

# Structural Investigations of Acrylonitrile–Vinyl Acid Copolymers by NMR Spectroscopy

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**ABSTRACT:** <sup>1</sup>H, <sup>13</sup>C [<sup>1</sup>H]-, and 2D HETCOR NMR spectroscopy have been employed to characterize polyacrylonitrile (PAN) homopolymer and copolymers of methacrylic acid (MAA) and itaconic acid (IA) prepared by solvent–water suspension polymerization technique in a mixture containing DMF (solvent) and water. The chemical composition of P(AN–MAA) copolymers was determined using <sup>1</sup>H-NMR and that of P(AN–IA) using quantitative <sup>13</sup>C[<sup>1</sup>H]-NMR spectra. P(AN–IA) copolymers show two separate signals due to two carboxylic groups in different magnetic environments of IA, whereas P(AN–MAA) shows only one in the region of  $\delta$  6.32–7.60 ppm in <sup>1</sup>H-NMR and  $\delta$  171.0–176.0 ppm in <sup>13</sup>C[<sup>1</sup>H]-NMR spectra. Evidence of acrylamide formation by the partial hydrolysis of AN groups is obtained by the small broad signal at  $\delta$  7.9 ppm in <sup>1</sup>H-NMR spectra. No carboxylic proton signal was observed in copolymers

containing 12 mol % of comonomer, which indicates the formation of anhydride. The microstructure was obtained in terms of the A- and M-centered triad sequences from <sup>13</sup>C[<sup>1</sup>H]- and <sup>1</sup>H-NMR spectra of the copolymers, which showed configurational and compositional sequences. For example, at higher comonomer content, the concentration of AAM and AAI sequencing increases. This is confirmed by 2D HETCOR NMR spectra also. The distribution of AN sequences is found to be random ( $n_o \sim n_m \approx 2.0$ ). The tacticity values are not affected by the comonomer content. The isotacticity remained almost same at 27% (mm, 26.5–29.3) in all acrylonitrile polymers irrespective of the nature of the comonomer and polymerization medium, that is, DMF/H<sub>2</sub>O ratio. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1211–1217, 2003

## INTRODUCTION

Among various polymerization methods, solution polymerization and solvent–water suspension polymerization are the most common techniques used for the synthesis of polymers for acrylic fibers.<sup>1</sup> Solution polymerization in dimethyl formamide (DMF) yields a low molecular weight polymer<sup>2,3</sup> (intrinsic viscosity  $[\eta] = 1\text{--}1.25 \text{ dL g}^{-1}$ ) due to the high chain transfer coefficient of DMF ( $2.8 \times 10^{-4}$  at 50°C). Polymers produced by aqueous suspension technique, although of sufficiently high molecular weight, show defects in the form of branching and enamionitrile formation as reported by Minagawa.<sup>4</sup> Solvent–water suspension polymerization in which the reaction medium is a mixture of solvent, such as DMF, and water is a good compromise between the molecular weight and molecular defects because water has a near-zero chain transfer coefficient.

NMR spectroscopy in solution has been used as a powerful experimental tool to determine the inter and

intramolecular chain structures such as sequence length distribution, tacticity, chemical composition, and molar mass distribution. Using <sup>13</sup>C[<sup>1</sup>H]-NMR spectroscopy, Bajaj et al.<sup>5</sup> found that poly(acrylonitrile) (PAN) prepared in water medium has a greater percentage (33.4%) of isotactic units than that prepared in water–acetone medium (28.3%). Prasad et al.<sup>6</sup> studied the effect of comonomers on the structure of polyacrylonitrile in radical polymerization. They concluded that the introduction of second and third comonomer hardly affected the steric configuration of PAN segments. Bajaj et al.<sup>7,8</sup> have also characterized the hydrolyzed acrylonitrile terpolymers and saponified products of acrylonitrile terpolymers by NMR spectroscopy. Minagawa et al.<sup>9</sup> showed that the tacticity of low molecular weight PAN polymers prepared by canal polymerization is higher compared to high molecular weight polymers, that is, for  $[\eta]$  of 2.67 dL g<sup>-1</sup>, isotacticity is 65% as against 48% for a polymer having intrinsic viscosity of 4.96 dl g<sup>-1</sup>.

Brar et al.<sup>10,11</sup> studied the compositional and configurational sequencing and glass-transition temperature of acrylonitrile copolymers by NMR spectroscopy. Brar et al.,<sup>12</sup> in another study of photo-polymerized acrylonitrile–methacrylic acid (AN–MAA) copolymers, also reported their structure and reactivity ratios using <sup>1</sup>H, <sup>13</sup>C[<sup>1</sup>H], and 2D TOCSY spectra.

