

Acrylonitrile–Acrylic Acids Copolymers.

I. Synthesis and Characterization

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SYNOPSIS

Acrylonitrile (AN) was copolymerized with acrylic acid (AA), methacrylic acid (MAA), and itaconic acid (IA) by the aqueous suspension method at 40°C with ammonium persulfate and sodium metabisulfite as the redox initiator. The reactivity ratios for the AN–AA and AN–IA systems were also calculated by the Finemann–Ross and the Kelen–Tüdös methods. Higher r_2 (AA) for the AN–AA system in comparison to r_2 (IA) for the AN–IA system indicates greater reactivity of AA toward the propagating species. The influence of comonomers on intrinsic viscosity, tacticity, and number-average sequence lengths was studied. ¹³C-NMR spectra revealed that AN copolymers having approximately 2 mol % of AA have a greater percentage (> 30%) of isotactic content than of homopolyacrylonitrile. Tacticity has also been calculated from infrared spectra of the polymers using stereospecific absorption bands at 1250 and 1230 cm⁻¹. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyacrylonitrile (PAN) is modified to improve its properties by incorporation of suitable comonomers¹ during polymerization. Modification of PAN by acidic comonomers increases its hydrophilicity² and helps in the cyclization of nitrile groups during heat treatment for thermal stabilization of acrylic fibres.^{3,4} Therefore, the incorporation of certain acidic comonomers is prevalent in the synthesis of the copolymers used for the manufacture of special acrylic fibres (SAF) and as precursors of carbon fibers.⁵ The copolymerization of acrylonitrile (AN) with some acidic comonomers, viz., acrylic acid and itaconic acid, along with a third monomer is reported in the patent literature.^{6,7} AN may be polymerized with a number of comonomers by various methods such as solution, emulsion, aqueous suspension, and solvent water suspension polymerization.⁵ Studies reported on the polymerization of PAN homopolymer include various aspects such as (i) the effect of the method of polymerization on properties of the

polymer⁸ and (ii) the effect of the various initiators.^{9–11} For aqueous suspension polymerization, three loci of polymerization have been reported by Peebles.¹² 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 is a monomer-poor phase. The distribution of comonomers between these two liquid phases would influence the course of polymerization. Initiation and some propagation would occur in the aqueous phase prior to the precipitation of the growing radical. The second locus of polymerization occurs at the particle–solution interphase known as the surface polymerization. The third loci of polymerization would be interior polymerization through buried free radicals, which is controlled by the diffusion of monomer to the active site. However, interior polymerization becomes less important as the polymerization temperature approaches 60°C and above.

Vijayendran¹³ further 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 latices produced by emulsion polymerization. According to the author, IA, being the most hydrophilic, remains in the aqueous phase, while

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MAA, being the most hydrophobic, becomes buried in the particle core. Mamazhanov et al.¹⁴ reported the synthesis of AN-MA-AA (or MAA) polymers and their spinning using a 12–20% sodium thiocyanate solution. Dependence of the cationic dye sorbed in the fiber on the AA or MAA content has been shown.

In the case of suspension polymerization initiated through redox initiators, the important reaction parameters are the (a) persulfate/bisulfite ratio, (b) water-to-monomer ratio, (c) reaction temperature, and (d) pH of the reaction medium. The reactivity ratios of the comonomers in these systems involving AN as a principal component have also been determined.^{9,15,16} The present work deals with a study of copolymerization of AN with the acidic comonomers AA, MAA, and IA in aqueous medium, using redox initiators. The tacticity is determined by ¹³C-NMR spectroscopy, whereas the compositions of the copolymers were ascertained by CHN and infrared spectroscopy.

EXPERIMENTAL

Materials

Acrylonitrile (AN) (BDH) was freed from inhibitor by washing with 0.1 *N* sodium hydroxide solution and then with water until completely freed from sodium hydroxide. The washed AN was kept over fused calcium chloride overnight and then distilled under nitrogen atmosphere at 77°C before use.

Acrylic acid (AA) and methacrylic acid (MAA) (Fluka) were purified by distilling under vacuum at 60°C/15 mm and 77°C/12 mm, respectively. Itaconic acid (IA) (Loba) (mp 166–167°C) and the initiators, viz., ammonium persulfate (BDH) and sodium metabisulfite (BDH), were used as received.

Polymerization

Copolymerization of AN with AAs was carried out in a four-neck flask using deionized water as a reaction medium, at 40°C under nitrogen atmosphere. The mol fraction of the comonomers in the reaction feed was varied from 0.004 to 0.037, and the water-to-monomer ratio was kept as 10. Ammonium persulfate and sodium metabisulfite (0.0576 and 0.0557 mol % with respect to monomer feed) were used as redox initiators. The pH of the reaction medium was adjusted to 3.5 by the addition of dilute sodium bicarbonate solution. The monomer mixture was

added slowly to the reaction mixture in 25–30 min and the polymerization was continued for 90 min (including the time required for the addition of the monomer mixture) with good agitation. The polymer was isolated by filtration, washed successively with water and methanol, and dried under vacuum at 50°C.

The similar polymerization conditions were used to determine the reactivity ratios of the AN-AA and AN-IA systems, but the mol fractions of the comonomers were varied from 0.020 to 0.1975, and the monomer mixture was added to the reaction medium in a single lot. The polymerization was terminated after 10 min by addition of ethylenediaminetetraacetic acid (EDTA).

