effect of Reaction Medium on Polymerization of AN with MAA and IA

Polymer	Code	DMF-H ₂ O Ratio (w/w)	Comonomer in Feed (Mol %)	Polymer Conversion (wt %)	R_{p60} (% min ⁻¹)	Elemental Analysis		[η] (dLg ⁻¹)
						Nitrogen (wt %)	Acid Content (Mol %)	
PAN	P0	20/80	0	80	1.33	25.18	—	1.76
Poly(AN-co-MAA)	P1	20/80	2	74	1.23	23.14	7.8	2.80
Poly(AN-co-MAA)	P2	40/60	2	49	0.82	23.51	7.1	2.50
Poly(AN-co-MAA)	P3	60/40	2	24	0.40	23.1	8.1	1.36
Poly(AN-co-MAA)	P4	80/20	2	22	0.37	22.75	9.0	0.69
Poly(AN-co-IA)	P5	20/80	2	60	1.00	23.33	5.1	2.90
Poly(AN-co-IA)	P6	40/60	2	35	0.58	23.26	5.3	2.67
Poly(AN-co-IA)	P7	60/40	2	22	0.37	22.91	5.9	1.45
Poly(AN-co-IA)	P8	80/20	2	18	0.30	22.12	7.3	0.67

R_{p60} = Average rate of polymerization at 60 min.

transfer coefficient of DMF (2.8×10^{-4} at 50°C). The termination reaction coefficient, kt , would also depend on the viscosity of the reaction medium or the solubility of the growing polymer chains in either the water phase or the DMF phase in the reaction medium depending on its composition. In water-rich reaction medium (DMF:H₂O = 20:80), the growing polymer radical would precipitate out, and polymerization would proceed heterogeneously because of the insolubility of the polymer—thus following more of the suspension polymerization technique. In DMF-rich polymerization medium (80:20), the polymer would swell and remain partially soluble in the DMF phase. On the basis of this assumption, a three-loci polymerization mechanism is proposed.

According to this theory, oligomeric radicals may be formed in the aqueous phase in the initial stages of polymerization, which precipitate out after attaining a certain critical molecular weight and then act as primary particles. Propagation would then occur either in the water phase, the DMF phase, or at the interface of the DMF-water mixture depending on the solubility of the monomers. The effect of the reaction medium (suspension, emulsion, and solution) on the copolymerization of acrylonitrile and methyl acrylate, acrylonitrile with 3-chloro 2-hydroxypropyl acrylate, and methacrylate has been investigated.¹⁵ Tsai and Lin¹⁷ also demonstrated the influence of monomer-solvent association²³⁻²⁴ in the polymerization of acrylonitrile with 2-ethylhexyl acrylate and itaconic acid in an acetone-DMSO reaction mixture.

Effect of Methacrylic or Itaconic Acid Comonomer Content

Figure 1 represents the conversion curves with the same profile; that is, they are initially auto-accelerated. Conversions increase linearly as a function of time up to high conversions and finally tend to level off. However, it should be noted that

1. the rate of polymerization is low in a DMF-water mixture (80% DMF), while in 80%

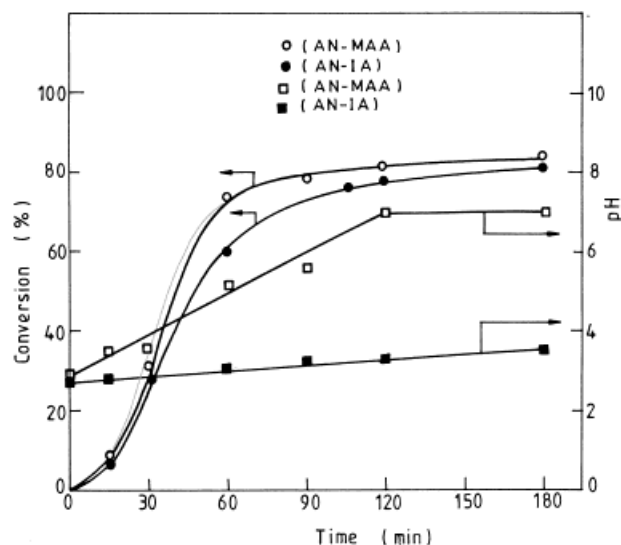


Figure 1 Rate of conversion and change in pH during AN copolymerization in DMF-water (20:80 w/w) medium. AN = 98 mol %, MAA-IA = 2 mol %. Temperature = 70°C. Monomer to solvent ratio is 1:5. AIBN = 2.5 wt % with respect to monomer.

Table II Effect of Comonomers on Reaction Rate of AN-MAA or IA Copolymerization

Polymer	R_{p15} (% min ⁻¹)	R_{p30} (% min ⁻¹)	R_{p60} (% min ⁻¹)	R_{p90} (% min ⁻¹)	R_{p120} (% min ⁻¹)	R_{p150} (% min ⁻¹)	R_{p180} (% min ⁻¹)
Poly(AN-MAA) P1	0.54	1.03	1.23	0.86	0.68	0.55	0.47
Poly(AN-IA) P5	0.49	0.93	1.00	0.82	0.4	0.53	0.45

R_{p15} = Rate of polymerization at 15 min.

