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### Donor-Acceptor Complexes in Copolymerization. XVI. NMR Analyses of Alternating and Random Copolymers of Styrene and $\alpha$ -Methylstyrene with Acrylonitrile and Methacrylonitrile

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## Donor-Acceptor Complexes in Copolymerization. XVI. NMR Analyses of Alternating and Random Copolymers of Styrene and $\alpha$ -Methylstyrene with Acrylonitrile and Methacrylonitrile

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### SUMMARY

An NMR investigation was carried out on random and alternating copolymers of acrylonitrile (AN) with  $\alpha$ -methylstyrene (MS) and methacrylonitrile (MAN) with  $\alpha$ -methylstyrene and styrene (S). The alternating MS-AN copolymer, prepared by complexation with  $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ , was found to have a predominantly coisotactic configuration which was attributed to the interaction between the  $\text{CH}_3$  and CN groups. The cotacticity of the alternating copolymer was found to be independent of the temperature of polymerization and the amount of  $\text{AlEt}_{1.5}\text{Cl}_{1.5}$  used for complexation. The NMR spectra of random MS-AN copolymers of varying compositions indicated a high value (0.85) for the coisotacticity probability parameter ( $\sigma$ ). The equimolar random MS-AN copolymer was also found to have essentially alternating sequences which was attributed to their low reactivity ratios. The equimolar alternating MS-MAN copolymer was found to have a random stereochemical configuration in which the coisotactic placement was slightly preferred over the cosyndiotactic placement. The NMR spectrum of the equimolar free radical initiated MS-MAN copolymer lacked the fine structure observed in the spectrum of the alternating copolymer which was attributed to the presence of other sequences. The equimolar alternating

S-MAN copolymer was found to have a high coisotactic configuration similar to that observed in the MS-AN copolymer. The equimolar free radical initiated S-MAN copolymer had a random sequence distribution.

## INTRODUCTION

The alternating tendency in the free radical copolymerization of vinyl monomers has been well documented. In an earlier report [1] NMR was used to provide evidence for the alternating tendency in random copolymers of acrylonitrile with styrene, isoprene, and butadiene. The results from the NMR analyses were matched with the sequence distribution of the comonomers expected from the reactivity ratios. In these systems the alternating tendency was predominant, which was explained on the basis of their low reactivity ratios, particularly when the reactivity ratio for one of the comonomers was close to zero.

In the present investigation some other comonomer pairs having low reactivity ratios have been examined. The copolymers chosen were  $\alpha$ -methylstyrene-acrylonitrile,  $\alpha$ -methylstyrene-methacrylonitrile, and styrene-methacrylonitrile. The reactivity ratios for these monomer pairs are listed in Table 1. In this report an attempt has been made to elucidate

Table 1. Reactivity Ratios

$M_1-M_2$	$r_1$	$r_2$	Ref.
$\alpha$ -Methylstyrene-acrylonitrile	0.1	0.06	2
$\alpha$ -Methylstyrene-methacrylonitrile	0.12	0.35	3
Styrene-methacrylonitrile	0.17	0.26	18

the sequence distribution and cotactic configurations of the random copolymers with the help of NMR. Evidence for the cotactic configurations has been provided from the NMR spectra of the alternating copolymers. A discussion is also presented on the relative influence of the various factors contributing to the cotacticity of one of the alternating copolymers.

## EXPERIMENTAL

 **$\alpha$ -Methylstyrene–Acrylonitrile Copolymer (MS-AN)**

The random copolymers were prepared in bulk at 70°C using benzoyl peroxide as the initiator. The reaction was terminated at less than 6% conversion.

The 1:1 alternating copolymer was prepared by the method described previously [4]. A mixture of  $\alpha$ -methylstyrene, acrylonitrile, and benzoyl peroxide, if any, was placed in a reaction flask, flushed with nitrogen, and maintained at 25°C. A toluene solution of ethyl aluminum sesquichloride was injected by means of a hypodermic syringe through a self-sealing rubber cap. The reaction mixture was stirred in a nitrogen atmosphere until approximately 10% conversion when the reaction was terminated by the addition of methanol. The product was dissolved in a mixture of acetone and benzene and precipitated into a large excess of cyclohexane.