Characterization

The polymers synthesized were characterized by intrinsic viscosity measurements made at 25 ± 0.5°C in *N*:*N*-dimethylformamide. The copolymer composition was determined from their nitrogen content, as estimated on the Perkin-Elmer 240C elemental analyzer.

IR spectra of the polymers were recorded on Nicolet 5-DX FTIR spectrophotometer. The transmission mode was used on finely powdered samples prepared as KBr pellet.

¹³C-NMR spectra of the polymers were recorded on a JEOL FX-100 NMR spectrophotometer operating at 25 MHz. The 8–10% (w/v) solution of the polymer in DMSO-*d*₆ at 60°C was used for this purpose.

RESULTS AND DISCUSSION

Reactivity of Comonomers

The comonomer contents in the monomer feed (M_2) and in the copolymers (m_2) are given in Table I. In the case of the AN-AA system, the incorporation of comonomer decreases with the increase in the mol fraction of the AA (M_2) in the monomer feed up to 0.12, and beyond this, it remains almost unchanged. Furthermore, in the AN-IA system, at a given feed ratio, the amount of IA incorporated into the copolymer is less compared to the AN-AA system, which decreases with increase in the M_2 value. This suggests that the copolymer composition changes with the change in the monomer feed.

The acidic comonomers under study, i.e., AA and IA, are weak acids, and, hence, their degree of dis-

Table I Suspension Copolymerization of AN with AA and IA

Batch No.	Comonomer Content in the Monomer Feed (Mol Fraction)	Comonomer Content in the Copolymer (Mol Fraction)	Nitrogen Content in the Copolymer (wt %)	Percentage Incorporation of Comonomer $m_2/M_2 \times 100$
	M_2	m_2		
AA				
A/1	0.037	0.1013	23.75	273.78
A/2	0.076	0.111	23.45	146.05
A/3	0.115	0.121	23.20	105.22
A/4	0.156	0.160	22.18	102.50
A/5	0.197	0.210	20.86	106.56
A/6	0.239	0.252	19.75	105.44
IA				
I/1	0.021	0.022	25.81	104.76
I/2	0.043	0.042	25.29	97.67
I/3	0.067	0.066	24.67	98.51
I/4	0.093	0.068	24.60	73.12
I/5	0.119	0.072	24.50	60.50
I/6	0.179	0.081	24.26	45.25

sociation (which leads to the formation of carboxylate ions $[\text{CH}_2=\text{C}(\text{R})\text{COO}^-]$ in aqueous medium largely depends upon their concentration. At lower concentration, i.e., at lower comonomer content in the feed, the degree of dissociation is high and decreases with increase in the concentration of the comonomer. This may be supported by the apparent

significant drop in the pH of the reaction medium (e.g., from 3.5 to ≈ 2.25 in the case of the AN-AA system) on the initial addition of the acidic comonomers (up to 0.02 mol fraction) and thereafter by a progressive slow decrease in the pH, which is also true for the other systems studied, i.e., AN-MAA and AN-IA. Thus, the increase in the co-

Table II Composition of AN-AA Copolymers

Polymer	Code	Comonomer in the Feed (mol %)	Yield (wt %)	Nitrogen Content (wt %)	Comonomer Content (mol %)		I.V. ^a (dL g)
					CHN	IR	
PAN	P	—	54.0	24.99	—	—	2.87
P(AN-co-AA)	PA1	0.99	69.0	24.74	0.99	1.06	2.32
P(AN-co-AA)	PA2	1.48	75.0	24.47	2.07	2.17	2.40
P(AN-co-AA)	PA3	2.22	81.0	24.32	2.65	2.93	2.61
P(AN-co-AA)	PA4	2.96	88.0	24.19	3.18	3.46	2.54
P(AN-co-AA)	PA5	3.70	93.0	24.15	3.35	3.66	2.70
P(AN-co-MAA)	PM1	0.62	65.0	24.74	0.97	1.08	3.07
P(AN-co-MAA)	PM2	1.24	72.0	24.59	1.52	1.41	3.11
P(AN-co-MAA)	PM3	1.86	77.5	24.46	2.10	2.25	3.16
P(AN-co-MAA)	PM4	2.48	82.0	24.25	2.95	2.99	3.36
P(AN-co-MAA)	PM5	3.10	88.0	24.00	3.95	3.57	3.44
P(AN-co-IA)	PI1	0.41	58.0	24.81	0.69	0.74	3.04
P(AN-co-IA)	PI2	0.82	63.0	24.67	1.27	1.37	2.84
P(AN-co-IA)	PI3	1.23	65.0	24.53	1.83	1.82	2.75
P(AN-co-IA)	PI4	1.64	68.0	24.45	2.15	2.04	2.65
P(AN-co-IA)	PI5	2.05	73.0	24.36	2.51	2.37	2.58

^a I.V.: intrinsic viscosity.