- water, higher values are obtained, as reported earlier, and
- between the two copolymerization systems the overall rate of polymerization is lower in the AN-IA system.

The rate of polymerization, $R_{p(15)}$, is 0.54% min⁻¹ for the AN-MAA system and 0.49% min⁻¹ for the AN-IA copolymerization after 15 min (Table II), which increases to 1.23% min⁻¹ and 1% min⁻¹, respectively, after 60 min of polymerization. The rate of copolymerization is greatly influenced by the concentration and polarity of the acid (the monomers) and the partition coefficient of the acid monomers between the aqueous and organic phases. Because itaconic acid is more hydrophilic, it remains in the aqueous phase, while methacrylic acid, which is more hydrophobic, becomes buried in the growing particle core.

It is interesting to note that in the AN-MAA system (P₁), with an increase in methacrylic acid content (P₁₁) in the DMF:H₂O = 20:80 reaction medium, the pH drops from 2.88 to 2.4 (Table III), resulting into negligible copolymer formation.

However, with an increase in DMF content for 2 mol % methacrylic acid or itaconic acid in the feed, the pH of the initial reaction mixture increases from 2.88 to 5.54 in the former and from 2.68 to 4.08 in the AN-IA system. In this case, although there is an increase in pH, the polymer conversions are reduced. The acid comonomers under study—MAA and IA—are weak acids, and therefore their degree of dissociation, which leads to the formation of carboxylate anions in the aqueous medium, would depend largely on their concentration and the solvating power/interaction of MAA-IA with the DMF organic phase. Hence, low polymer conversion in a DMF-rich reaction medium or in a higher-acid comonomer in the feed could be attributed to the dissociation of the acid comonomer, the higher chain transfer coefficient of the DMF, and the formation of complexes between the electron-acceptor free radicals and the solvents. Formation of such complexes leads to a drop in the density of the unpaired electron in the radical, resulting in lower reactivity vis-a-vis low polymer conversion in a DMF-rich reaction medium.

Table III Effect of pH on Copolymer Yield

Polymer Code	DMF-H ₂ O (w/w)	Acid Comonomer Feed (mol %)	Initial pH of Reaction Mixture	Polymer Conversion (%)
Poly(AN/MAA)				
P11	20:80	5	2.40	Negligible
P12	20:80	3	2.76	45
P1	20:80	2	2.88	73.5
P2	40:60	2	3.28	49
P3	60:40	2	4.15	24
P4	80:20	2	5.54	22
Poly(AN/IA)				
P5	20:80	2	2.68	60
P6	40:60	2	2.77	35
P7	60:40	2	3.26	22
P8	80:20	2	4.08	18

Table IV Quantitative Analysis of Comonomer Content Using Spectroscopy

Polymer Code	Comonomer Feed	FTIR		NMR				Acid Content (mol %)	Acid Content from Acidimetry (mol %)
		Absorbance Ratio $\frac{A_{CO}}{A_{CN}} = \frac{1735 \text{ cm}^{-1}}{2243 \text{ cm}^{-1}}$	Acid Content (mol %)	¹ H Signal Intensity at		¹³ C Signal Intensity at			
				1.24 ppm —CH ₃	2.1 ppm —CH ₂	174 ppm —C=O	121 ppm —C=N		
P1	2	0.56	3.2	0.84	14.060	—	—	4.0	3.2
P2	2	0.76	3.7	0.847	12.663	—	—	4.5	3.7
P3	2	0.90	5.1	1.657	18.801	—	—	5.9	5.1
P4	2	1.48	6.1	1.646	17.853	—	—	6.0	6.1
P5	2	0.72	2.2	—	—	1	16.665	2.9	2.0
P6	2	0.86	2.3	—	—	1	15.630	3.1	2.3
P7	2	0.90	2.6	—	—	1	14.875	3.3	2.6
P8	2	1.14	3.9	—	—	1	12.614	3.8	3.2
P9	10	1.55	8.4	—	—	1	9.963	9.1	13.0
P10	10	1.93	6.7	—	—	1	4.460	10.1	13.1

P₉ = Poly(AN-MAA)P₁₀ = Poly(AN-IA)

Polymer Characterization

Elemental Analysis

The copolymer composition determined using various techniques is given in Tables I and IV. It can be noted from the elemental analysis data that the nitrogen content in the homopolymer (25.18 wt %) is less than expected for a 100% PAN, which should contain 26.4% nitrogen. Hence, the comonomer content calculated by elemental analysis is always found to be higher than that determined from NMR, IR, and acidimetric titration. Possible reasons for this are:

- the addition of 2-cyanopropyl radicals during initiation (degradation product of AIBN) and termination; and
- some acrylonitrile groups may get hydrolyzed to acrylamide and acrylic acid (the presence of acrylamide units is confirmed by the presence of a sharp peak at 1660 cm⁻¹ in FTIR and a small signal at $\delta = 7.9$ ppm in ¹H-NMR).

Acidimetric Titration

The quantitative analysis of the carboxylic acid groups was carried out using acidimetry, and the results are given in Table II. These values are

comparable with the comonomer content obtained through the FTIR and NMR spectral studies.

