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International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

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To cite this Article Prasad, J. V. , Satpathy, U. S. , Jassal, M. , Pantar, A. and Satish, S.(1992) 'Studies of the Effect of Comonomers on the Microstructure of Polyacrylonitrile in Radical Polymerization Using NMR Spectroscopy', *International Journal of Polymeric Materials*, 18: 1, 105 – 115

To link to this Article: DOI: 10.1080/00914039208034817

URL: <http://dx.doi.org/10.1080/00914039208034817>

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Studies of the Effect of Comonomers on the Microstructure of Polyacrylonitrile in Radical Polymerization Using NMR Spectroscopy†

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(Received February 26, 1992)

The free radical polymerization method has been employed to synthesize homopolymers of acrylonitrile (AN), its copolymers with methylacrylate (MA) and terpolymers containing itaconic acid (IA) in homogeneous solution (aqueous solution of sodium thiocyanate and dimethylsulfoxide media) and aqueous redox slurry system. ^{13}C NMR was used to characterize these polymers in terms of steric configurations in order to study the effect of co and ter monomers on microstructure of polyacrylonitrile both at low and high conversions. The study showed no significant change in microstructure of polyacrylonitrile on the introduction of MA and IA. Different techniques of polymerization for ACN-MA-IA had no effect on the microstructure of terpolymer. ^1H NMR and IR techniques were used to determine the composition of copolymers and a good agreement was observed between the results from the two techniques. The presence of unsaturated carboxylic acid monomer (IA) was confirmed by ^1H NMR.

KEY WORDS Polyacrylonitrile, comonomers, microstructure NMR.

INTRODUCTION

There is increasing interest in understanding the mechanism of polymerization and structure of acrylonitrile-methylacrylate copolymers (ACN-MA) as they are precursors for carbon fibres.¹ The physicochemical and chemical properties of these polymers are critically dependent on monomeric composition and steric configurations of polyacrylonitrile (PAN). Atactic stereochemical configuration of the polymer chain inhibits the access of nitrile groups after polymerization to certain degree and consequently terminating polymerization and affecting the degree of polymerization.² Earlier work³ showed that polymerization conditions affect steric configurations of monomers in polymers such as increase in syndiotactic fraction of PAN can be observed due to decrease in polymerization temperature. The

†IPCL Communication No. 185.

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complexities of the structure of these polymers are controlled primarily by the kind of initiation (free radical or otherwise), the propagation and the termination reactions competing with secondary reactions. The initiation reaction affects composition and configuration of monomers whereas, propagation influences primarily the composition with a minor effect on configurations unless very wide temperature ranges are considered. Addition of third comonomer itaconic acid (IA) to these polymers increases ionic initiation of CN cyclization⁴ and its estimation is sometimes critical.

Many techniques viz. NMR,⁵ IR⁶ and PGC-MS⁷ were used to study the structural features of these polymers. Among them NMR is more powerful and reliable technique⁸ to reveal information regarding stereochemical configurations and monomer sequence distributions in acrylic copolymers.

In the present paper it has been aimed to study the effect of co and ter monomers on the steric configurations of polyacrylonitrile synthesized by free radical polymerization in solution (aqueous and DMSO media) and suspension techniques at high and low conversions. ¹³C NMR was used to study the difference in number average sequence lengths⁹ and first order Markovian probabilities¹⁰ arising from different polymerization processes. Appearance of well resolved and isolated signal of one of the two carboxyl groups of IA in ¹H NMR enabled a semiquantitative estimation of the third monomer in the terpolymers. In order to quantify the monomeric composition in copolymers and terpolymers two different complementary techniques ¹H NMR and IR were used. Elemental analysis (C, H and N) was also employed to confirm the monomer incorporation.

EXPERIMENTAL PROCEDURES

Commercial polymer samples (A1-A4) from DuPont (USA) and Poly Science (USA) and polymers synthesized by free radical initiated method were used in the present studies. The IR spectra of these samples were recorded on Beckman 4220 IR spectrometer using KBr disk and solvent cast film method. Elemental analysis of these polymers was carried out on Carlo Erba Elemental Analyzer Model No. 1106. DSC studies of the polymers were carried out on DuPont Thermal Analyzer 990.

The synthetic methods and conditions of polymerization for homopolymers, copolymers and terpolymers are mentioned below. Detailed experimental conditions are shown in Table I.