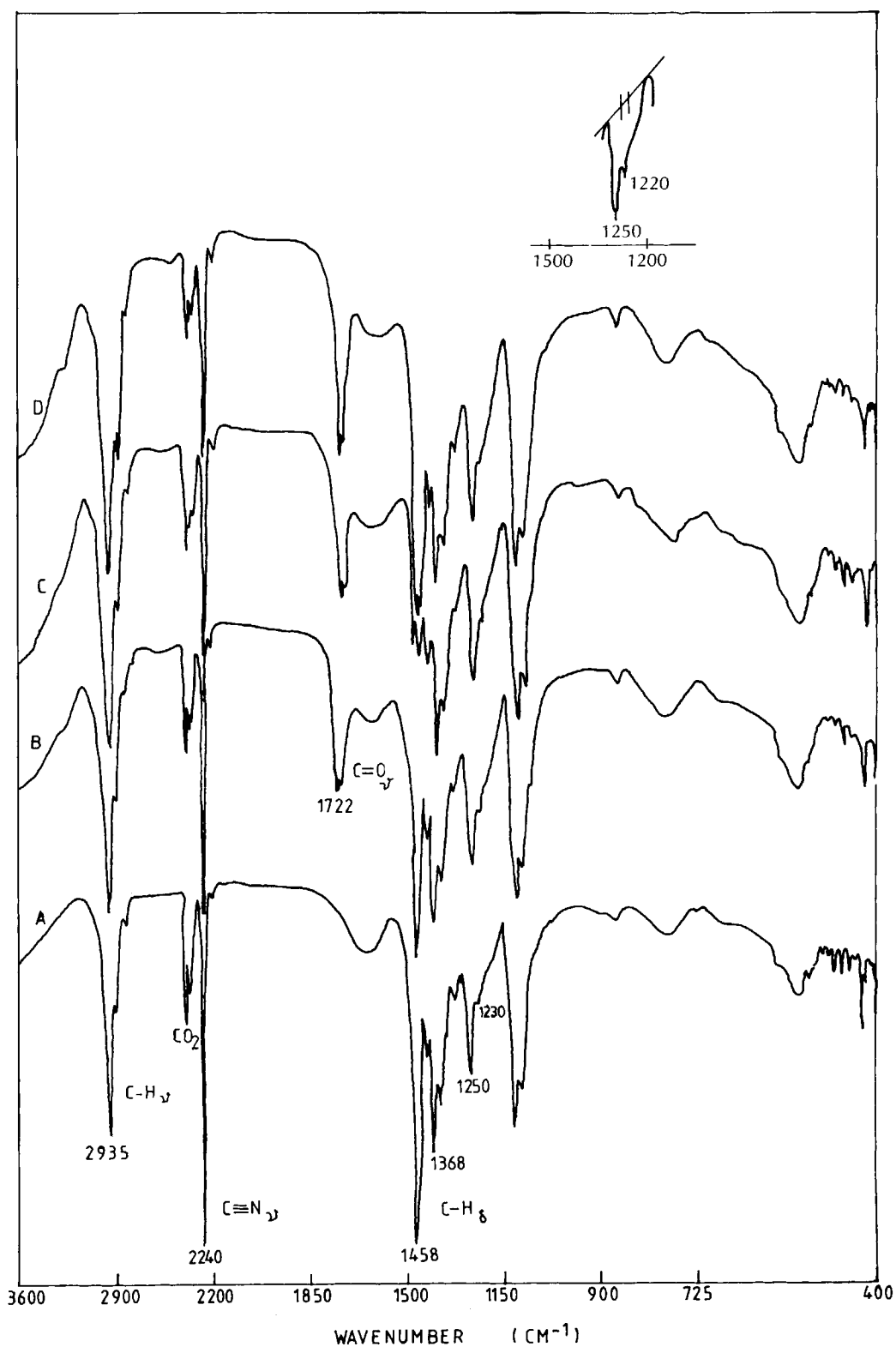


Figure 1 IR spectra of (A) polyacrylonitrile (PAN), (B) acrylonitrile-acrylic acid copolymer (PA1), (C) acrylonitrile-methacrylic acid (PM1), and (D) acrylonitrile-itaconic acid copolymer (PI1).

