

Configurational sequence lengths in polyacrylonitrile and poly(acrylonitrile-CO-haloalkyl acrylate/methacrylate)s determined by ^{13}C n.m.r.

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The tacticity and number average sequence length of like (\bar{n}_o), meso (\bar{n}_m) and racemic (\bar{n}_r) acrylonitrile (AN) triad units in polyacrylonitrile (PAN) prepared in both water and water-acetone (2:1 v/v) media and AN-3-chloro, 2-hydroxypropyl acrylate/methacrylate, AN-2-bromoethyl methacrylate and AN-2-chloroethyl acrylate copolymers have been calculated using ^{13}C n.m.r. spectra of the polymer solutions concerned at a field strength of 24.99 MHz. The spectra reveal that PAN prepared in water medium has a greater percentage (33.4%) of isotactic units than PAN prepared in water-acetone (2:1 v/v) medium (28.3%). The tacticity distribution of AN sequences in PAN and the copolymers is found to be random ($\bar{n}_m \approx \bar{n}_r \approx 2.0$) and the number average sequence length of AN sequences in a copolymer containing 14.8 mole% of 3-chloro, 2-hydroxypropyl methacrylate was 15.2.

(Keywords: PAN; poly(AN-CO-haloalkyl acrylate/methacrylate); ^{13}C and ^1H n.m.r.; tacticity; number average sequence length)

INTRODUCTION

The spectral findings of AN homo and its copolymers by using ^1H n.m.r. technique has been restricted, despite the use of deuterated polymers and extensive homonuclear spin-spin decoupling techniques, since they do not become amenable to determinations of the relative concentrations of steric dyads and triads in the polymer chain easily¹⁻⁴. Recently, ^{13}C n.m.r. spectroscopy has largely displaced ^1H n.m.r. because of the development of Fourier transform (FT) instrumentation with spectrum accumulation that has permitted the practical observation of carbon-13 in natural abundance, its much greater range of chemical shifts and the consequent sensitivity to details of polymer structure such as end-groups, branches, head-to-head and monomer sequences^{5,6}.

Balard *et al.*⁷ have observed that for PAN the carbon atom of the cyano group was the most stereosensitive, whereas, for oligomers it is the carbon atoms of the chain. They are also of the view that ^{13}C n.m.r. allows for the direct estimation of the relative concentrations of the different isomers in a mixture and is, therefore, the best spectroscopic technique for controlling the efficiency of the methods used to separate oligomeric diastereoisomers. Schaefer's⁸ work on polyacrylonitrile prepared with organometallic catalyst, is indicative of a modest increase in stereoregular contents (found using ^{13}C n.m.r. spectra) as compared to that in the PAN prepared by using redox initiator. Both ^1H and ^{13}C n.m.r. techniques have

been employed to elucidate the comonomer sequence distribution of poly(AN-CO-methacrylic acid)⁹. More recently, the compositions of AN-N-vinyl pyridine copolymers² have been determined using an ^{13}C n.m.r. technique.

The present paper reports measurements, using the ^{13}C n.m.r. technique, of tacticity and number average sequence length of AN units in PAN made in water and water-acetone (2:1 v/v) media, and AN-haloalkyl acrylate/methacrylate copolymers made in water-acetone (2:1 v/v) medium. Some qualitative studies on ^1H n.m.r. of PAN and poly(AN-CO-2-bromoethyl methacrylate) is also discussed.

EXPERIMENTAL

PAN was prepared in both water and water-acetone (2:1 v/v) media using $\text{K}_2\text{S}_2\text{O}_8$ and $\text{Na}_2\text{S}_2\text{O}_5$ initiators at 40°C. All copolymers were prepared in water-acetone (2:1 v/v) medium. Intrinsic viscosities of the copolymers range between 0.7 and 1.2 dl g⁻¹. Other details of synthesis of PAN and poly(AN-CO-haloalkyl acrylate/methacrylate) have been reported elsewhere^{10,11}. The n.m.r. spectra of the homo- and copolymers were recorded on a Jeol JNM FX-100 Fourier transform spectrometer.

The ^{13}C n.m.r. spectra (at 24.99 MHz) were recorded using a 10-15% (w/v) solution of the polymer at 130° ± 1°C in DMSO and DMSO-d₆ (20:1 v/v) solvent mixture. 2500-8000 free induction decays (FID) (depend-

ing on the amount of polymer in solution) were accumulated using a pulse width of 14 μ s. An acquisition time of 6 s and a spectral width of 7500 Hz (300 ppm) were employed.