Intrinsic Viscosity

The $[\eta]$ (intrinsic viscosity) values of the copolymers decrease with an increase in DMF content in the reaction medium (Table I) because of the high chain transfer coefficient of DMF, which facilitates the termination of growing radicals. The $[\eta]$ values of P₀, P₁, and P₅ produced under similar conditions show that the introduction of an acidic comonomer (MAA or IA) increases the intrinsic viscosity value from 1.75 to 2.8 for P₁ and 2.9 dLg⁻¹ for P₅. It can be seen that in the 80% water medium, the IA copolymer has the higher $[\eta]$ value, 2.9 dLg⁻¹, while in the 80% DMF medium the MAA copolymer has a higher $[\eta]$ value, 0.69 dLg⁻¹. This may be because of the higher solubility of IA acid in a water medium.

Figure 2 shows the plot of intrinsic viscosity measurements of poly(AN-MAA) and poly(AN-IA) copolymers in DMF. While measuring the intrinsic viscosity, it can be observed that in the higher dilution region there is a definite deviation from the rectilinearity of the concentration dependence of the reduced viscosity. This phenomenon may be explained by the polyelectrolytic effect, caused by ionogenic groups such as MAA and IA

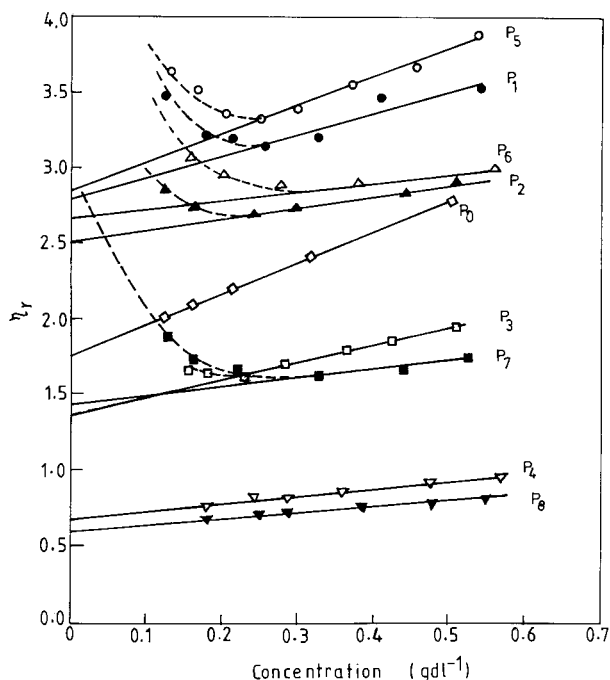


Figure 2 Intrinsic viscosity measurement of acrylonitrile homo- and copolymers in DMF at 25°C.

in the copolymer, which at a higher dilution in DMF may undergo greater ionization. Smirnova et al.²⁵ reported that in a binary copolymer containing no acid, the polyelectrolytic effect is not observed. A similar result was obtained when measurements were carried out for PAN homopolymers such as P₀.

Another important observation is that P₄ and P₈, which are copolymers of MAA (acid content of 6.1 mol %) and IA (acid content of 3.2 mol %), respectively, do not show any polyelectrolytic property. This may be because of their low molecular weight, and so they cannot act as a polyelectrolyte—that is, the polyelectrolyte effect depends not only on the acid content but also on the molecular weight.

FTIR Studies

The overlay of IR spectra obtained for PAN and its copolymers is shown in Figure 3. The IR absorption bands and their tentative assignments are given in Table V. Results of the quantitative analysis of comonomers (MAA and IA) carried out by FTIR using the calibration curves reported by Muller²⁶ are given in Table IV. In this case, the absorbance ratio of the signals at 1734 cm⁻¹ to that at 2243 cm⁻¹ was plotted against the mole

fraction of the acid component in a mixture of AN and the respective acid. The absorbance ratio of the carbonyl peaks at 1734 cm⁻¹ to that of the nitrile peak at 2243 cm⁻¹ is a measure of the acid comonomer content in the copolymer. The acid comonomer content calculated using FTIR is in good agreement with other techniques such as NMR and acidimetry at a lower comonomer content (P₁–P₈). But at higher acid levels, such as P₉–P₁₀, the comonomer content appears to be lower than that calculated from other techniques. This may be because of the broadening of the acid peak (1734 cm⁻¹) due to hydrogen bonding at a