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Brar and Hekmatyar,<sup>13</sup> using <sup>1</sup>H- and <sup>13</sup>C[<sup>1</sup>H]-NMR spectroscopy, determined microstructure of acrylonitrile terpolymers containing styrene and methacrylate. The sequence length distribution of the acrylonitrile-, styrene-, and methyl methacrylate-centered triads determined by <sup>13</sup>C[<sup>1</sup>H]-NMR were found in good agreement with the triad sequence calculated by statistical method. Prasad et al.<sup>6</sup> also studied the structural characterization of terpolymers containing acrylonitrile, methylacrylate and itaconic acid (IA). The well-resolved signal at  $\delta$  9.63 ppm in <sup>1</sup>H-NMR spectrum was assigned to the carboxyl proton of itaconic acid. Other authors<sup>12,14</sup> in their studies on acrylonitrile-vinyl acid copolymer systems did not mention the carboxyl proton signal in <sup>1</sup>H-NMR. However, the carboxyl carbon signal has been observed in <sup>13</sup>C[<sup>1</sup>H]-NMR spectra.

The determination of chemical composition and microstructure (tacticity and comonomer sequencing) in PAN-based polymers is essential particularly for acrylonitrile fibers used as precursors for the production of carbon fibers. The present study is an attempt to analyze and quantify the effect of comonomers and reaction medium on the composition and microstructure of acrylonitrile-vinyl acid copolymers synthesized by solvent-water suspension polymerized using NMR spectroscopy.

## EXPERIMENTAL

Acrylonitrile copolymers of methacrylic acid (MAA) and itaconic acid were prepared by solvent-water suspension polymerization using different DMF-water mixtures (varying from 80:20 to 20:80 w/w). The intrinsic viscosity of the polymers ranges from 0.69 to 2.9 dL g<sup>-1</sup>. Other details of the synthesis of PAN, P(AN-MAA), and P(AN-IA) have been reported elsewhere.<sup>15</sup>

All the 1D and 2D NMR spectra were recorded in DMSO-d<sub>6</sub> at 80°C. The <sup>1</sup>H- and <sup>13</sup>C[<sup>1</sup>H]-NMR spectra of the copolymers were recorded on a Bruker DPX-300 spectrometer operating at 300.13 and 75.5 MHz, respectively. 2D HETCOR spectrum was also recorded in DMSO-d<sub>6</sub> at 80°C using the standard pulse sequence. A total of 32 scans were accumulated with a relaxation delay of 2 s for each of the 512 *t*<sub>1</sub> experiments.

The copolymer composition was determined by <sup>1</sup>H NMR spectra for P(AN-MAA) using methylene (—CH<sub>2</sub>) proton signals of AN and methyl (—CH<sub>3</sub>) proton signals of MAA and by quantitative <sup>13</sup>C [<sup>1</sup>H]-NMR spectra for P(AN-IA) using —CN carbon signals of AN and —COOH carbon signals of IA, respectively.

## RESULTS AND DISCUSSION

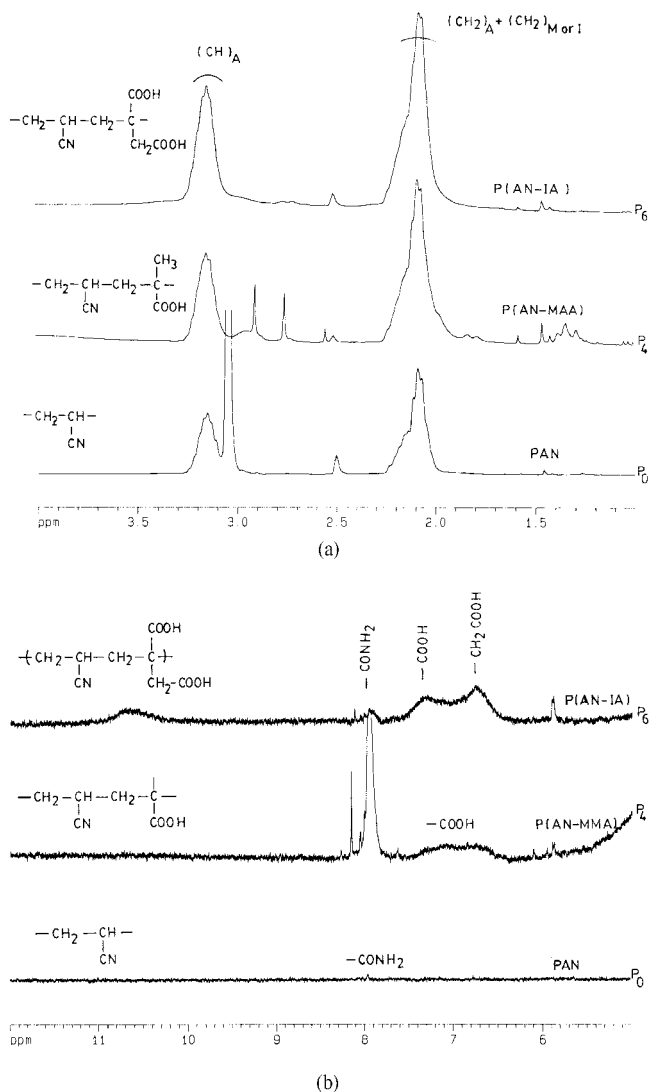
### Chemical composition

The chemical composition of P(AN-MAA) copolymers was determined by measuring the intensity of the signals at  $\delta$  1.2–1.5 ppm due to  $\alpha$ -CH<sub>3</sub> group of methacrylic acid and at  $\delta$  1.7–2.3 ppm due to —CH<sub>2</sub> groups of both AN and MAA (Fig. 1). The comonomer content was calculated using the following equation:

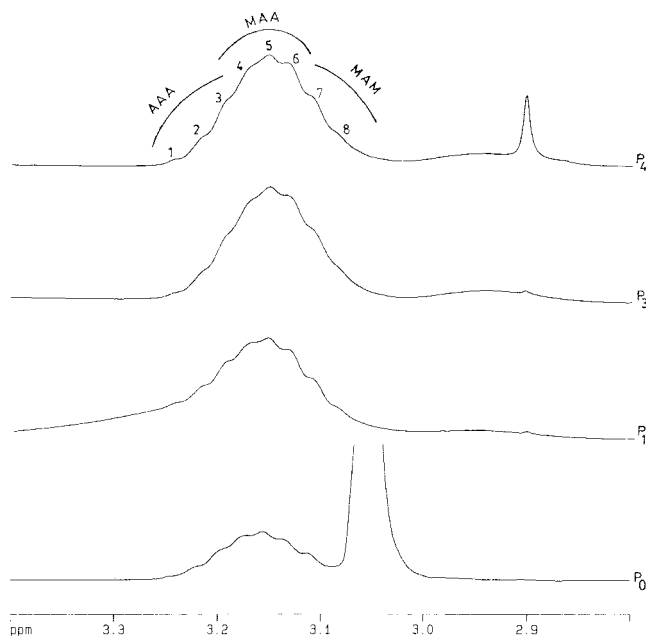
$$\% \text{ MAA} = \frac{I[(\text{CH}_3/3) \times 2]}{I[\text{CH}_2(\text{AN}) + \text{CH}_2(\text{MAA})]} \times 100$$

where  $I[(\text{CH}_3/3) \times 2] = I[\text{CH}_2]$  of MAA.

There is no methyl group in P(AN-IA) copolymers. Also, as it has been found that carboxylic—OH proton



**Figure 1** 300 MHz <sup>1</sup>H-NMR spectra of AN homo- and copolymers in DMSO-d<sub>6</sub> at 80°C: (a) expanded methine, methylene and methyl region; (b) expanded nitrile and carboxyl region.



**Figure 2** 300 MHz  $^1\text{H-NMR}$  spectra of methine region of P(AN-MAA) copolymers with different mol % in copolymer in DMSO- $d_6$  at  $80^\circ\text{C}$ .

signal could not be compared with the methylene-CH signals, proton NMR could not be used in determining the chemical composition of P(AN-IA) copolymers. So, in this case, quantitative  $^{13}\text{C}[^1\text{H}]$ -NMR was used to calculate the comonomer content in copolymers, making use of the intensities of carbon signals at  $\delta$  171.0–176.0 ppm due to both the carboxylic carbonyl groups of itaconic acid unit and at  $\delta$  118.8–120.0 ppm due to the nitrile group of AN unit. Thus, the chemical composition of these copolymers was calculated using the following equation:

$$\% \text{IA} = \frac{I[-\text{COOH}]/2}{I[-\text{CN}] + I[-\text{COOH}]/2} \times 100$$

where  $I[-\text{COOH}/2]$  is taken because there are two  $-\text{COOH}$  groups in every IA molecule.