The ^1H n.m.r. spectra (at 99.55 MHz) were recorded using a 5% (w/v) solution of the polymer at $130^\circ \pm 1^\circ\text{C}$ in DMSO-d_6 solvent. 100 free induction decays (FID) were accumulated using a pulse width of 21 μ s, an acquisition time of 5 s and a spectral width of 1000 Hz. TMS was used as internal standard.

RESULTS AND DISCUSSION

The noise decoupled ^{13}C n.m.r. spectra of PAN prepared in water and water-acetone (2:1 v/v) media are shown in Figure 1. Herein, the methine, methylene and nitrile carbon resonances appear at $\delta 27.019$, $\delta 32.807$ and $\delta 119.044$ respectively. It is evident from the spectra that both methine and nitrile carbon resonances show resolvable stereochemical splittings. These splittings are particularly pronounced in the expanded spectra, included in Figure 1. The nitrile carbon peaks at $\delta 119.339$, $\delta 119.044$ and $\delta 118.826$ are assigned to iso (mm), hetero (mr/rm) and syndio (rr) tactic triad configurations in order of increasing field strength. The methine triad peaks at $\delta 26.506$, $\delta 27.019$ and $\delta 27.385$ are assigned to iso, hetero and syndio tactic triads respectively. (These assignments are based on the reported values for PAN by Schaefer⁸). The methine carbon of PVC, and poly(isopropyl acrylate) is found to give a triad splitting similar to the methine carbon of PAN¹².

The tacticity values have been calculated from the relative intensity of the peaks as obtained from the computer data. And the number average sequence length of like (\bar{n}_o), meso (\bar{n}_m) and racemic (\bar{n}_r) configurations have been calculated using the following relations¹³:

$$\bar{n}_o = [(\text{rr}) + 1/2(\text{mr})]^{-1}$$

$$\bar{n}_m = \frac{(\text{mm}) + 1/2(\text{mr})}{1/2(\text{mr})}$$

$$\bar{n}_r = \frac{(\text{rr}) + 1/2(\text{mr})}{1/2(\text{mr})}$$

Table 1 gives the tacticity and \bar{n}_o , \bar{n}_m and \bar{n}_r and values for PAN prepared in water and water-acetone (2:1 v/v) media including the values of P_m which provide the best fits for the fractions assuming that Bernoullian statistics apply. The tacticity values record a small difference (0.5–7.7%) when these are calculated based on methine or nitrile carbon resonance splittings. Such small differences are anticipated since the present calculations are based on a triad sensitivity⁸.

PAN prepared in water-acetone (2:1 v/v) medium reveals 46.3% atactic, 28.3% isotactic and 25.4% syndio tactic AN units, respectively. It is interesting to note that when the medium is changed from water-acetone to water, the isotactic content increased to 39.4% with the syndiotactic content decreasing to 15.5%. The higher value of syndiotactic configurations in PAN prepared in