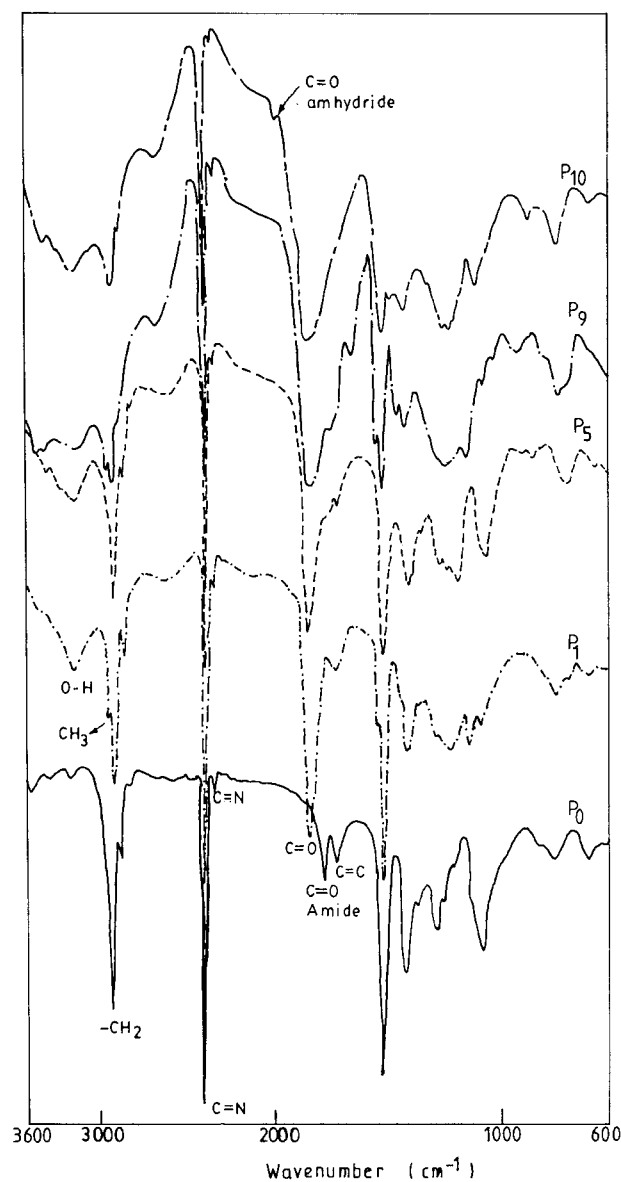


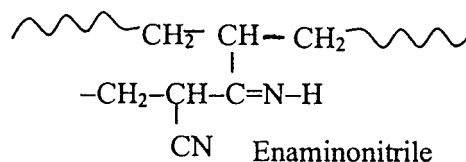
Figure 3 FTIR spectra of acrylonitrile homo- and copolymers.

Table V IR Absorption Bands and Assignments

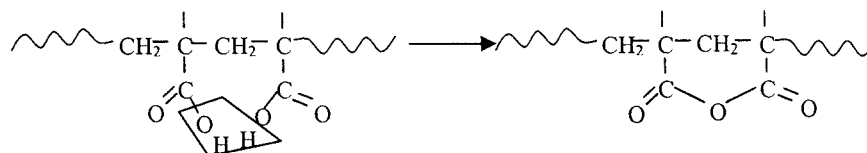
Peak Position (cm ⁻¹)	Assignments
3532–3555	$\sqrt{N-H}$ of amide formed by partial hydrolysis of PAN
3232–3348	$\sqrt{O-H}$ of acid hydroxyl group (itaconic acid shows doublet in this region)
2982	$\sqrt{C-H}$ of $-CH_3$ methacrylic acid; found only in Poly(AN-MAA) is P1-P4 and P9
2938–2941	$\sqrt{C-H}$ of $-CH_2-$ in AN
2873–2875	$\sqrt{C-H}$ of $-CH_2-$ in acids
2243	$\sqrt{C\equiv N}$ of AN
2192	$\sqrt{C=N}$
1859–1860	$\sqrt{C=O}$ anhydride
1734–1738	$\sqrt{C=O}$ of acid
1662	$\sqrt{C=O}$ of amide
1625–1636	$\sqrt{C=C}$ due to termination by disproportionation. *confirmed by the decoloration of very dilute bromine water
1455–1456	δ_{C-H} of $-CH_2-$
1396	δ_{C-H} of $-CH_3$, seen only in case of Poly(AN-MAA)
1363	δ_{C-H} of AN
1319	$\sqrt{C-O}$ of acid
1252	δ_{C-H_w} of $-CH_2-$ (stereo specific)
1195	$\sqrt{C-CN}$
945–1075	$\sqrt{C-CH_3} + \sqrt{C-CH_2-COOH}$
902	γ_{CH_2} of itaconic acid (rocking)
798	γ_{CH_2} of carbon chain (rocking)
670	γ_{C-CN} (rocking)

higher MAA-IA content or due to the anhydride group formation during polymerization (in diad/triad sequences).

In addition to the expected major peaks associated with the acrylonitrile repeat units, weak absorption bands at 2192, 1860, 1660 and 1638 cm⁻¹ can be observed. Patron et al.²⁷ and Minagawa²⁸ observed that the enamionitrile structure is produced during acrylonitrile polymerization as a defect. The band at 2192 cm⁻¹, present in all the spectra, has been assigned to the C=NH stretching of the enamionitrile structure, as reported by various authors.^{5,6,27}



IR absorption bands at 1860 and 1660 cm⁻¹ are assigned to C=O stretching due to anhydride and acrylamide units formed, respectively. The former arises from the dehydration of two acid groups (ABB sequence, B = acid group) and the latter by the partial hydrolysis of acrylonitrile units during polymerization.



Bajaj et al.²⁸ have also reported the formation of anhydride in methacrylic acid-ethyl acrylate copolymers as a result of water elimination involving adjacent acid groups.