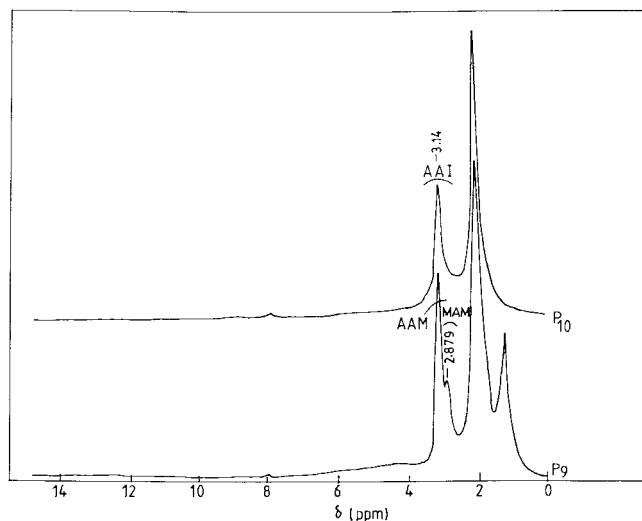
### $^1\text{H}$ NMR studies

The  $^1\text{H-NMR}$  spectrum of P(AN-MAA) and P(AN-IA) copolymer in DMSO- $d_6$  at  $80^\circ\text{C}$  is shown in Figure 1. In case of P(AN-MAA) copolymer ( $P_4$ ),  $\alpha$ -methyl ( $-\text{CH}_3$ ), methylene ( $-\text{CH}_2$ ), and carboxylic acid ( $-\text{COOH}$ ) protons are assigned at  $\delta$  1.2–1.6, 1.7–2.3, and 6.3–7.8 ppm (broad), respectively. The methine ( $-\text{CH}$ ) proton resonance shows a broad signal at  $\delta$  2.97–3.28 ppm. In case of P(AN-IA) copolymer ( $P_6$ ), methylene and carboxylic acid protons signals are shown around  $\delta$  1.9–2.3 and 6.3–7.8 ppm, respectively (Fig. 1). The latter is a broad doublet corresponding to two carboxylic acid groups of IA ( $-\text{COOH}$  and  $-\text{CH}_2-\text{COOH}$ ) present in different magnetic environments. As reported by Brar et al.,<sup>12</sup> the triad sequencing of methine group in the copolymer shows three signals around  $\delta$  2.97–3.28 ppm due to the MAM, AAM, and AAA triad compositional sequences. However, in the present study, the signals around  $\delta$  3.28–3.20, 3.20–3.14, and 3.14–2.97 ppm are assigned to AAA, MAA, and MAM triad compositional sequences, respectively, as shown in Figure 2. Also, the comonomer content in the copolymer is increased from 4 to 6 mol % when the DMF level increases from 20% to 80% (Table I). Further splitting within these triads are assigned due to configurational sequences as reported by Brar et al.<sup>12,14</sup>

Figure 3 shows the  $^1\text{H-NMR}$  spectrum of P(AN-MAA) and P(AN-IA) copolymers with more than 10 mol % of comonomer content. The signal at  $\delta$  3.25 ppm, which was previously assigned to the methine group of AAA sequencing in copolymers, appears to be overlapped with signal at 3.14 ppm.  $P_{10}$ , P(AN-IA), contains only one  $-\text{CH}$  signal at  $\delta$  3.14 ppm, which was assigned to AAI sequencing (I, itaconic acid). This

**TABLE I**  
Characterization of Acrylonitrile-Vinyl Acid Copolymers

Polymer	Code	DMF/H <sub>2</sub> O (w/w)	MAA/IA in the feed (mol %)	MAA/IA in the polymer (mol %)	$[\eta]$ dL g <sup>-1</sup>
PAN	P <sub>0</sub>	20:80	0	0	1.76
P(AN-MAA)	P <sub>1</sub>	20:80	2	4	2.8
P(AN-MAA)	P <sub>2</sub>	40:60	2	4.5	2.5
P(AN-MAA)	P <sub>3</sub>	60:40	2	5.9	1.36
P(AN-MAA)	P <sub>4</sub>	80:20	2	6	0.69
P(AN-IA)	P <sub>5</sub>	20:80	2	2.9	2.90
P(AN-IA)	P <sub>6</sub>	40:60	2	3.0	2.67
P(AN-IA)	P <sub>7</sub>	60:40	2	3.3	1.45
P(AN-IA)	P <sub>8</sub>	80:20	2	3.8	0.67
P(AN-MAA)	P <sub>9</sub>	20:80	10	12.5	
P(AN-IA)	P <sub>10</sub>	20:80	10	12	



**Figure 3** 300 MHz  $^1\text{H}$ -NMR spectra of P(AN-MAA) and P(AN-IA) copolymers with 12 mol % of comonomer.

shows that the probability of AAA sequencing is reduced with an increase in the comonomer content.

Another observation is that there is no proton signal due to carboxylic hydrogen at  $\delta$  6.3–7.8 ppm (Fig. 3), although it is expected to be very intense as the comonomer content in both  $P_9$  and  $P_{10}$  is more than 10 mol %. When the comonomer content is increased, presumably they get arranged in AIA IA form (Scheme 1).

As they come closer, they may undergo dehydration, leading to the formation of anhydride.<sup>16</sup> The  $-\text{COOH}$  groups are converted to anhydride  $-\text{CO}-\text{O}-\text{CO}-$ , which does not have any proton, hence no signal at  $\delta$  6.3–7.8 ppm.

The  $^1\text{H}$ -NMR spectra [Figs. 1(b) and 3] show a small broad signal at  $\delta$  7.9 ppm, which may be assigned to  $\text{NH}_2$  groups due to acrylamide formation by partial hydrolysis of nitrile groups. Ebdon et al.<sup>17</sup> also reported the formation of acrylamide due to partial hydrolysis of acrylonitrile during its polymerization using redox initiator.