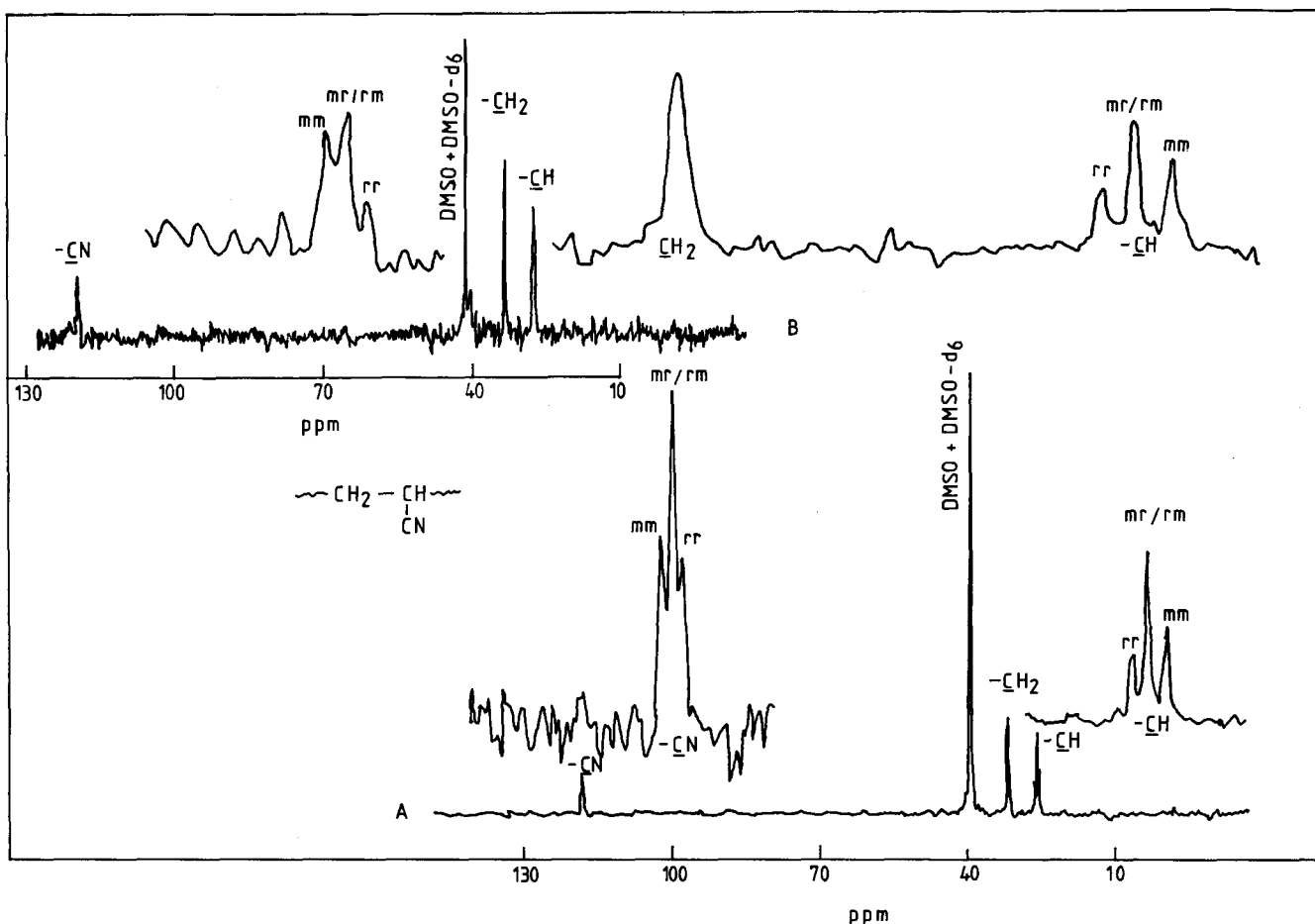


Figure 1 ^{13}C spectra of PAN prepared in (a) water-acetone (2:1 v/v) and (b) water media along with nitrile and methine carbon expansions in $\text{DMSO} + \text{DMSO-d}_6$ (20:1) mixture at 130°C

Table 3 Triad tacticity of AN homosequences in poly (AN-CO-3-chloro, 2-hydroxypropyl acrylate) (PA). ($m_2 = 14.5$ mole %)

Chemical shift (δ)	Assignment	Tacticity (%)	\bar{n}_o , \bar{n}_m and \bar{n}_r values*	P_m^*
24.618	CH AAM triad			
26.506	iso	(mm) = 26.7	$\bar{n}_m = 2.060$	0.52
27.018	CH hetero	(mr/rm) = 50.5	$\bar{n}_o = 2.081$	
27.385	syndio	(rr) = 22.8	$\bar{n}_r = 1.903$	
32.807	CH ₂ AA diad			
34.453	AM diad			
46.848	CHOH			
66.705	CH ₂ Cl			
68.756	OCH ₂			
118.826	syndio	(rr) = 24.1	$\bar{n}_r = 1.949$	0.50
119.046	CN hetero	(mr/rm) = 50.8	$\bar{n}_o = 2.020$	
119.338	(AAA triad) iso	(mm) = 25.0	$\bar{n}_m = 1.984$	
119.850	syndio			
120.215	CN hetero	unresolved		
120.620	(AAM triad) iso			
173.337	C=O			