Solution polymerization in DMSO medium

The copolymerization of AN with MA and terpolymerization with IA were carried out in DMSO medium using azobis isobutyronitrile (AIBN) as initiator at 70°C in a jacketed glass reactor. After 6 hrs of polymerization the polymer was precipitated with demineralized water. It was further washed with demineralized water followed by excess of hot water. The polymer in the form of noodle like threads was dried at 60°C overnight. Adopting the same technique, homopolymers were synthesized.

TABLE I
 Polymerization conditions of PAN, ACN-MA copolymers and ACN-MA-IA ter polymers

Monomers and condition	Solution (DMSO)			Aqueous Solution of (NaSCN)			Suspension		
	Homo	Co	Ter	Homo	Co	Ter	Homo	Co	Ter
ACN %	100	95.7	91.96	100	94	93	100	93	93
MA %	—	4.3	8.04	—	6	6	—	7	6
IA %	—	—	2.69	—	—	1	—	—	1
Initiator (g)	—	AIBN (0.031)	AIBN (0.235)	AIBN (0.225)	AIBN (0.3)	AIBN (0.3)	KPS/MBS (0.056/0.106)	KPS/MBS (0.056/0.106)	KPS/MBS (0.045/0.89)
Time (h)	6	6	6	5	5	5	4	4	4
Temperature	70°C	70°C	70°C	70°C	70°C	70°C	50°C	50°C	50°C
% Yield	48	40.35	48	60.12	66.42	69	78.25	83.5	82.5
Solvent (g)	446	640	300	510	510	510	800	800	800
pH	—	—	—	7	7	7	2.28	2.35	2.3

Polymerization in aqueous sodium thiocyanate(NaSCN) solution

Copolymers of AN and MA and terpolymers containing IA were prepared by radical polymerization of 51% aqueous solution of NaSCN with AIBN as initiator at 70°C. The polymer was precipitated with a mixture of water and methanol (1:1). Polymer was filtered off, washed with boiling distilled water to remove NaSCN and later with methanol. It was initially dried at room temperature and later vacuum dried at 60°C. Homo and copolymers were synthesized using the similar method.

Polymerization in aqueous redox slurry system

The terpolymerization of AN, MA and IA was carried out in aqueous medium (pH 2–5, adjusting with dil. H₂SO₄) using potassium persulfate/sodium metabisulphite redox pair at 50°C under nitrogen atmosphere for 4 hrs in a glass reactor. After polymerization the reaction mixture was filtered, polymer was washed thoroughly with distilled water and dried at 50–60°C to constant weight. Similarly homo and copolymers were synthesized.

NMR Spectroscopy

¹³C and ¹H NMR spectra were recorded on a JOEL JNM FX 100 FT NMR spectrometer, with ¹³C and ¹H nuclei resonating at 25 MHz and 100 MHz respectively. Copolymers were dissolved in (CH₃)₂ SO-d₆ (90°C) at a concentration of 15 w/v (%). All the chemical shifts were referenced to HMDS. Pulse width was 13 μs corresponding to a pulse angle 90° and the pulse repetition time was 8 s. Close agreement between the number average sequence lengths estimated from methine and nitrile signals confirmed the adequacy of pulse repetition time. For ¹³C NMR the spectral width was 5000 Hz, acquisition time as 1.55 s and the number of transients accumulated were 1500–2500. For ¹H NMR the spectral width was 2000 Hz, pulse delay was 5 s and 20 pulses were accumulated.

RESULTS AND DISCUSSION

The detailed experimental conditions of synthesis of various polymers and their elemental composition are shown in Tables I and II respectively. Evidently, there is a decrease in percentage of nitrogen (N) for copolymers and terpolymers, prepared under different techniques (viz. solution and suspension) which qualitatively shows the incorporation of comonomer (i.e. MA) in polyacrylonitrile (PAN) skeleton. In order to confirm the copolymer formation with methylacrylate and terpolymers formation with methylacrylate and itaconic acid, these polymers were subjected to thermal analysis by differential scanning calorimetry (Figure 1). Table III shows the thermal initiation temperature (T_i) and thermal peak temperature (T_p) for the homo, co and ter polymers. It is clear from these data that incorporation of co and termonomers has decreased the T_i and T_p values. Identification of co and ter comonomer incorporation was carried out using similar method by Grassi *et al.*¹¹