The peak at 1638 cm⁻¹ may be assigned to the stretching vibration of $-C=C-$, perhaps because of the termination by disproportionation. This was confirmed by the discoloration of very

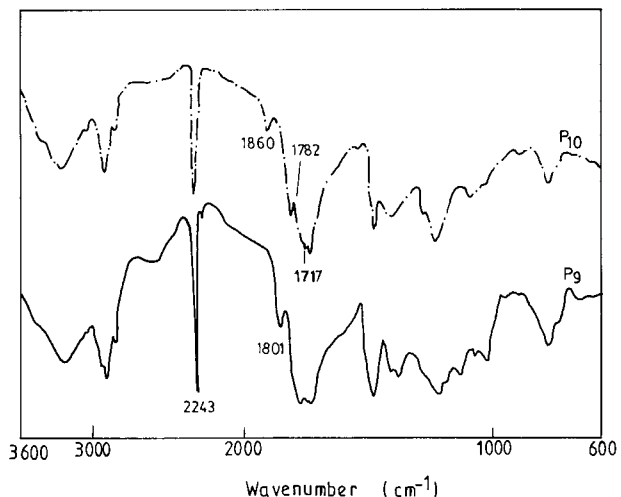


Figure 4 FTIR spectra of heated acrylonitrile copolymers.

dilute bromine water. In copolymers the peaks at 1660 and 1638 cm^{-1} are not sharp enough, as they appear to be overlapped with the carbonyl

stretching band of acid groups at 1734–1738 cm^{-1} , which broaden at higher comonomer concentrations due to hydrogen bonding. But in the case of the homopolymer P0, both peaks are quite significant, perhaps because of partial hydrolysis of the nitrile groups during polymerization.

Figure 4 shows the IR spectra of heated P9 and P10 containing more than 10 mol % of MAA and IA, respectively. In the unheated P9 sample, the anhydride peaks are not visible, but in the heated sample (heated at 170°C for 15 min), a sharp and very prominent peak has developed at 1801 cm^{-1} due to anhydride formation. On the other hand, P10, which contains two carboxylic groups of itaconic acid, shows two peaks, at 1860 and 1782 cm^{-1} . The peak at the lower absorption frequency (1782 cm^{-1}) may be due to an anhydride carbonyl group attached to the $-\text{CH}_2-$ side group, and the higher-absorption frequency peak (1860 cm^{-1}) may be because of the carbonyl group attached to the tertiary carbon as follows:

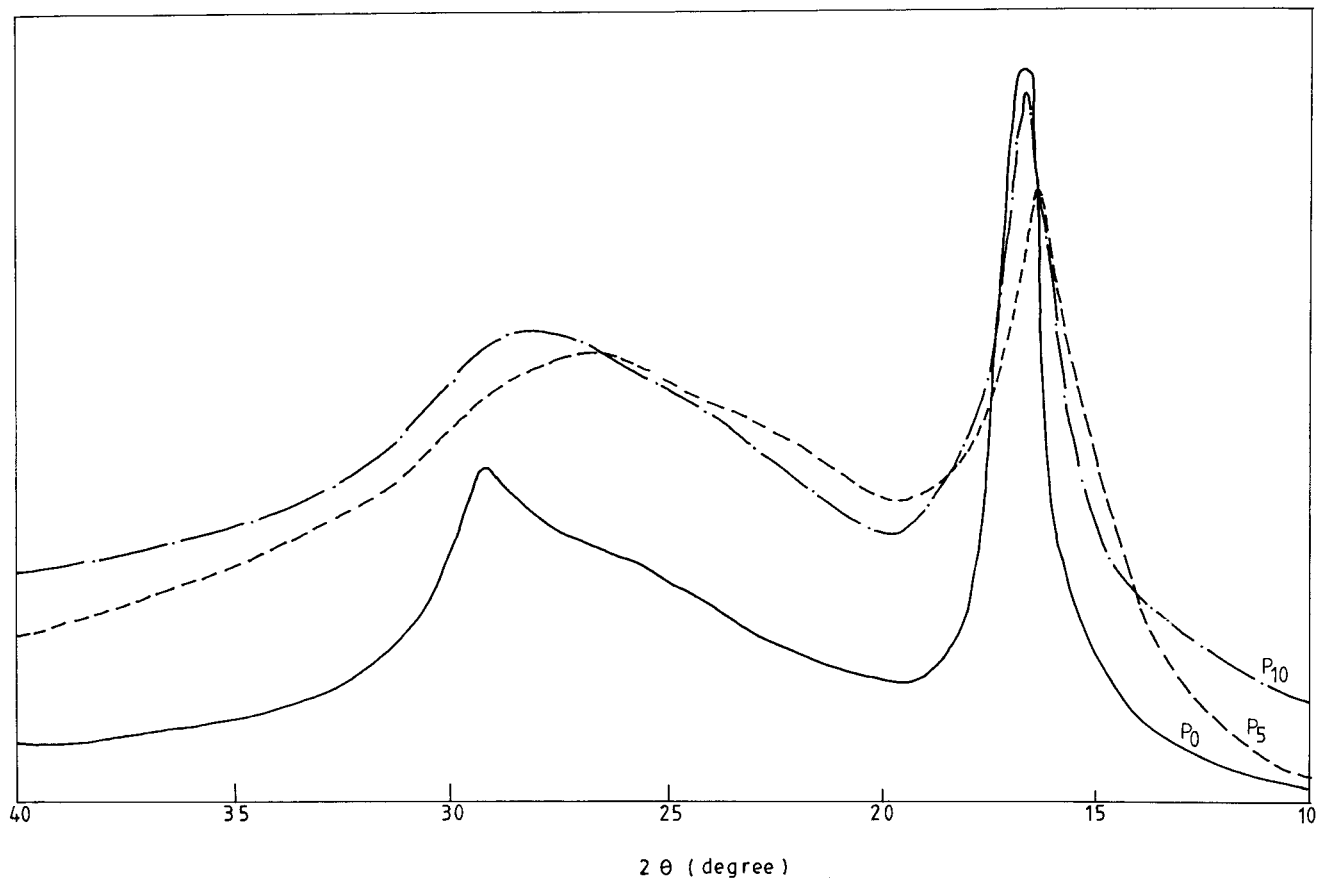
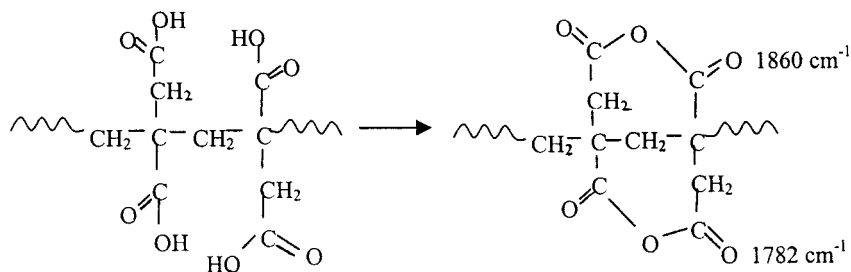