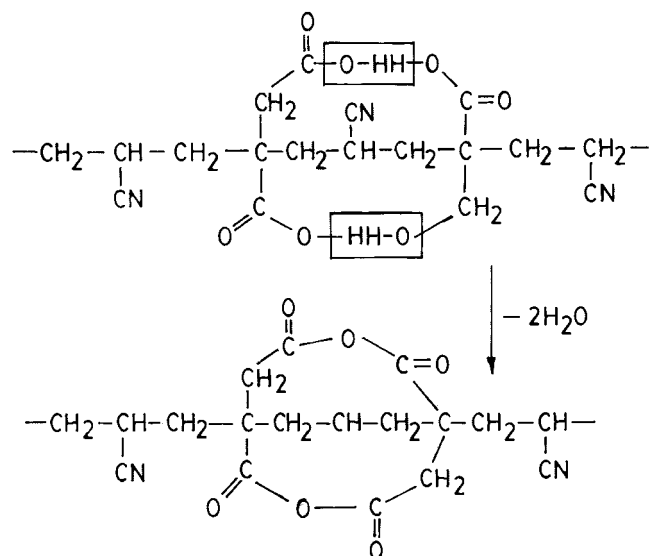
### $^{13}\text{C}$ [ $^1\text{H}$ ] NMR studies

The  $^{13}\text{C}$ [ $^1\text{H}$ ]-NMR spectra of P(AN-MAA) and P(AN-IA) copolymers are shown in Figure 4. The signals due to methine, methylene, nitrile, and carboxyl resonance appears around  $\delta$  26.3–27.8, 32.0–33.2, 118.8–120.0, and 171.0–176.0 ppm, respectively. As observed in the  $^1\text{H}$ -NMR spectrum, P(AN-MAA) copolymer shows only one carbonyl carbon signal, whereas P(AN-IA) shows two carbonyl signals due to two carboxylic groups of itaconic acid. The methine, nitrile, and carbonyl signals are stereospecific<sup>10</sup> and show splitting,

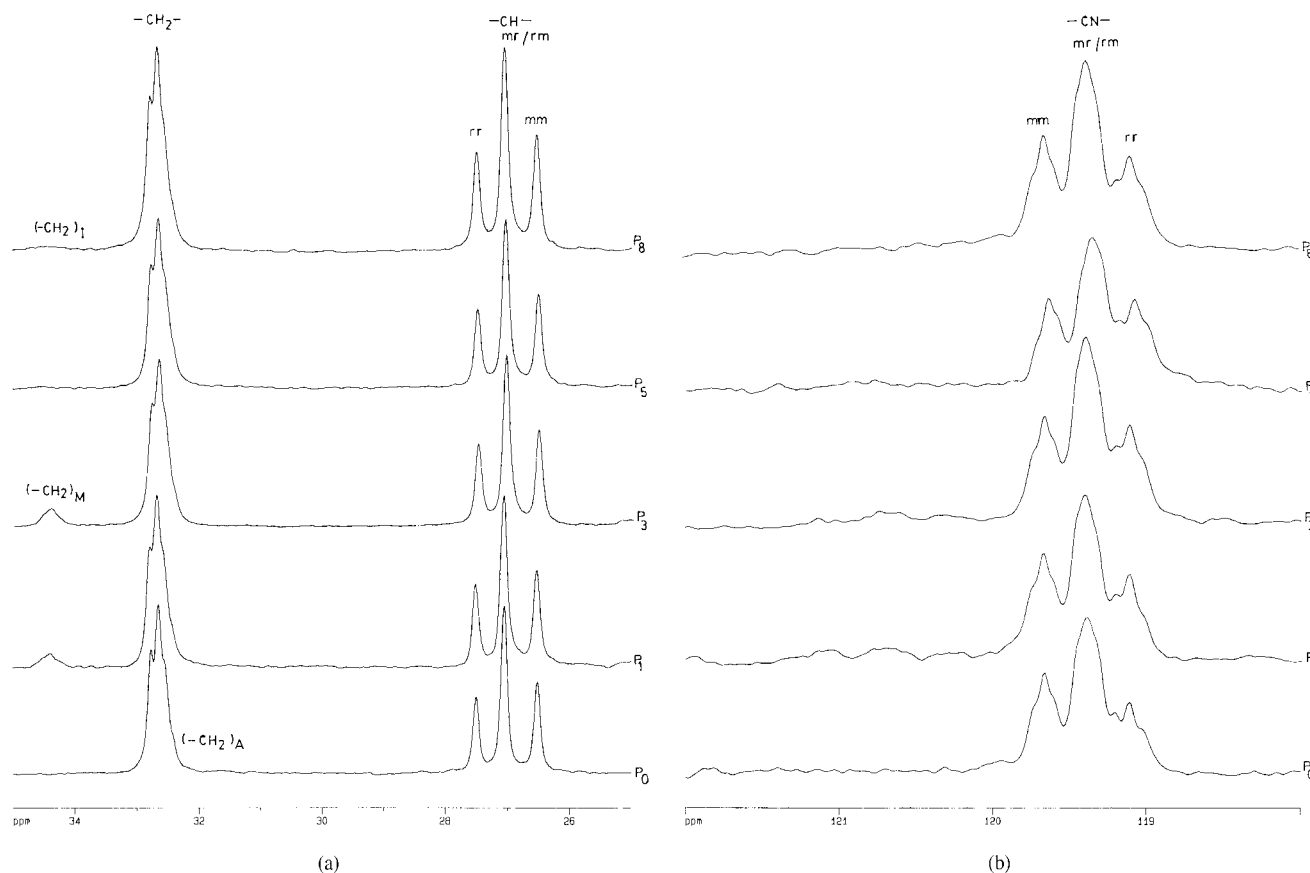
which are due to the compositional or configurational sequences.