Further, barring special cases, it is generally observed that the compositional

TABLE II
Elemental analysis of homo, co and ter polymer

Sample	D.M.S.O.			Aqueous solution of NaSCN			Suspension	
	C	H	N	C	H	N	C	H
Homopolymer (PAN)	67.1	5.88	25.63	64.37	5.57	25.29	66.81	5.58
Copolymer (ACN-MA)	64.52	5.62	23.57	64.43	5.59	23.34	66.41	5.78
Terpolymer (ACN-MA-IA)	64.65	5.75	23.69	64.44	5.97	23.95	64.92	5.63

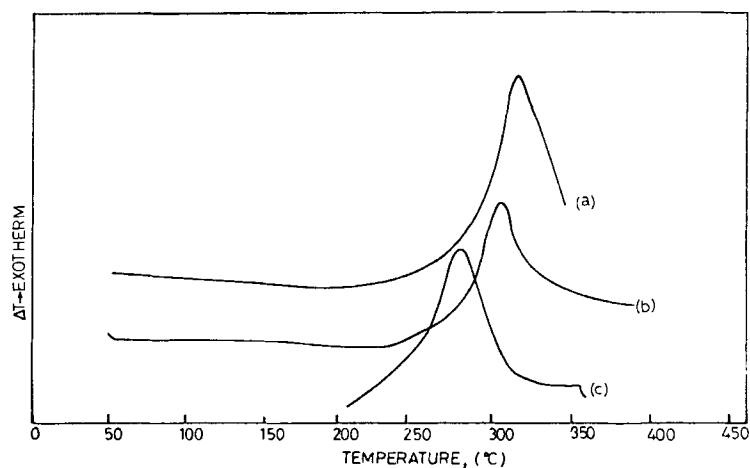


FIGURE 1 DSC thermograms of (a), homopolymer (PAN) (b), ACN-MA copolymer, and (c), ACN-MA-IA ter polymer.

TABLE III
DSC-Results of PAN, (AN-MA) copolymers and AN-MA-IA terpolymers

Sr. No.	Polymer	Concentration of MA, wt %	Thermal Properties	
			T_i	T_p
1	PAN	0	235	318
2	(AN-MA)	2	230	308
3	(AN-MA)	6	230	302
4	(AN-MA-IA)	6	210	278

microstructure analysis of radical initiated copolymers appears quite complex because of overlapping of the compositional and configurational sequence resonances. Figure 2 shows the ^1H NMR spectra of AN homopolymer, AN-MA copolymer and AN-MA-IA terpolymer prepared under homogeneous (DMSO medium) conditions. The spectra of the samples prepared in aqueous NaSCN medium and other

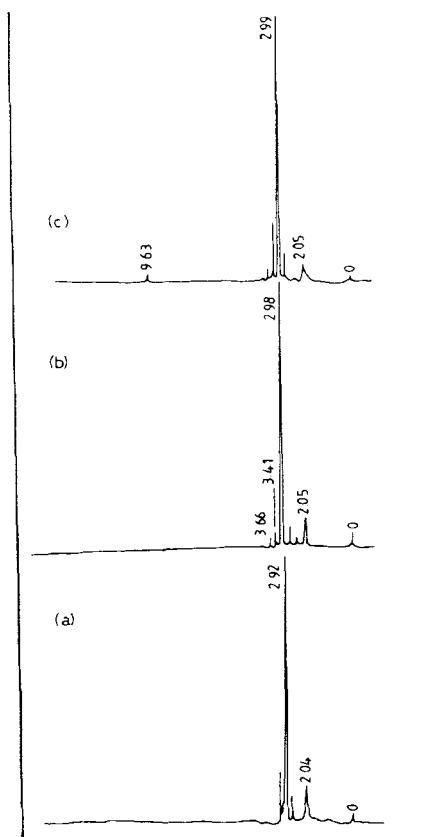


FIGURE 2 ^1H NMR spectra of (a), homopolymer (PAN) (b), ACN-MA copolymer, and (c), ACN-MA-IA terpolymer.