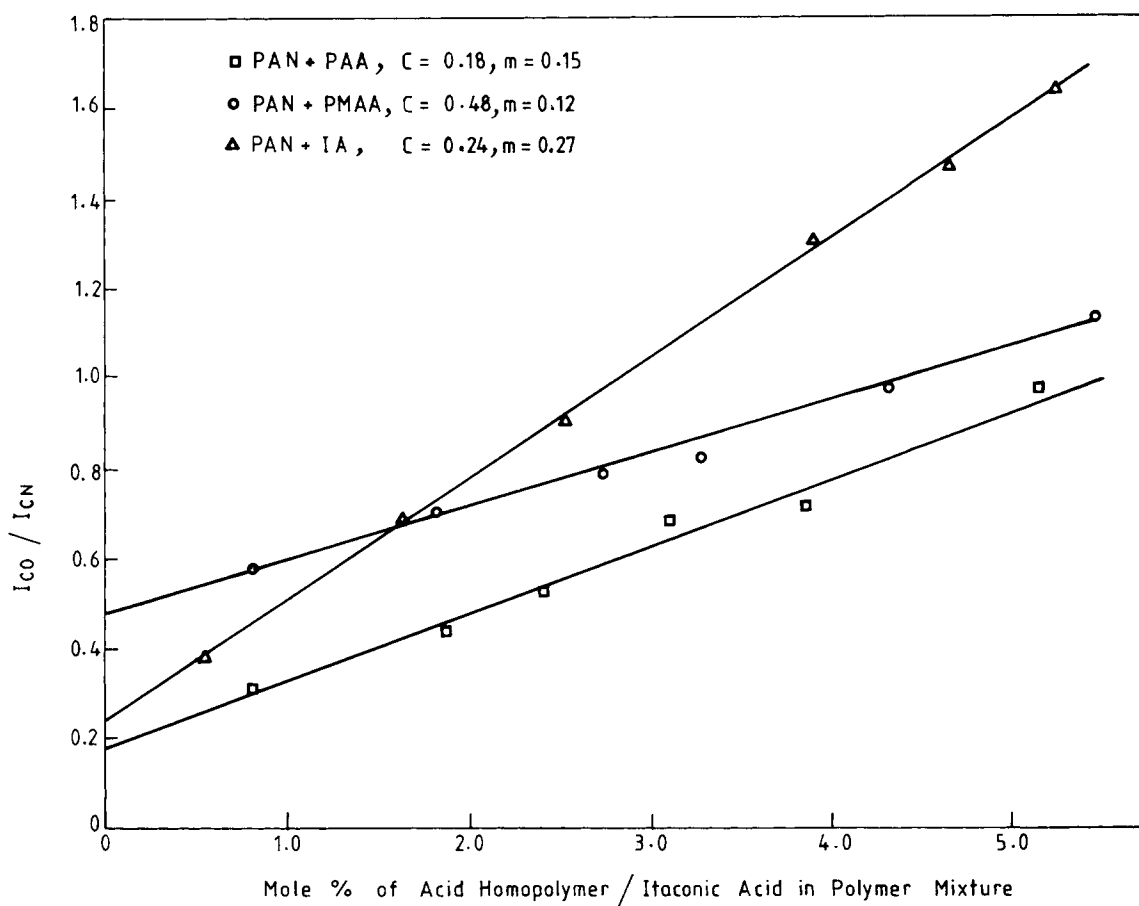


Figure 2 Contents of acid homopolymer/acid as a function of ratio of intensities of ν_{CO} to ν_{CN} , IR stretch bands.

monomer content may also cause a decrease in the concentration of carboxylate ions, which appear to be more reactive toward the reaction-initiating species R^* as well as to the radical of the growing polymer chain due to the electronic interactions such as resonance.¹⁷ This could be the possible reason for the decrease in the percentage incorporation of the comonomer with the increase in the comonomer content in the feed. Furthermore, IA is less reactive than is AA; the lower reactivity of the IA molecule may be attributed to its comparatively bulky size, which might pose hindrance in its approach to the radical end of the growing polymer chain.

The reactivity ratios of the monomers were determined by the Finemann-Ross¹⁹ and Kelen-Tüdös²⁰ method by using the data as shown in Table I. The values obtained are given below:

Finemann-Ross method:

$$r_1(\text{AN}) = 0.27 \quad \text{and} \quad r_2(\text{AA}) = 3.07$$

$$r_1(\text{AN}) = 0.87 \quad \text{and} \quad r_2(\text{IA}) = 2.52$$

Kelen-Tüdös method:

$$r_1(\text{AN}) = 0.34 \quad \text{and} \quad r_2(\text{AA}) = 3.25$$

$$r_1(\text{AN}) = 0.84 \quad \text{and} \quad r_2(\text{IA}) = 6.73$$

The values of reactivity ratios for AN (r_1) are less than unity in both the systems, which implies that the growing radical AN prefers to combine with the comonomer unit. On the other hand, the reactivity ratio for the comonomer (r_2) is greater than unity in both the systems, thereby suggesting that the growing comonomer radical $\sim\text{AA}^*$ or $\sim\text{IA}^*$ has greater affinity toward its own monomer unit. Hence, both the growing radicals, i.e., $\sim\text{AN}^*$ as well as $\sim\text{AA}^*$ and $\sim\text{IA}^*$ have preference for acidic monomer. Furthermore, the value of relative reactivity of AN ($1/r_1 = 3.70$) is higher for the AN-AA system than for the AN-IA system (1.5), which indicates that the growing AN radical has a higher reactivity toward AA as compared to IA.

As shown in Table II, the yield of the copolymers synthesized under the identical experimental con-