Figure 5 Wide-angle X-ray diffraction pattern of acrylonitrile homo- and copolymers.

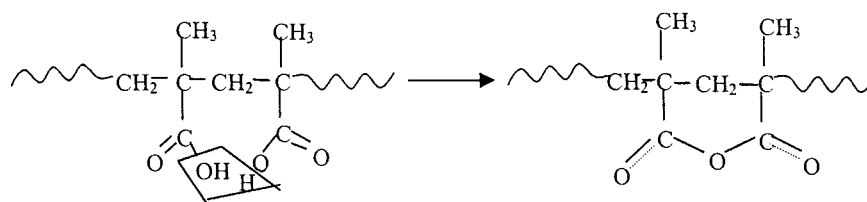
Table VI Wide-Angle X-ray Diffraction of PAN and Its Copolymers

Polymer Code	Crystallinity (χ_c)	Peak I			Peak II	
		$2\theta^\circ$	D (Å)	L_c (Å)	$2\theta^\circ$	D (Å)
P0	51	16.7	5.31	64.3	29.3	3.05
P1	46	17.0	5.21	61.8	29.4	3.03
P2	43	17.0	5.21	56.4	29.6	3.02
P3	41	17.2	5.16	55.5	29.2	3.06
P4	37	16.9	5.25	51.9	29	3.06
P5	44	16.8	5.28	47.2	29	3.08
P6	49	17.1	5.19	48.7	29	3.08
P7	40	16.8	5.27	57.4	29	3.08
P8	41	17.0	5.27	45.9	29	3.08
P9	34	16.8	5.28	47.3	29	3.08
P10	31	16.6	5.34	28.7	28.6	3.12



In poly(AN-MAA) copolymers, only one anhydride carbonyl stretching frequency is observed, at 1802 cm^{-1} . This absorption band is between the two IR absorption frequency values of the

carbonyl groups of the itaconic acid anhydride, that is, between 1860 and 1782 cm^{-1} . This may be because of the presence of a α -methyl group of MAA, which is an electron-donating group.



WAXD Studies

Figure 5 shows the wide-angle X-ray diffraction pattern of acrylonitrile homo- and copolymers. The PAN homopolymer P_0 shows a very sharp reflection at $2\theta = 17^\circ$, while the P_5 and P_{10} copolymers have a broader peak. Similarly, the peak at $2\theta = 29^\circ$ is comparatively sharper in the case of the homopolymer, while that of the copolymers is diffused, representing the lower crystallinity of copolymers. The crystallinity of the homopolymer

produced in a 20:80 DMF-water mixture is 51%, which decreases with an increase in comonomer content. Among the poly(AN-MAA) copolymers, P_9 showed the least crystallinity, 34%, because of the maximum amount of comonomer content (13 mol % from acidimetry). A similar drop in the crystallinity is observed in poly(AN-IA) polymers. However, IA-containing copolymers have a lower crystallinity than the poly(AN-MAA) copolymers. Although P_9 has a crystallinity value of 34%, P_{10} , which also contains around 13 mol %