In the nitrile ( $-\text{CN}$ ) carbon signal, the signals due to iso-, hetero-, and syndiotactic triads are assigned from high to low chemical shift ( $\delta$  120.1–118.8 ppm), respectively, whereas in the methine ( $-\text{CH}$ ) carbon signals, these triads appear from low to high chemical shift ( $\delta$  26.3–27.8 ppm). The nitrile ( $-\text{CN}$ ) and carbonyl ( $> \text{C}=\text{O}$ ) carbon signals show configurational and compositional sequence specificity. PAN homopolymer [Fig. 4 (b)] shows well-resolved triplet in the nitrile region. When a comonomer is introduced, the resolution of nitrile splitting becomes broad specifically at  $\delta$  119.2–118.8 due to overlapping of compositional sequences of AN-MAA-IA copolymers. In  $P_1$ , P(AN-MAA) copolymer with 4 mol % of MAA, apart from the above-mentioned AAA signal, two small signals are also observed. These signals are sharper in  $P_9$ , having 12.5 mol % of methacrylic acid. The signals at  $\delta$  120.8 and 121.4 ppm may be due to a combination of AAM and MAM triad units. Carbonyl carbon resonance of  $P_1$  shows a sharp signal at  $\delta$  176.0 and a shoulder at 176.1 ppm. These signals may be assigned to the two triads units, AMA and MMA, respectively. The probability for the third triad units is very low, as the comonomer content is only 4 mol %. But as the comonomer content is increased to 12.5 mol % in  $P_9$ , the signal due to AMA at  $\delta$  176 ppm disappears, and the intensity at  $\delta$  176.1 ppm due to MMA increased. Also, an additional triad sequence has been shown at  $\delta$  177.4 ppm, which may be due to MMM triad.

$P_6$  and  $P_{10}$  are P(AN-IA) copolymers, which also show splitting in the carbonyl carbon region: one in the region of  $\delta$  171.5–173.5 ppm due to  $-\text{CH}_2-$



**Scheme 1**



**Figure 4** 75.5 MHz  $^{13}\text{C}[^1\text{H}]$ -NMR spectra of AN homo- and copolymers in  $\text{DMSO-d}_6$  at  $80^\circ\text{C}$ : (a) expanded  $-\text{CH}$  (methine) and  $-\text{CH}_2$  (methylene) regions; (b) expanded  $-\text{CN}$  (nitrile) region.

$\text{COOH}$  group, and the other at  $\delta$  174.5–176.5 ppm due to  $-\text{COOH}$  group of itaconic acid (Fig. 5). Each resonance signal shows splitting as they show compositional sequencing, and the assignment seems to be difficult. The configurational sequence length for the copolymers were calculated as described by Randall<sup>18</sup> from the relative intensities of the respective peaks of methine and nitrile carbon resonance splitting. These average sequence lengths were calculated by using the following equations:

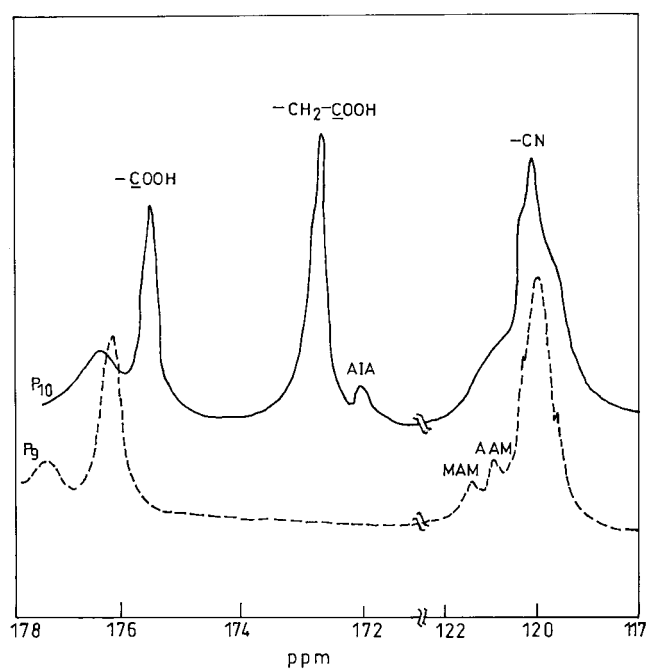
$$\bar{n}_0 = \frac{1}{rr + mr/2}$$

$$\bar{n}_m = \frac{mm + mr/2}{mr/2}$$

and

$$\bar{n}_r = \frac{rr + mr/2}{mr/2}$$

Tables II and III show the stereoregularity calculated from the CN and CH signals, respectively. The



**Figure 5** 75.5 MHz expanded  $^{13}\text{C}[^1\text{H}]$ -NMR spectra of  $>\text{C}=\text{O}$  (carbonyl) regions of AN homo- and copolymers in  $\text{DMSO-d}_6$  at  $80^\circ\text{C}$ .