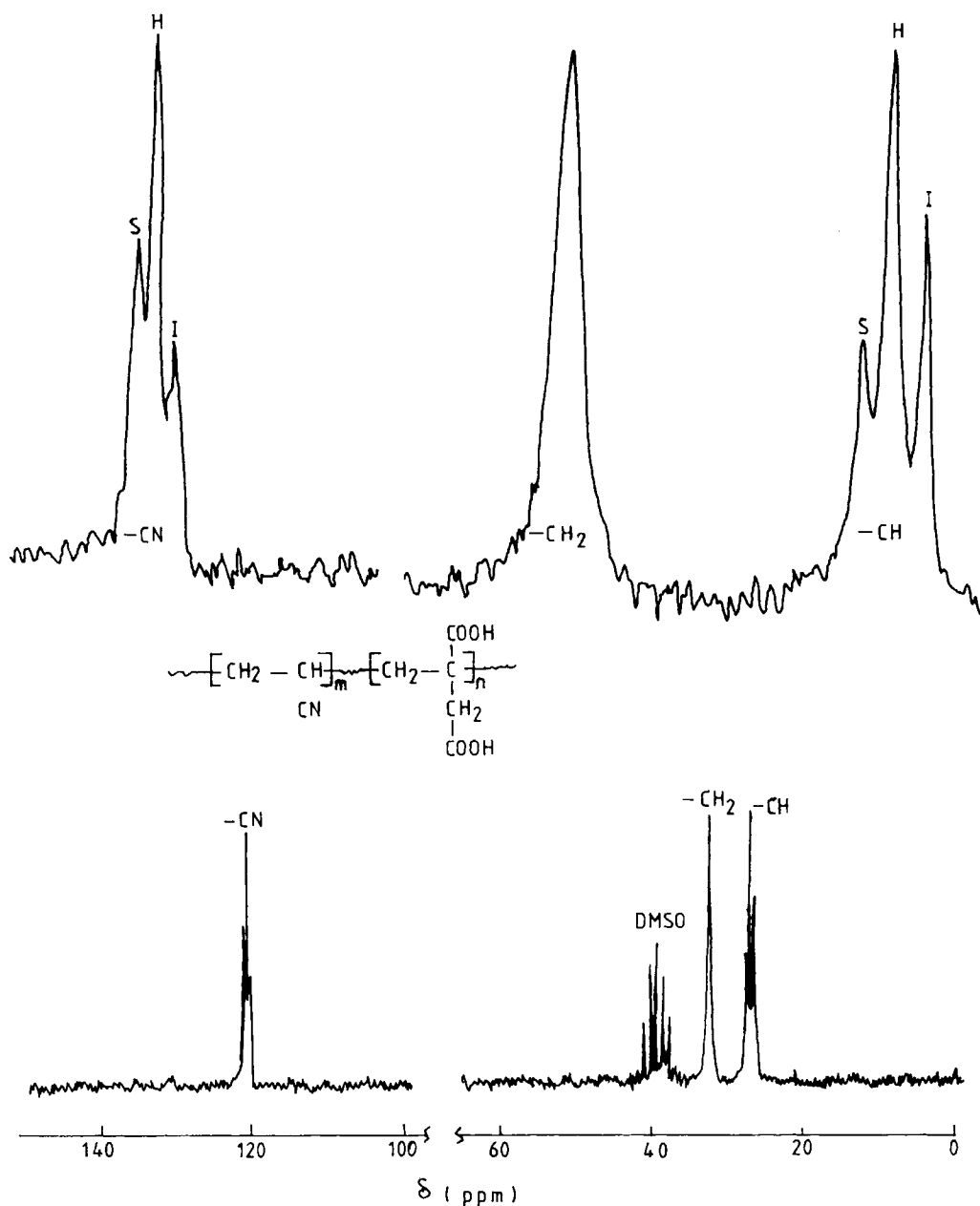


Figure 3 25 MHz ^{13}C -NMR spectra of (A) polyacrylonitrile (PAN) and (B) acrylonitrile-itaconic acid copolymer (PI4) recorded in $\text{DMSO-}d_6$ at 60°C .

ditions increased on increasing the mol fraction of acidic comonomer in the feed from 0.005 to 0.037. This shows that the comonomers enhance the overall rate of polymerization in the following order:



Thus, as compared to the PAN homopolymer, the incorporation of any of these three acidic comonomers enhances the rate of polymerization. This increase in the extent of polymerization in the pres-

ence of acidic comonomers may be attributed to the role of the comonomer in the initiation step of the reaction, which is generally known to occur in the aqueous phase if inorganic compounds are used as initiators. However, with an increasing number of polymer particles, polymerization in the aqueous phase becomes less important¹⁸ and seems to occur at the surface of the oligomer or polymer particles. The free radical generated as a result of the combination of comonomer with reaction-initiating species R^{\cdot} is more stable as compared to that formed