*As given in Table 1

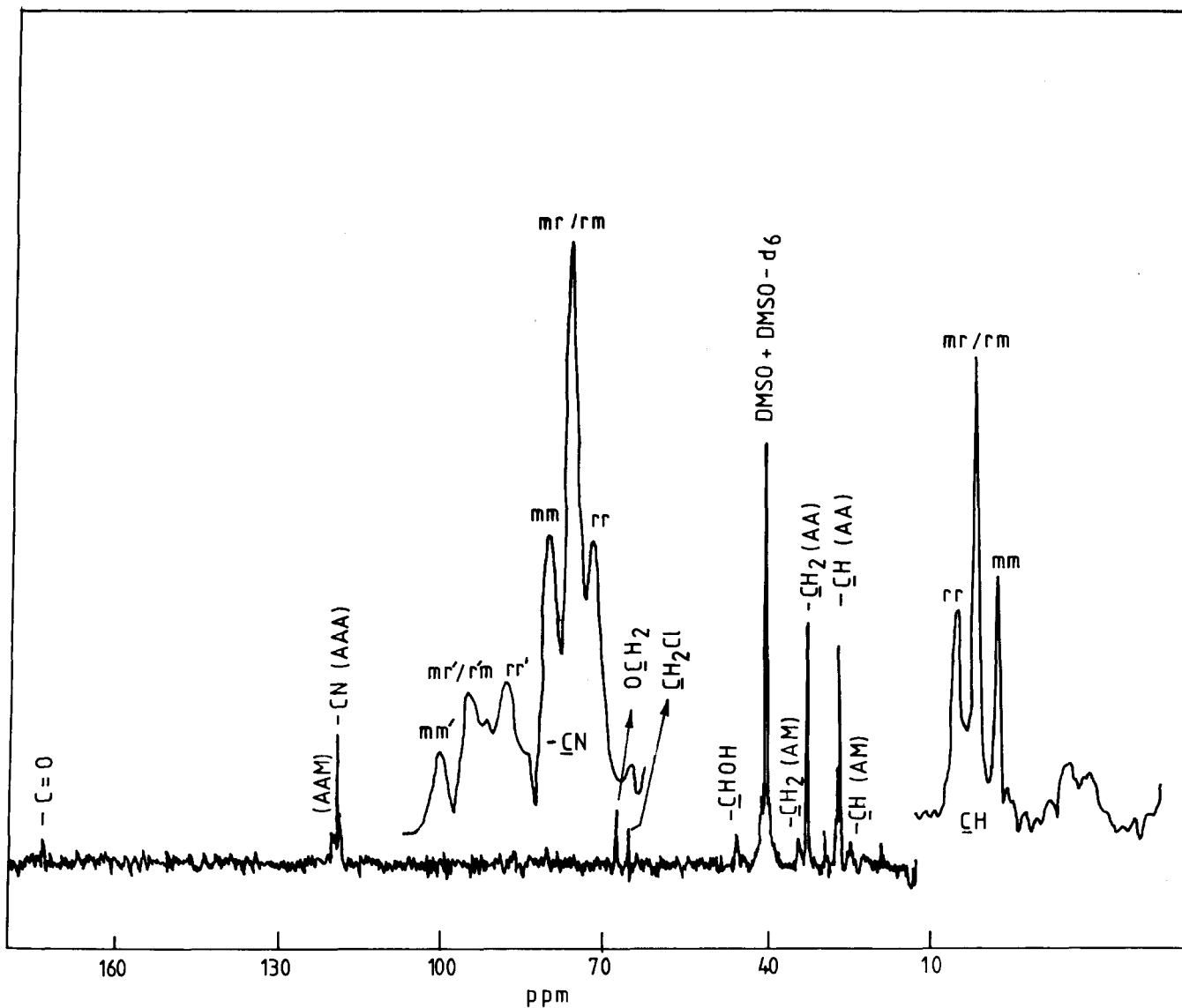


Figure 2 ¹³C spectra of a copolymer of AN with 3-chloro, 2-hydroxypropyl acrylate ($m_2 = 14.5$ mole%) along with nitrile and methine carbon expansions in DMSO + DMSO- d_6 (20:1) mixture at 130°C

details that are a result of resonances coming from the homo polyacrylonitrile. However, in the present work the signal at $\delta 173.578$ assigned to the carbonyl carbon of the acrylate/methacrylate comonomer could be observed with a total accumulated pulses of around 5000 and above.

In the above spectrum, the nitrile carbon peak when expanded gave two triplets assignable to AAA and AAM triads where A is acrylonitrile and M is the comonomer unit⁹.