Table VII NMR Assignments in Acrylonitrile Copolymers

Chemical Shift (δ)	Nature of Resonance	Assignment
¹ H-NMR		
Poly(AN-MAA)		
1.2-1.4	Multiplet	-CH ₃
1.7-2.5	Singlet	-CH ₂
3-3.45	Doublet	-CH
12.5-13.5	Broad singlet	-COOH _H
Poly(AN-IA)		
1.8-2.4	Doublet	-CH
3-3.45	Singlet	-CH ₂
12.1-13.5	Two singlets	-COOH _H

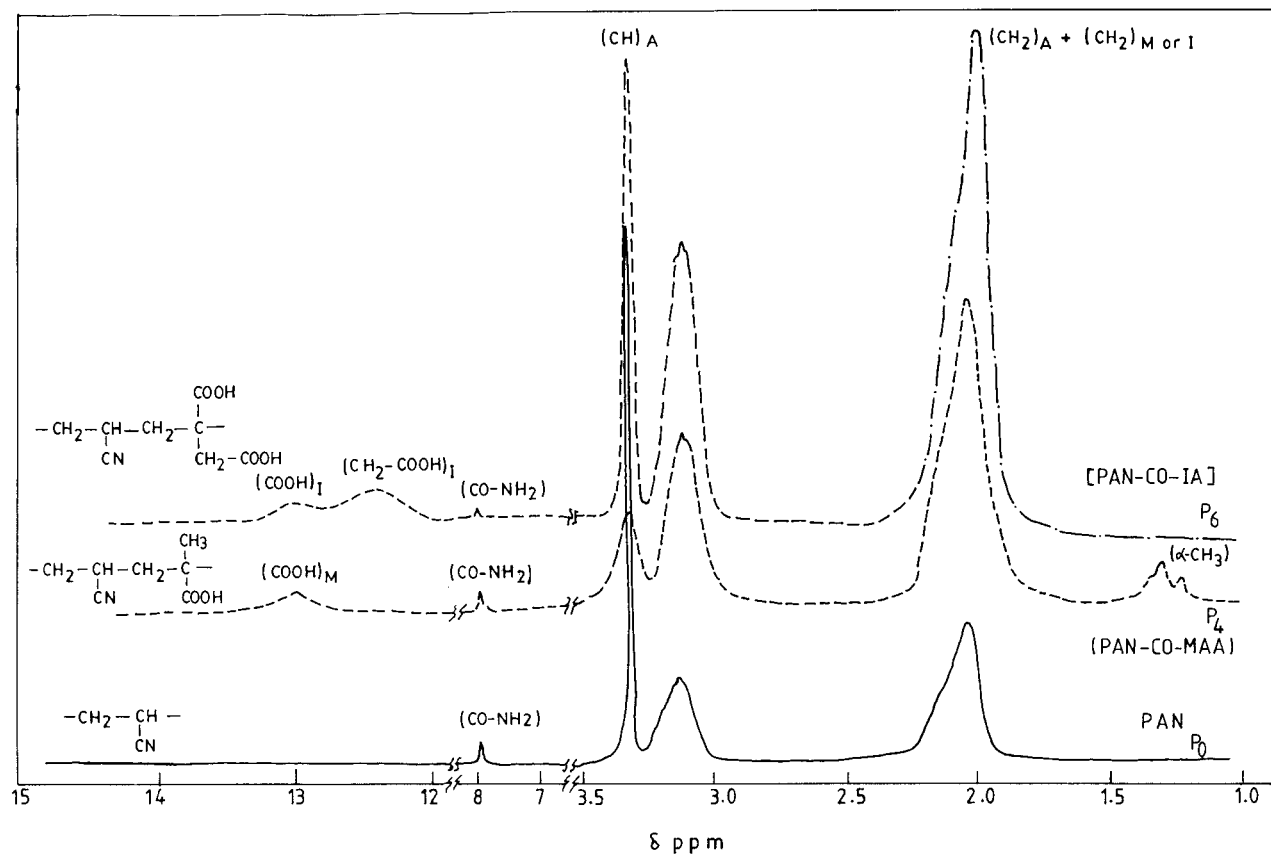
IA, has a 31% value (Table VI). The lower crystallinity of itaconic acid-containing copolymers may be due to its bulky side group, which may affect the crystal lattice formation. In addition, poly(AN-IA) copolymers showed a lower crystal size ($L_c = 28.7\text{\AA}$ for P_{10}) than P_9 , poly(AN-MAA) ($L_c = 47.22\text{\AA}$), confirming the broader crystal dis-

persion in case of IA-containing copolymers (Table VI). However, the d values agree well with the reported experimental values for PAN and its copolymers.²⁹

¹H- and ¹³C-NMR Studies

The proton NMR spectra of poly(AN-MAA) copolymers (P_1 - P_4 and P_9) show signals due to α -methyl (-CH₃), methylene (-CH₂), and carboxylic acid (-COOH_H) protons (Fig. 6), which are assigned at δ 1.2-1.4, 1.7-2.5, and 12.5-13.5 (broad) ppm, respectively. In the case of poly(AN-IA) copolymers (P_5 - P_8 and P_{10}), methylene (-CH₂) and carboxylic acid (-COOH_H) protons are assigned at 1.8-2.4 and 12.1-13.5 ppm, respectively. The latter (-COOH_H) signals shows two broad singlets corresponding to the two carboxylic acid groups of itaconic acid (-COOH and -CH₂-COOH) present in different magnetic environments.