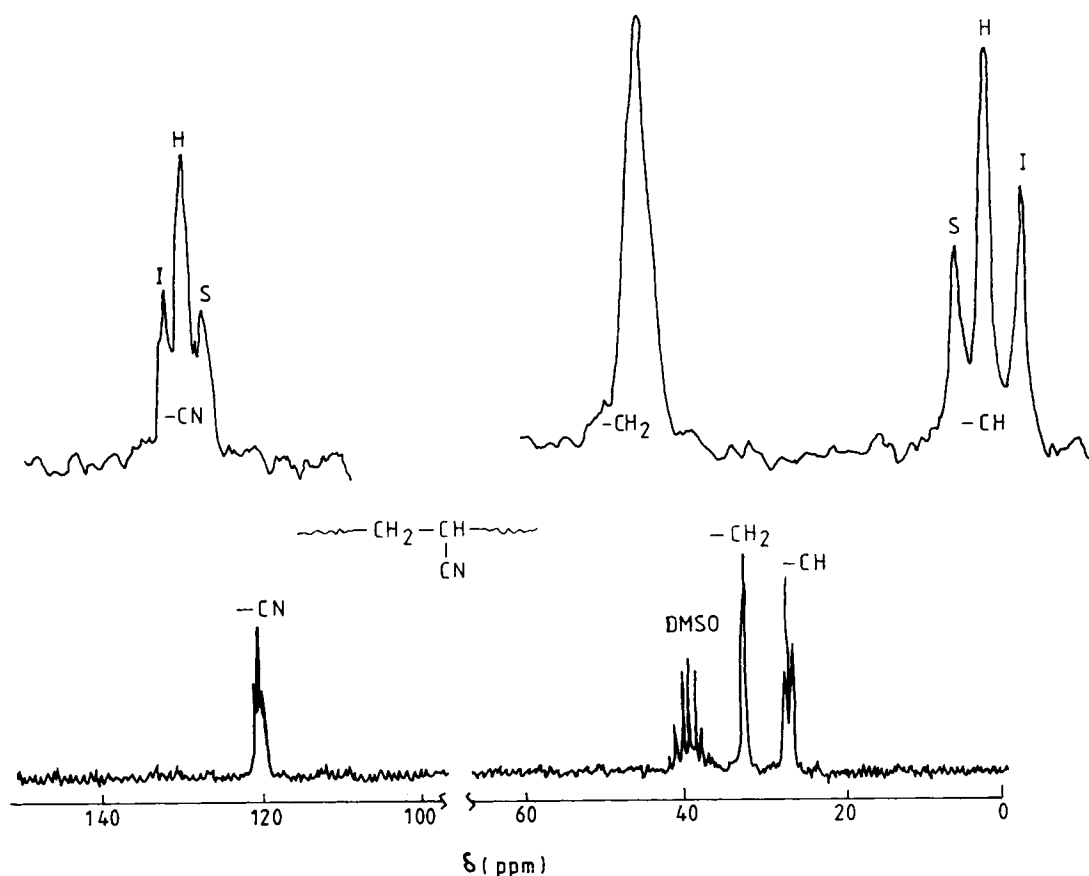


Figure 3 (Continued from the previous page)

with combination with AN. Hence, initiation through the comonomer gives an enhanced rate of polymerization, which accounts for the greater yield of these copolymers than that of the homopolymer. Furthermore, as seen from the values of the reactivity ratios (stated above), the activation energy of the reaction would be smaller when the initiating species R^* involves the acidic comonomer units. This lowering of activation energy would account for the faster rate of polymerization in the presence of the comonomers. In addition to this, the preferential initiation through comonomers, i.e., AA, MAA, and IA, is probably due to their higher solubility as compared to AN in the reaction medium, i.e., water, which also contains the reaction-initiating species, i.e., R^* (SO_4^+ and SO_3^+ in case of persulfate/bisulfite system). Therefore, the comonomer has a better chance to combine with the reaction-initiating species (R^*) and to initiate the reaction. Pichot et al.¹⁶ also made similar observations in their study on the emulsion polymerization of AN with MAA and confirmed that the higher rate of polymerization in the presence of MAA was due to the preferential initiation involving the MAA molecule.

Intrinsic Viscosity

The values of intrinsic viscosity for P(AN-MAA) copolymers (3.07–3.44) irrespective of their composition are higher than that for the PAN homopolymer (2.87 dL g⁻¹), whereas the intrinsic viscosities of P(AN-AA) and P(AN-IA) copolymers are lower than that of PAN. The P(AN-AA) and P(AN-MAA) copolymers exhibited an increasing trend in their intrinsic viscosities with increase in the comonomer content from 0.01 to 0.04 mol fraction, whereas it is just the opposite for P(AN-IA) copolymers (Table II). The increase in the values of intrinsic viscosity with the increase of comonomer content in the case of the P(AN-AA) and P(AN-MAA) copolymers may be explained on the basis of the increase in the hydrodynamic volume, which influences the intrinsic viscosity. The addition of the comonomer to the polymer chain may increase the molecular dimensions by decreasing the freedom of rotation around the comonomer units in the molecular chain, and, thus, the hydrodynamic volume increases, which leads to the increase in the values of intrinsic viscosity. However, the hydrodynamic vol-

ume of P(AN-AA) and P(AN-IA) copolymers should be more as compared to that of PAN, but, as stated above, their intrinsic viscosities are lower than the $[\eta]$ intrinsic viscosity of PAN, i.e., 2.87 dL g⁻¹. This is probably due to the decrease in their degree of polymerization (DP), i.e., the molecular weight. This suggests that the incorporation of AA and IA comonomers causes the decrease in the DP of the polymer. However, the hydrodynamic volume of P(AN-AA) as well as of P(AN-IA) copolymers should increase on increasing the comonomer content and, therefore, the intrinsic viscosity, but the intrinsic viscosity of P(AN-IA) copolymers showed a decreasing trend.

FTIR Studies

The comparison of IR spectra of PAN with its copolymers is shown in Figure 1. The broad band in the range 3100–2700 cm⁻¹ with its maximum at 2935 cm⁻¹ is assigned to C—H stretching in CH, CH₂, and CH₃.²¹ The position of the C≡N absorption band at 2240 cm⁻¹ remains unchanged in all the copolymers, indicating the presence of uninterrupted long sequences of AN units in all the copolymers.²² A shoulderlike appearance at 2190 cm⁻¹ near the characteristic absorption for C≡N (at 2240 cm⁻¹) may be attributed to the stretching vibration of C=NH (Ref. 23) formed during polymerization.²⁴

The bands in the regions 1460–1440, 1370–1350, and 1270–1220 cm⁻¹ were assigned to the C—H vibrations of different modes.²³ Minagawa et al.²⁵ reported that the absorption bands at 1250 and 1230 cm⁻¹ are stereospecific and appear due to the wagging mode of the methine (CH) group coupled with rocking mode of the (CH₂) methylene group.