TABLE IV
Compositional data from various techniques

Samples	^1H NMR			I.R.		
	AN	MA	IA	AN	MA	IA
Copolymer (DMSO)	94.2	5.8	—	94.05	5.95	—
Terpolymer (DMSO)	93.96	5.5	0.54	93.75	6.35	—
Copolymer (Aqueous NaSCN)	93.9	6.10	—	93.56	6.44	—
Terpolymer (Aqueous NaSCN)	93.61	5.7	0.61	93.01	6.09	—
Copolymer (Suspension)	93.6	6.4	—	93.75	6.25	—
Terpolymer (Suspension)	93.58	5.8	0.62	93.07	6.03	—

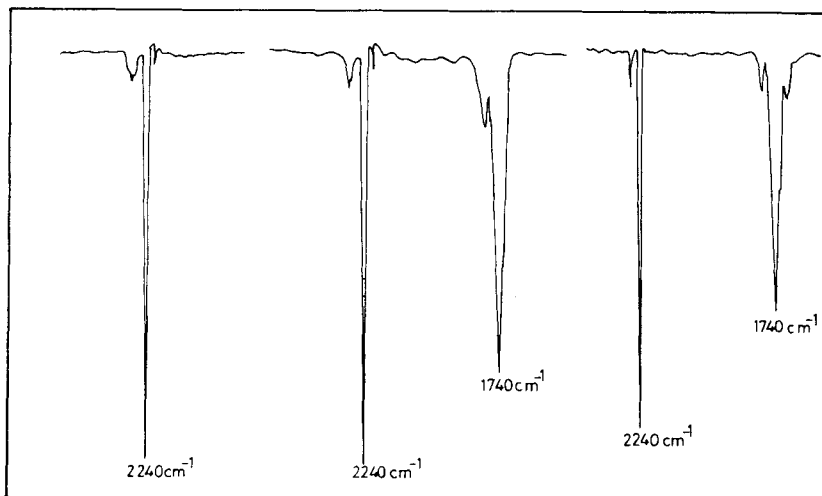


FIGURE 3 IR spectra of (a), homopolymer (PAN) (b), ACN-MA copolymer, and (c), ACN-MA-IA terpolymer.

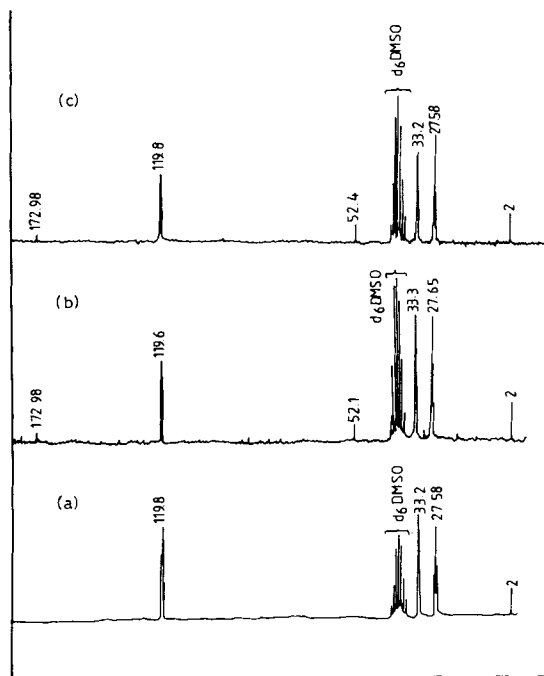


FIGURE 4 ¹³C NMR spectra of (a), homopolymer (PAN) (b), ACN-MA copolymer, and (c), ACN-MA-IA terpolymer.

suspension conditions are similar to the spectra in Figure 1. Since all these polymers predominantly have acrylonitrile their spectra possess features resembling to that of ¹H NMR spectra of pure polyacrylonitrile (PAN). Strong absorption at 2.92 δ corresponds to methine protons in PAN segments. A broad envelop at 2.04 δ has

TABLE V
Structural parameters from ^{13}C NMR for PAN, ACN-MA and ACN-MA-IA polymers