In ¹³C-NMR spectra signals appear at 26-29, 32-35, 118-122, and 171-176 ppm because of methine, methylene, nitrile, and carbonyl carbon

**Figure 6** ¹H-NMR spectra of acrylonitrile homo- and copolymers.

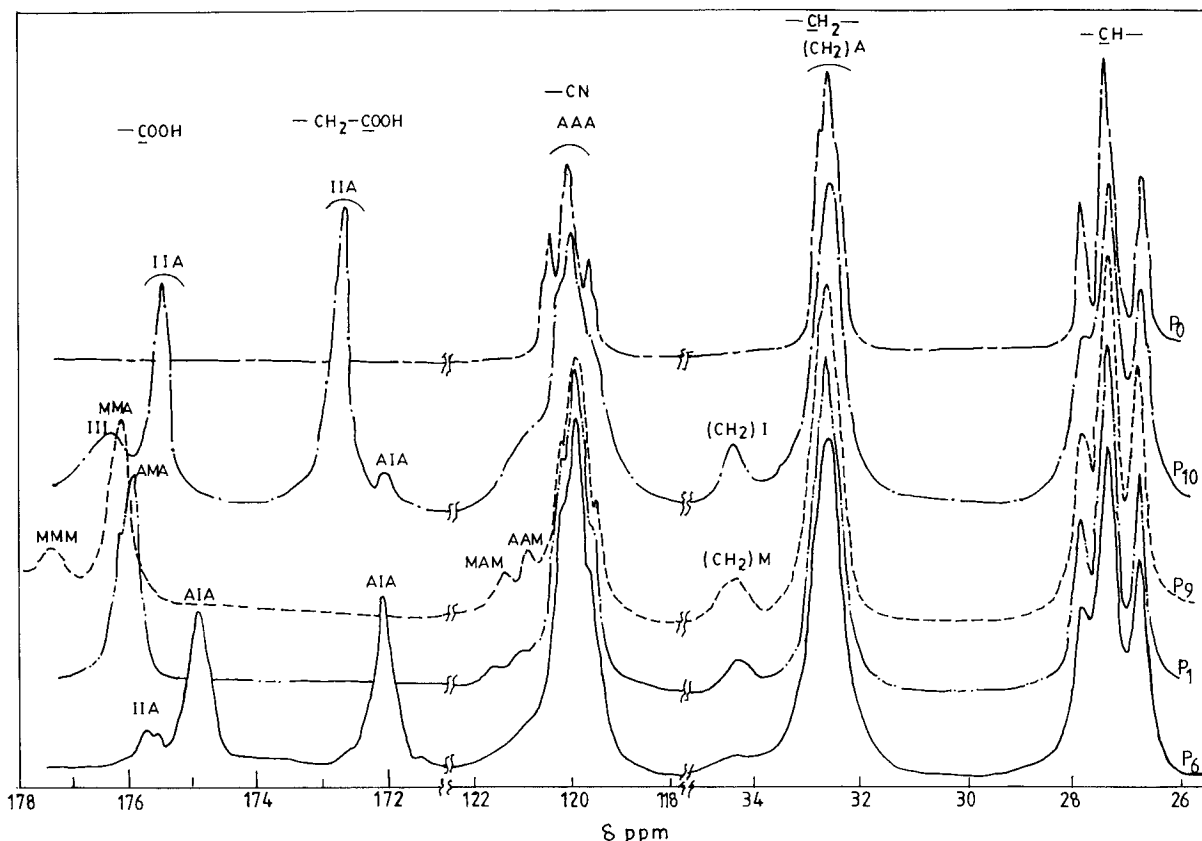


Figure 7 ^{13}C -NMR spectra of acrylonitrile homo- and copolymers.

resonance, respectively (Fig. 7). The methine, nitrile, and carbonyl signals are stereospecific and showed stereochemical splitting. The number-average sequence length values n_m (meso configuration) and n_r (racemic configuration) of $\text{C}\equiv\text{N}$ group tacticity were calculated using the equation given by Randell.³⁰ These values of the homo- and copolymers are around 2.0, which suggest random distribution of the nitrile group configuration.

CONCLUSIONS

- The average rate of polymerization at 60 min (R_{p60}) decreases with an increase in DMF concentration because of the high radical-solvent interaction and/or radical stability.
- The R_p of the AN-IA system is lower than that of the AN-MAA system, as the former has lower pH because of two carboxylic acid groups per molecule.
- The higher the DMF content in the reaction medium, the lower is the intrinsic viscosity of resulting copolymer. Polyelectrolyte behav-

ior can be observed for higher-molecular-weight acrylonitrile copolymers.

- Copolymers containing a higher amount of comonomers (≈ 10 mol %) undergo anhydride formation on heating, with water elimination from adjacent carboxyl groups.
- IA copolymers show two ^1H -NMR signals at the acid proton region, while MAA copolymers show only one. The splitting of signals confirms AN-MAA-MAA and AN-IA-IA triad sequences, which helps in the anhydride formation.
- The crystallinity and crystal size decrease with an increase in comonomer content. MAA copolymers are more crystalline compared to IA copolymers.

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