The strong band in the range of 1730–1720 cm⁻¹ is present in the copolymers due to the C=O stretching.²⁶ For determining the composition of these copolymers through the IR spectra,²⁷ the mechanical mixtures of PAN (homopolymer) and homopolymers of AA and MAA were prepared. The IR spectra of these mixtures were recorded to make the calibration plot (Fig. 2). Since the homopolymerization of IA is difficult,²⁸ the IR spectra of mechanical mixtures of PAN and IA were used for calibration purposes. The ratio of the intensity of the C=O stretching band at 1730–1720 cm⁻¹ to the C≡N stretching band at 2240 cm⁻¹ [I_{CO}/I_{CN}] was plotted against the contents of polyacrylic acid (PAA)/polymethacrylic acid (PMAA)/itaconic

acid (IA) in the mixture (Fig. 2) and a linear relationship was obtained, which can be expressed in mathematical form as below by using the straight-line equation, $Y = MX + C$:

$$Y = 0.18 + 0.15X \text{ (for mixtures containing PAA)}$$

$$Y = 0.48 + 0.12X \text{ (for mixtures containing PMAA)}$$

$$Y = 0.24 + 0.27X \text{ (for mixtures containing IA)}$$

where Y is the ratio of the intensity of the C=O stretching to the C≡N stretching band and X is the contents (in mol %) of PAA/PMAA/IA. The values of Y obtained from the IR spectra of the copolymers were put in the above equation to estimate the comonomer content in the copolymers. These results were found in to be in good agreement with those obtained through nitrogen analysis (Table II).

NMR Studies

The ¹³C-NMR spectra of PAN and P(AN-IA) copolymer are shown in Figure 3. The signals due to methine, methylene, and nitrile carbon appeared at 27.221, 32.82, and 119.65 ppm. The methine and nitrile signals are stereospecific and showed stereochemical splitting,^{29,30} which is quite clear in the expanded spectra. In the nitrile carbon signal, the peaks due to iso-, hetero-, and syndiotactic triads appear from higher to lower field, respectively, whereas in the methine carbon signal, these peaks appear from lower to higher magnetic field, and a similar observation has also been made by Minagawa et al.²⁵ The tacticity values and configurational sequence lengths (Table III) for these copolymers were calculated as described elsewhere³¹ from the relative intensities of the respective peaks of methine and nitrile carbon resonance splitting, as obtained from the computer data. The PAN homopolymer as well as the AN copolymers showed that the nm and nr values are around 2.0, which suggests that they have a random distribution of the nitrile group configuration.²⁹

The isotacticity of the copolymers, calculated on the basis of nitrile and methine signals, differs marginally (Table IV) from each other due to triad sensitivity.²⁹ The isotacticity of these copolymers was also determined from the intensity of the IR bands at 1250 and 1230 cm⁻¹ for the homopolymer. The isotacticity of the homopolymer calculated from the