TABLE II  
Tacticity of P(AN-MAA) and P(AN-IA) Copolymers by NMR Spectroscopy Using  $-\text{C}\equiv\text{N}$  Signals

Polymer code	Monomer feed (mol %)	Copolymer composition (mol %)	$-\text{C}\equiv\text{N}$ tacticity stereo regularity			Sequence length distribution		
			Isotactic <i>mm</i>	Atactic <i>mr</i>	Syndiotactic <i>rr</i>	$\bar{n}_o$	$\bar{n}_m$	$\bar{n}_r$
P <sub>0</sub>	AN, 100	AN, 100	26.01	52.31	21.68	2.09	2.00	1.83
P <sub>1</sub>	AN, 98 MAA, 2	AN, 96 MAA, 4	27.09	51.54	21.37	2.12	2.05	1.83
P <sub>2</sub>	AN, 98 MAA, 2	AN, 95.5 MAA, 4.5	23.56	48.90	25.54	2.00	1.96	2.05
P <sub>3</sub>	AN, 98 MAA, 2	AN, 94.1 MAA, 5.9	33.79	50.51	25.70	1.96	2.34	2.02
P <sub>4</sub>	AN, 98 MAA, 2	AN, 94 MAA, 6	22.86	48.80	28.34	1.90	1.94	2.16
P <sub>5</sub>	AN, 98 IA, 2	AN, 97.1 IA, 2.9	22.53	47.99	29.48	1.87	1.94	2.23
P <sub>6</sub>	AN, 98 IA, 2	AN, 97 IA, 3	22.71	52.42	22.87	2.04	1.94	1.87
P <sub>7</sub>	AN, 98 IA, 2	AN, 96.7 IA, 3.3	25.98	48.20	25.82	2.00	2.08	2.07
P <sub>8</sub>	AN, 98 IA, 2	AN, 96.2 IA, 3.8	23.16	50.81	26.03	1.94	1.91	2.03

isotacticity (*mm*) values in all the cases is around 27%. This shows tacticity values are not effected by the comonomer content in the present system.

The homo- and copolymers showed  $\bar{n}_m$  (number average sequence length distribution of mesoconfiguration) and  $\bar{n}_r$  (recimic configuration) values around 2.0, which suggests that they have random distribution of the nitrile group configuration.

## 2D HETCOR

Figure 6 shows the 2D HETCOR NMR spectra of acrylonitrile copolymers containing nearly 12 mol % of MAA-IA. Figure 6(a) is the HETCOR spectrum of P(AN-MAA) copolymer. It exhibits two  $-\text{CH}$  ( $^{13}\text{C}[^1\text{H}]$ ) signals of AN units due to the merging of two contours, at  $\delta$  28.25 and 25.5 ppm. The corresponding CH ( $^1\text{H}$ ) signals are at  $\delta$  3.15 and 2.88 ppm, respectively. The cross-peaks at  $\delta$  28.25/3.15 ppm are

assigned to AAA + MAA and the cross-peak at  $\delta$  25.5/2.88 ppm is assigned to MAM triad compositional sequences. The further splitting is due to the various configurational triads sequences such as *mm*, *mr*, and *rr* within these triad sequences. The splitting to a triplet may be caused by different conformational sequences. The triplet behavior is more clear in the case of P(AN-IA) copolymer [Fig. 6 (b)].

A multiplet is observed in the methyl region from  $\delta$  20.5 to 23.75 ppm for P(AN-MAA) copolymer. This may be due to the methyl groups of methacrylic acid units and the methyl groups of 2-cynopropyl end groups derived from the initiator, AIBN.

## CONCLUSIONS

The copolymers of acrylonitrile and vinyl acids of different compositions show various compositional and configurational sequences by  $^1\text{H}$ -,  $^{13}\text{C}[^1\text{H}]$ -, and