The NMR spectra of the copolymers were examined in  $\text{CDCl}_3$  at 75°C at 100 MHz.

 **$\alpha$ -Methylstyrene–Methacrylonitrile Copolymer (MS-MAN)**

The equimolar random copolymer was prepared in bulk at 75°C using benzoyl peroxide as the initiator.

The 1:1 alternating copolymer was prepared in the same manner as the  $\alpha$ -methylstyrene–acrylonitrile copolymer.

**Styrene–Methacrylonitrile Copolymer (S-MAN)**

The equimolar random copolymer was prepared in bulk from an equimolar charge of monomers at 75°C using benzoyl peroxide as the initiator.

The alternating copolymers was prepared in the same manner as the  $\alpha$ -methylstyrene–acrylonitrile copolymer.

The NMR spectra of the copolymers were examined in pyridine at 90°C at 100 MHz.

## RESULTS AND DISCUSSION

 **$\alpha$ -Methylstyrene–Acrylonitrile Copolymer (MS-AN)**

Figure 1 presents the NMR spectrum of the alternating  $\alpha$ -methylstyrene–acrylonitrile copolymer whose elemental analyses indicated an equimolar

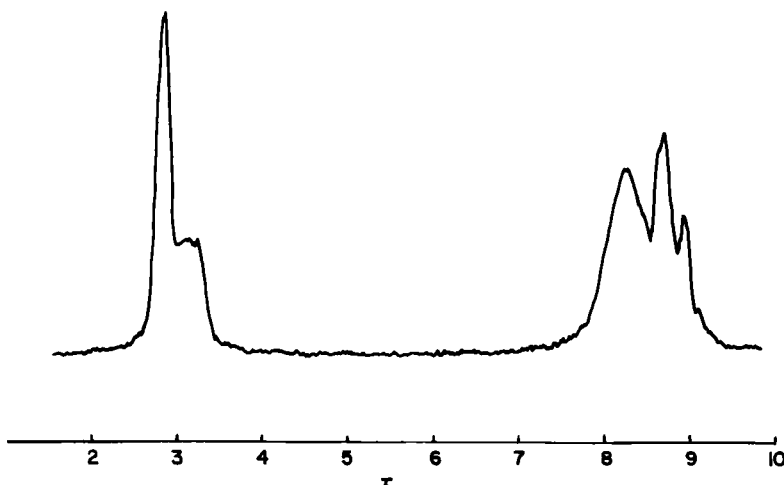


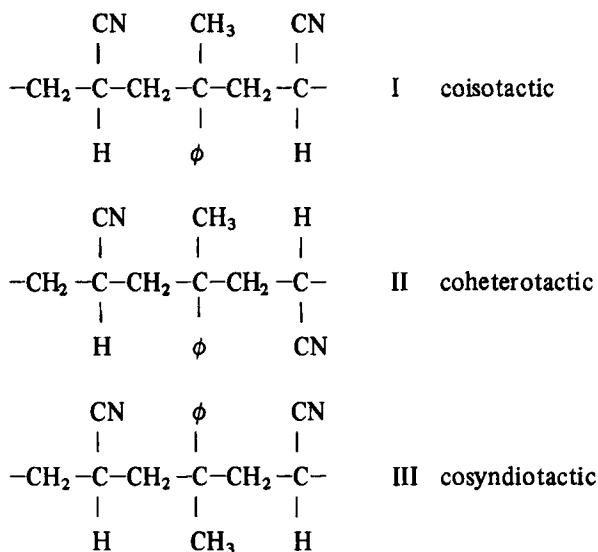
Fig. 1. NMR spectrum of 1:1 alternating  $\alpha$ -methylstyrene-acrylonitrile copolymer prepared by complexation with  $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ .

composition. The phenyl protons appeared in the range 2.5-3.5  $\tau$  with a broad multiplicity essentially as two peaks. The phenyl protons in the NMR spectrum of the poly- $\alpha$ -methylstyrene, when run in several solvents, are known to be split [5]. It is evident that the phenyl proton peaks have shifted downfield in comparison to that observed in poly- $\alpha$ -methylstyrene (3.0-3.7  $\tau$ ) because of the adjacent acrylonitrile units. Although the phenyl protons appear as two peaks, this should not be considered as due to the presence of  $\alpha$ -methylstyrene blocks. Similar splitting of phenyl protons is known to be present in the NMR spectra of alternating styrene-methyl acrylate [6] and styrene-acrylonitrile [1] copolymers. It is also generally understood that this could arise due to other environmental groups [7].

The methylene protons of  $\alpha$ -methylstyrene and both the methylene and methine protons of acrylonitrile appear together as a single broad peak in the range 7.40-8.55  $\tau$ . The assignment is made on the basis of relative peak area measurements and because the methylene protons of acrylonitrile and  $\alpha$ -methylstyrene units appear at  $\sim 8.0$   $\tau$  and the methine proton of acrylonitrile appears at a still lower field. The appearance in this broad range is due to the combined influence of the shielding effect of the adjacent phenyl units on the methylene and methine protons of acrylonitrile and the deshielding effect of the acrylonitrile units on the methylene protons of  $\alpha$ -methylstyrene. It is of interest to note that no

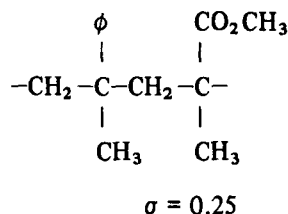
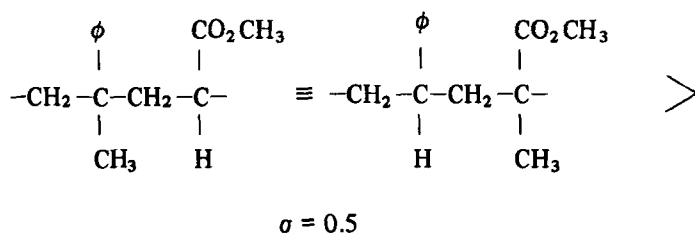
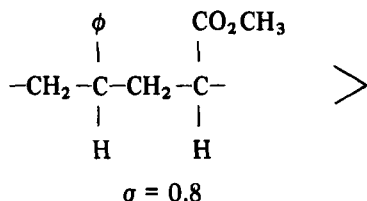
absorption is evident below  $7.4 \tau$ . The extent of such up-field absorption of the methine proton of acrylonitrile is known to be less in copolymers of acrylonitrile with methyl methacrylate [8], ethyl acrylate [9], isoprene [1], butadiene [1], styrene [1], etc. In the alternating styrene-acrylonitrile copolymer the methine proton of acrylonitrile appears as a single peak. Evidently, the  $\alpha$ -methylstyrene units provide a larger shielding effect.

The  $\alpha$ -methyl protons appear at the highest field strength in the spectrum and as three peaks at 8.72, 8.94, and 9.12  $\tau$ . These peaks are assigned to the coisotactic (I), coheterotactic (II), and cosyndiotactic (III) configurations of  $\alpha$ -methylstyrene centered triads. Since the nitrile group is the only substituent in acrylonitrile, the configurations are assigned as shown.