Sample	Tacticities						Number Average Sequence Lengths					
	CN			CH			CN			CH		
	<i>mm</i>	<i>mr</i>	<i>rr</i>	<i>mm</i>	<i>mr</i>	<i>rr</i>	\bar{n}_m	\bar{n}_r	\bar{n}_m	\bar{n}_r	\bar{n}_m	\bar{n}_r
Homopolymers (DMSO)	29.41	46.52	24.06	27.52	49.59	22.94	2.26	1.97	2.11	2.11	1.93	
Copolymer (DMSO)	29.22	46.1	24.68	27.18	48.6	24.27	2.27	2.07	2.9	2.9	2.7	
Terpolymer (DMSO)	29.31	46.23	24.46	27.31	48.5	24.19	2.25	2.01	2.91	2.91	2.7	
Homopolymer (NaSCN)	29.85	44.78	25.37	27.66	48.93	23.4	2.33	2.13	2.13	2.13	1.96	
Copolymer (NaSCN)	29.41	46.22	24.37	30.41	47.97	21.62	2.27	2.06	2.27	2.27	1.9	
Terpolymer (NaSCN)	26.67	46.67	26.67	26.87	49.25	23.88	2.14	2.14	2.09	2.09	1.97	
Homopolymer (Suspension)	30.19	48.11	21.7	28.48	48.73	22.79	2.26	1.9	2.27	2.27	1.93	
Copolymer (Suspension)	28.75	48.75	22.5	28.46	47.97	23.58	2.18	1.92	2.19	2.19	1.98	
Terpolymer (Suspension)	25.31	44.44	30.25	32.53	46.39	21.08	2.14	2.36	2.4	2.4	1.91	
A1 ^a	29.15	43.54	27.31	28.19	46.98	24.83	2.34	2.26	2.2	2.2	1.83	
A2 ^a	30.33	45.9	23.77	28.86	47.65	23.49	2.32	2.04	2.21	2.21	1.99	
A3 ^a	28.68	45.74	25.58	29.38	47.49	22.6	2.25	2.12	2.24	2.24	1.95	
A4 ^a	28.58	45.84	25.58	29.28	47.49	22.7	2.24	2.11	2.23	2.23	1.96	
TP ^b	31.1	45.3	23.6	31.4	47.4	21.2	2.37	2.04	2.33	2.33	1.9	

^aCommercial samples.

^bLow conversion.

TABLE VI

First order markovian probabilities for PAN, ACN-MA and ACN-MA-IA polymers

Samples	CN				CH			
	$P_{n/r}$	$P_{r/m}$	$P_{m/m}$	$P_{r/r}$	$P_{n/r}$	$P_{r/m}$	$P_{m/m}$	$P_{r/r}$
Homopolymer (DMSO)	0.44	0.49	0.56	0.57	0.47	0.52	0.53	0.48
Copolymer (DMSO)	0.44	0.48	0.56	0.52	0.47	0.5	0.53	0.50
Terpolymer (DMSO)	0.43	0.47	0.57	0.53	0.46	0.57	0.52	0.57
Homopolymer (NaSCN)	0.43	0.47	0.57	0.53	0.47	0.57	0.53	0.49
Copolymer (NaSCN)	0.44	0.49	0.56	0.57	0.47	0.52	0.53	0.48
Terpolymer (NaSCN)	0.47	0.47	0.53	0.53	0.48	0.57	0.52	0.49
Homopolymer (Suspension)	0.44	0.53	0.56	0.47	0.46	0.52	0.54	0.48
Copolymer (Suspension)	0.46	0.52	0.54	0.48	0.46	0.5	0.54	0.50
Terpolymer (Suspension)	0.47	0.42	0.53	0.58	0.42	0.52	0.58	0.48
A1 ^a	0.43	0.44	0.57	0.56	0.45	0.49	0.55	0.57
A2 ^a	0.43	0.49	0.57	0.57	0.45	0.50	0.55	0.50
A3 ^a	0.44	0.47	0.56	0.53	0.45	0.50	0.55	0.50
A4 ^a	0.43	0.48	0.55	0.52	0.44	0.57	0.54	0.48
TP ^a	0.42	0.49	0.58	0.57	0.43	0.53	0.57	0.47

^aCommercial samples.^bLow conversion.

been assigned to methylene protons. Signal at 2.48 δ has been attributed to the solvent d_6 DMSO. Methyl protons in methylacrylate are observed as a shoulder at 3.66 δ . The signals corresponding to methylene and methine protons appear at 2.09 δ . A well resolved and distinct signal at 9.03 δ has been assigned to the carboxyl proton. The relative intensities of the signals at 3.1 δ , 3.66 δ and 9.03 δ corresponding to methine, methyl and carbonyl protons in acrylonitrile, methylacrylate and itaconic acid respectively led to semi quantitative estimation of these monomers as shown in Table IV.