The triad tacticity of AN homosequences in the above copolymers and the \bar{n}_o , \bar{n}_m and \bar{n}_r values are given in Tables 2 and 3. These values (\bar{n}_m and \bar{n}_r) are found to be around 2.0, which suggests that the distribution of nitrile configuration in them is also random similar to that in PAN. In the PM copolymer the tacticity values which were based on the nitrile carbon triplet assigned to AAM triad, were found to be 38.5% racemic (\bar{n}_r) and 23.0% meso (\bar{n}_m). Herein, due to the presence of the bulky substituted propyl group in the 3-chloro, 2-hydroxypropyl methacrylate comonomer, the racemic additions are favoured.

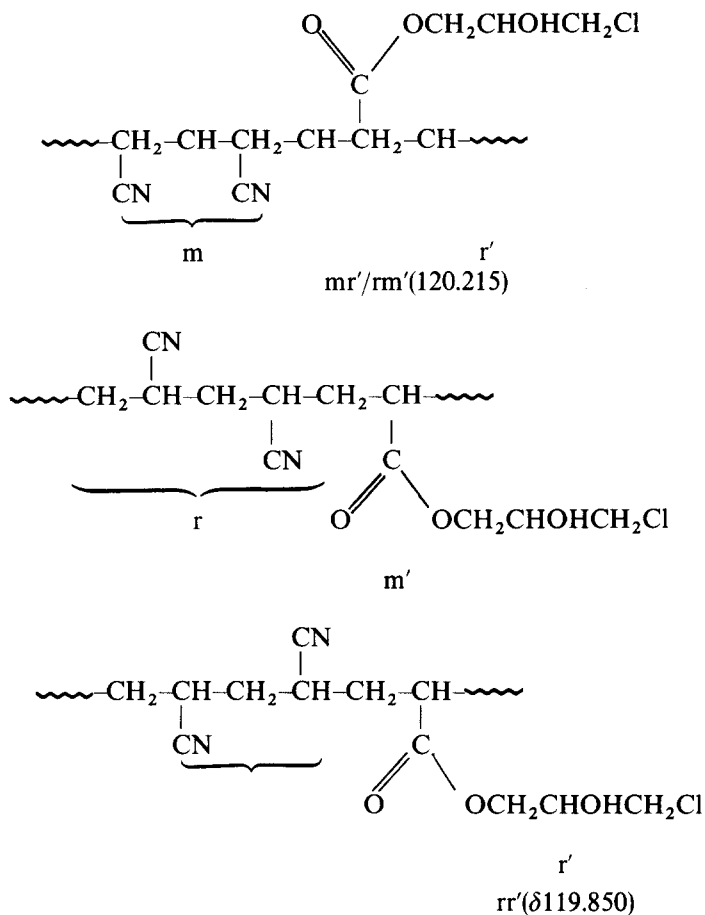
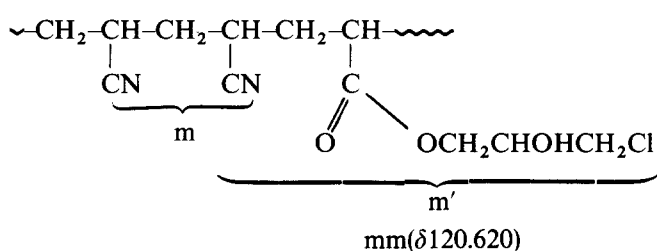


Table 4 Triad tacticity of AN homosequences in (A) poly (AN-CO-2-bromoethyl methacrylate) ($m_2 = 6.1$ mole %) and (B) poly(AN-CO-2-chloroethyl acrylate) ($m_2 = 4.5$ mole %)