TABLE III  
Triad Tacticity of PAN Copolymers Using C—H Signals

Polymer code	Signal position			Tacticity			Sequence length		
	<i>mm</i> I	<i>mr/rm</i> H	<i>rr</i> S	<i>mm</i> I	<i>mr/rm</i> H	<i>rr</i> S	$\bar{n}_o$	$\bar{n}_m$	$\bar{n}_r$
P <sub>0</sub>	26.53	27.06	27.51	27.8	53.2	19.0	2.19	3.05	1.71
P <sub>1</sub>	26.53	27.06	27.51	26.5	52.3	21.2	2.11	2.01	1.81
P <sub>2</sub>	26.53	27.05	27.50	26.8	51.2	22.0	2.10	2.05	1.86
P <sub>3</sub>	26.53	27.05	27.50	27.2	50.1	22.7	2.09	2.08	1.91
P <sub>4</sub>	26.52	27.03	27.48	29.3	49.6	21.1	2.18	2.18	1.85
P <sub>5</sub>	26.52	27.04	27.49	27.6	50.5	21.9	2.12	2.09	1.87
P <sub>6</sub>	26.52	27.04	27.48	27.8	49.0	23.2	2.10	2.14	1.95
P <sub>7</sub>	26.52	27.04	27.49	27.0	52.2	20.8	2.13	2.04	1.80
P <sub>8</sub>	26.54	27.05	27.50	28.8	49.5	21.7	2.15	2.16	1.88

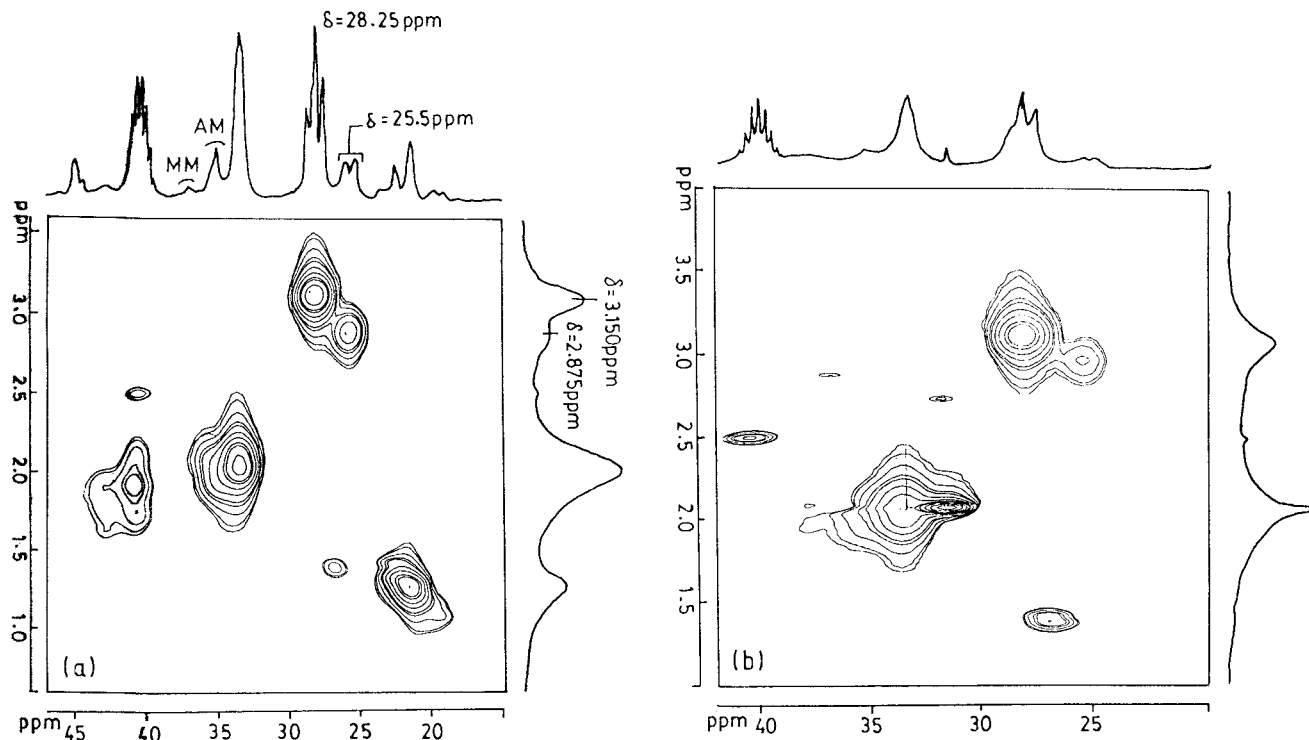


Figure 6 2D HETCOR spectra of AN copolymers containing 12 mol % MAA/IA: (a) P(AN-MAA); (b) P(AN-MAA).

2D NMR techniques. Composition of P(AN-IA) copolymers has been determined using quantitative  $^{13}\text{C}[^1\text{H}]$ -NMR spectra, while that of P(AN-MAA) using  $^1\text{H}$ -NMR spectra. Copolymers show carboxylic proton signal at  $\delta$  6.3 to 7.8 ppm. Interestingly, P(AN-MAA) shows one signal, while P(AN-IA) shows two signals. Anhydride formation occurs when the carboxylic content is increased to 10 mol %, giving no proton signal. However, carbonyl carbon signal is observed in  $^{13}\text{C}[^1\text{H}]$ -NMR. Presence of AAM and AAI triad compositional sequencing has been established from 2D HETCOR NMR spectra.

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