Typical IR spectra of copolymers synthesized using three different methods are shown in Figure 3. In the IR spectrum characteristic absorption corresponding to carbonyl in MA and nitrile in AN appear at 1730 cm^{-1} and 2240 cm^{-1} respectively. The ratio of intensities of absorptions of CO and CN was used to estimate MA in copolymers (Table IV) of AN & MA. [Calibration curve was developed by IR techniques for copolymers and blends of known composition].

Figure 4 shows the ^{13}C NMR spectra of homopolymer of AN, AN-MA copolymers and AN-MA-IA terpolymers synthesized under homogeneous (DMSO medium) conditions. The spectra of the homo, co and terpolymers prepared under aq. NaSCN and suspension conditions match well with the spectra shown in Figure 2.

Since the methylacrylate (MA) content in these copolymers is less, in their ^{13}C NMR spectra showed discernible signals corresponding to OCH_3 and CO at 52 δ and 173 δ respectively. The other three signals at 119 δ , 33.2 δ and 28.83 δ arise from nitrile (CN), methylene and methine carbons respectively. Signal corresponding to methylene carbons of MA is merged in the signal at 33.2 δ . Absorptions due to methine group of MA fall in the region of signals of d_6 -DMSO. The nitrile carbons showed a good triad sensitivity and the two shoulders appearing at high and low fields have been assigned to *rr* and *mm* steric configurations. The dominant

central peak is assigned to *mr* configuration. The signal corresponding to methine carbons was found to resolve into three peaks. The two peaks at high and low fields were due to *mm* and *rr* configurations respectively and central peak was assigned to *mr*. Further in the ^{13}C NMR spectrum of copolymer the carbonyl carbons moved slightly upfield and OCH_3 absorbed at lower field and these shifts may be attributed to electron withdrawing nature of CN group.

The number average sequence lengths \bar{n}_m and \bar{n}_r (Equations 1 and 2), and the first order Markovian probabilities $P_{m/m}$, $P_{m/r}$, $P_{r/m}$ and $P_{r/r}$ (Equations 3, 4, 5 and 6) for all the synthesized and commercial polymers are shown in Tables V and VI.

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

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

$$P_{m/m} = P_m(1 - P_{m/r})$$

$$P_{m/r} = \frac{(mr)}{2(mm) + (mr)}$$

$$P_{r/m} = \frac{(mr)}{2(rr) + (mr)}$$

$$P_{r/r} = 1 - P_{r/m}$$

Evidently there is a marginal difference between the data obtained using nitrile and methine signals. On the other hand, the number average sequence lengths for all the synthesized polymers are not only close with each other but also match with those of commercial polymers. Even the polymers synthesized at lower conversion of 20% had their number average sequence lengths and steric configurations same as those of the other polymers synthesized at higher conversion of 80%. These observations indicate that the polymers obtained under different polymerization conditions have similar steric configurations of PAN segments. The configuration of PAN segments in homo, co and terpolymers remains same while the composition and monomers vary. Except the temperature of polymerization other alterations in the polymerization conditions such as variation of the diluent, monomer concentration initiator ratio and also the nature of the initiator (AIBN, KPS/MBS) affect primarily the termination reactions¹². Eventually it would affect the molecular weight and molecular weight distribution of the polymers obtained from various methods. Therefore any change in physicomechanical properties of these polymers may be attributed to difference in molecular weight and molecular weight distributions.

The composition of dyad, triad, tetrad and pentads of the second (MA) and third (IA) comonomers in the terpolymers may contribute to the change in properties.

Such information can be obtained from additional resolved splittings of signals due to CN groups, at higher compositions of MA and IA.

CONCLUSION

^{13}C NMR study of homopolymers of AN, its copolymers with MA and terpolymers containing MA and IA synthesized under homogeneous solution (aq. solution of NaSCN and DMSO media) and aq. redox slurry system both at high and low conversions showed that the introduction of second and third comonomer hardly affects the steric configuration of PAN segment. Accordingly the number average sequence lengths \bar{n}_m and \bar{n}_r , and first order Markovian probabilities of these polymers remain nearly constant. Copolymer composition determined by IR and ^1H NMR seems to have a reasonably good agreement. The presence of IA in these polymers was successfully identified by ^1H NMR spectroscopy.

Acknowledgment

The authors wish to thank Mrs. J. D. Shah and Miss Y. K. Patel for rendering experimental assistance and Mrs. V. J. Koshy for useful discussions. They gratefully acknowledge Dr. I. S. Bhardwaj, Director, R&D Centre for his encouragement and kind permission to publish this work.

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