Chemical shift (δ)	Assignment	Tacticity (%)	\bar{n}_o, \bar{n}_m and \bar{n}_r values*	P_m^*
A				
20.131				
20.311	CH ₃ (split)			
25.187	CH AAM triad			
26.946	iso	(mm) = 28.4	$\bar{n}_m = 2.237$	0.52
27.065	CH hetero	(mr/rm) = 45.9	$\bar{n}_o = 1.970$	
28.113	(AAA triad syndio)	(rr) = 25.7	$\bar{n}_r = 2.119$	
32.807	-CH ₂			
45.102	C			
63.946	CH ₂ Br			
69.808	OCH ₂			
119.779	syndio	(rr) = 23.9	$\bar{n}_r = 2.072$	0.56
120.072	CN hetero	(mr/rm) = 44.6	$\bar{n}_o = 2.165$	
120.438	iso	(mm) = 32.4	$\bar{n}_m = 2.408$	
B				
24.821	CHAAM triad			
26.772	iso	(mm) = 35.2	$\bar{n}_m = 2.644$	0.59
27.359	CH hetero	(mr/rm) = 42.9	$\bar{n}_o = 2.312$	
27.841	syndio	(rr) = 21.8	$\bar{n}_r = 2.016$	
32.702	CH ₂			
34.343				
65.851	CH ₂ Cl			
67.830	OCH ₂			
119.600	syndio	(rr) = 22.8	$\bar{n}_r = 2.060$	0.56
119.825	CN hetero	(mr/rm) = 43.0	$\bar{n}_o = 2.020$	
120.190	iso	(mm) = 34.0	$\bar{n}_m = 2.590$	

*As given in Table 1

Table 5 ^1H n.m.r. assignments in (A) PAN and (B) Poly(AN-CO-2-bromoethyl methacrylate)

Chemical shift (δ)	Nate of the resonance	Assignment
A		
2.103 (1.96-2.24)	envelope	CH_2
3.152 (3.02-3.36)	split, unresolved	CH
B		
1.160 1.480	Broad, doublet	CH_3
2.080 (1.68-2.32)	Broad	CH_2
3.150 (2.90-3.34)	Broad, partially burried in the solvent signal	CH
3.44	Weak, multiplet	CH_2Br
3.95	Weak	OCH_2

The number average sequence length (\bar{n}_0) distribution of acrylonitrile units in the above copolymers were calculated using the AA and AM/MA diad peaks of methylene carbons at $\delta 32.777$ and $\delta 33.396$, respectively. Poly(AN-CO-3-chloro, 2-hydroxypropyl methacrylate) has \bar{n}_0 equal to 15.3 while poly(AN-CO-3-chloro, 2-hydroxypropyl acrylate) has \bar{n}_0 of 14.0. This is related to the uninterrupted long sequences of AN units in the above copolymers.

The ^{13}C n.m.r. spectral parameters of poly(AN-CO-2-bromoethyl methacrylate) and poly(AN-CO-2-chloroethyl acrylate) are included in Table 4. Since the comonomer content in these copolymers is less, the carbonyl peak positions could be located with an accumulated pulses of around 8000, however, the AAM triad splittings observed in the spectra of PM and PA polymers could not be observed in the spectra of these copolymers. Again random distributions of mm, mr and rr triads of AN were observed in these copolymers.

The ^1H n.m.r. spectrum of PAN prepared in water-acetone (2:1 v/v), displayed a broad envelope between $\delta 1.96$ and $\delta 2.24$ and an unresolvable multiplet located between $\delta 3.02$ and $\delta 3.36$ (Table 5). The signal at $\delta 3.02$ – $\delta 3.36$ split upon expansion into an unsymmetrical quartet. Based on intensity measurements and chemical shifts these resonances with maxima at $\delta 3.152$ and $\delta 2.103$ are assigned, respectively, to CH and CH_2 protons in the homo PAN¹⁻³.

The ^1H n.m.r. spectrum of the poly(AN-CO-2-bromoethyl methacrylate) ($m_2 = 6.1$ mole%) recorded under similar conditions showed a broad envelope ($\delta 2.068$) due to

the CH_2 protons coming from the AN component and a partially split signal (due to the CH of AN) at $\delta 3.152$, a part of this envelope towards high field appear to be overlapped with the solvent signal. A weak multiplet resonance located at the extreme left end of the CH signal, at $\delta 3.44$ is attributed to CH_2Br (present in the bromoethyl methacrylate component). Other signals were located at $\delta 3.95$ (envelope, OCH_2), $\delta 1.160$, and $\delta 1.389$ (broad, doublet, methyl). The two broad signals at $\delta 1.160$ and $\delta 1.389$ are indicative of different monomer distribution, and their configurational arrangements.

Again, the methine and methylene proton signals in the copolymer spectrum appeared broad (CH_2 , $\delta 1.68$ – 2.32) as compared to the PAN (CH_2 , $\delta 1.96$ – 2.24). This is suggestive of the partial overlapping of the backbone protons present in both AN and comonomer units. Similar broadening has been reported for methine protons in the ^1H n.m.r. spectrum of AN-styrene copolymer¹⁸.

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