**Table III Triad Tacticity of PAN and AN Copolymers with AA, MAA, and IA
(on the Basis of the —CH Signal)**

Polymer Code	Composition Comonomer Contents (mol %)	Chemical Shift δ Scale	Assignment	Tacticity (%)	$n0$, nm , and nr Values
P	—	27.71	<i>mm</i> (iso)	30.57	$n0$ 2.23
		27.22	<i>mr/rm</i>	45.19	nm 2.36
		26.68	<i>rr</i>	22.23	nr 1.98
PA1	1.06	27.76	<i>mm</i> (iso)	27.69	$n0$ 2.02
		27.27	<i>mr/rm</i>	45.59	nm 2.21
		26.73	<i>rr</i>	26.70	nr 2.16
PA2	2.17	27.75	<i>mm</i> (iso)	30.49	$n0$ 2.14
		27.27	<i>mr/rm</i>	45.62	nm 2.34
		26.73	<i>rr</i>	23.88	nr 2.05
PA3	2.93	27.71	<i>mm</i> (iso)	26.39	$n0$ 2.00
		27.22	<i>mr/rm</i>	47.36	nm 2.11
		26.68	<i>rr</i>	26.24	nr 2.11
PA4	3.46	27.71	<i>mm</i> (iso)	22.57	$n0$ 1.92
		27.27	<i>mr/rm</i>	50.75	nm 1.89
		26.78	<i>rr</i>	26.68	nr 2.05
PA5	3.66	27.56	<i>mm</i> (iso)	22.42	$n0$ 2.02
		27.12	<i>mr/rm</i>	48.04	nm 1.94
		26.54	<i>rr</i>	25.43	nr 2.06
PM1	1.08	27.85	<i>mm</i> (iso)	26.21	$n0$ 1.96
		27.37	<i>mr/rm</i>	45.73	nm 2.15
		26.78	<i>rr</i>	28.05	nr 2.23
PM2	1.41	27.80	<i>mm</i> (iso)	26.76	$n0$ 1.99
		27.31	<i>mr/rm</i>	46.24	nm 2.16
		26.73	<i>rr</i>	26.99	nr 2.17
PM3	2.25	27.61	<i>mm</i> (iso)	30.68	$n0$ 2.23
		27.12	<i>mr/rm</i>	48.89	nm 2.26
		26.54	<i>rr</i>	20.41	nr 1.84
PM4	2.99	27.56	<i>mm</i> (iso)	28.45	$n0$ 2.14
		27.10	<i>mr/rm</i>	49.44	nm 2.15
		26.53	<i>rr</i>	22.10	nr 1.89
PM5	3.57	27.76	<i>mm</i> (iso)	26.36	$n0$ 2.11
		27.27	<i>mr/rm</i>	46.42	nm 2.14
		26.73	<i>rr</i>	24.21	nr 2.04
PI1	0.74	27.71	<i>mm</i> (iso)	27.76	$n0$ 2.08
		27.22	<i>mr/rm</i>	48.14	nm 2.15
		26.68	<i>rr</i>	24.10	nr 2.00
PI2	1.37	27.71	<i>mm</i> (iso)	30.64	$n0$ 2.18
		27.22	<i>mr/rm</i>	46.92	nm 2.31
		26.68	<i>rr</i>	22.43	nr 1.96
PI3	1.82	27.71	<i>mm</i> (iso)	32.59	$n0$ 2.28
		27.22	<i>mr/rm</i>	47.13	nm 2.38
		26.68	<i>rr</i>	20.28	nr 1.86
PI4	2.04	27.66	<i>mm</i> (iso)	32.17	$n0$ 2.22
		27.22	<i>mr/rm</i>	45.56	nm 2.41
		26.68	<i>rr</i>	22.26	nr 1.98
PI5	2.37	27.61	<i>mm</i> (iso)	28.01	$n0$ 2.07
		27.17	<i>mr/rm</i>	47.54	nm 2.18
		26.64	<i>rr</i>	24.45	nr 2.03

Table IV Percentage Tacticity of PAN and AN Copolymers with AAs

Polymer Code	Composition Comonomer Content (mol %)	Percentage Isotacticity of ¹³ C NMR Spectra		
		—CH Signal	—CN Signal	IR
P	—	30.57	28.20	27.64
PA1	1.06	27.69	25.09	39.21
PA2	2.17	30.49	29.80	44.00
PA3	2.93	26.39	28.66	47.90
PA4	3.46	22.57	25.07	50.37
PA5	3.66	22.42	25.52	54.10
PM1	1.08	26.21	28.10	32.81
PM2	1.41	26.76	28.61	39.56
PM3	2.25	30.68	31.79	44.66
PM4	2.99	28.45	30.69	49.21
PM5	3.57	26.36	28.19	51.09
PI1	0.74	27.76	30.14	34.50
PI2	1.37	30.64	30.16	45.05
PI3	1.82	32.59	31.41	47.05
PI4	2.04	32.17	30.43	51.22
PI5	2.37	28.01	28.45	58.41

IR spectra is in close agreement (Table IV) with that calculated from the NMR spectra. However, the isotacticity values of copolymers calculated by these two methods differ considerably and the difference is greater in copolymers having a higher comonomer content. This implies that the Minagawa method²⁵ holds good only for homopolymer and is not suitable for its application to copolymers as comonomers would influence the tacticity of neighboring AN units. In other words, C—H vibrations in comonomer molecules may influence the characteristics of IR absorption bands at 1250 and 1230 cm⁻¹, used for calculating the tacticity of CN groups.

The isotacticity increases initially in the copolymers with increase in the comonomer content and then it decreases (Table IV). Furthermore, the copolymers having about 2 mol % of carboxylic acid comonomers showed maximum isotacticity (above 30%). The copolymers P(AN-AA), P(AN-MAA), and P(AN-IA) having 2.17, 2.25, and 1.82 mol % of the AA, MAA, and IA, respectively, showed more than 30% isotacticity. The observed difference in the tacticity of homopolymers and copolymers may be attributed to the influence of comonomer units on certain interactions such as those of the monomer-reaction medium, radical-reaction medium, and, besides these two, the monomer-radical (monomer-radical of the growing chain), which affect the transition state in the propagation step.

These interactions are reported to alter the stereoregularity³² as well as the rate of the polymerization reaction.^{22,33}

CONCLUSIONS

In aqueous suspension polymerization, the incorporation of the acidic comonomers into the copolymer depends upon the comonomer content in the feed. The comonomers AA and IA have higher values for the reactivity ratios as compared to AN, which suggests that these comonomers are preferred over AN by the growing radical of the polymer chain. Furthermore, in the systems studied, the initiation of the polymerization is preferred through the comonomers. The IR absorption band at ≈ 2190 cm⁻¹ is assigned to the C=NH structure formed during polymerization due to the intramolecular cyclization. The IR spectra have been used to find out the tacticity of the homopolymer; however, this method does not hold good for the copolymers. The copolymers having ≈ 2 mol % of comonomer appear to have higher isotacticity as calculated from methine group signals in the ¹³C-NMR spectra.

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