The assignments are based on the cotactic configurations of methyl methacrylate copolymers and because in poly- $\alpha$ -methylstyrene the isotactic configuration appears at the lowest field strength [10]. It is apparent that in the alternating copolymer the coisotactic configuration is predominant. This would be ascribed to the interaction of the methyl group with the nitrile group in the neighboring monomer unit. This is in conformity with the probability of coisotacticity ( $\sigma$ ) [11] observed in the copolymers of various  $\alpha$ -substituted acrylates with styrene and  $\alpha$ -methylstyrene [12]. Thus, the coisotacticity parameter ( $\sigma$ ) decreased in the series styrene-methyl acrylate > styrene-methyl methacrylate  $\equiv$   $\alpha$ -methylstyrene-methyl

acrylate  $>$   $\alpha$ -methylstyrene–methyl methacrylate. Since Ito et al. [12] have based the assignment on the relative position of the carbomethoxy protons in the acrylate centered triad, considering the adjacent phenyl ring as the substituent, the increased methyl substitution on the  $\alpha$ -position of the acrylate or styrene units contributed to increased interaction between the methyl group (MS units) and the carbomethoxy group resulting in the decrease in the  $\sigma$  values. On this basis the coisotactic configuration in the

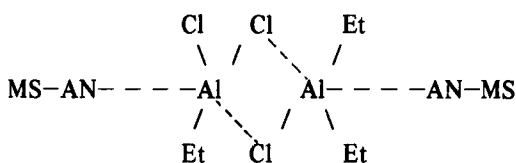


alternating  $\alpha$ -methylstyrene–acrylonitrile copolymer would be the more favored one. In a series of samples that were prepared at different temperatures and different amounts of  $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ , the relative amounts of the various configurations are unchanged and the coisotactic configuration is the predominant one. It is apparent from the results in Table 2 that the I, H, and S configurations are present in 66:27:7 ratio. Since the alternating copolymer is considered to be formed by the homopolymerization of the  $[\text{MS}^+ \cdot \text{AN}]$  charge transfer complex, it would reasonably indicate that the complex exists predominantly in the cis configuration.

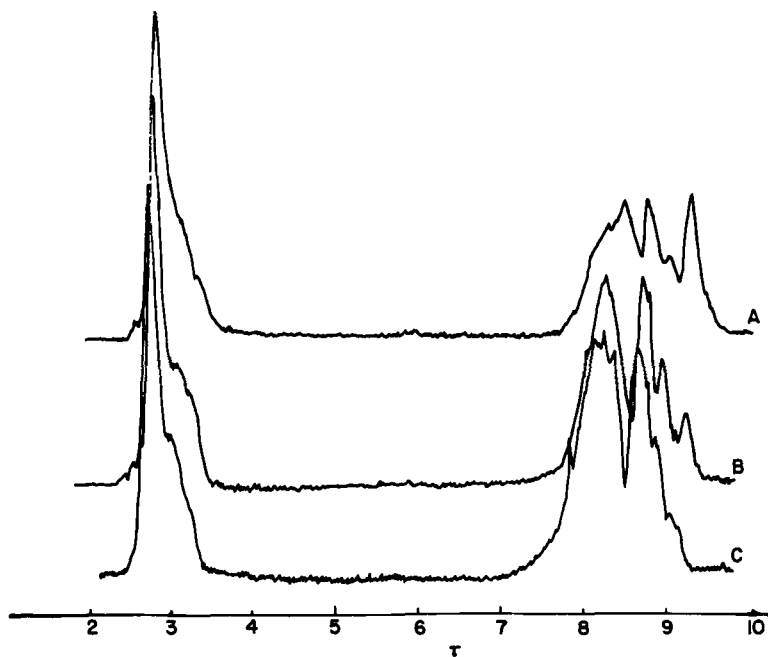
Table 2. Configurations in Alternating  $\alpha$ -Methylstyrene-Acrylonitrile Copolymer

AN/AlEt <sub>1.5</sub> Cl <sub>1.5</sub> , mole ratio	Temp. (°C)	I	H	S
18	20	66	27	7
2	0	65	26	9
2	20	66	26	8
2	40	65	29	6

The temperature independence of the tacticity is known to be a characteristic in the polymerization of methyl methacrylate in the presence of ZnCl<sub>2</sub> or SnCl<sub>4</sub> [13]. In the polymerization of methacrylonitrile, no change in tacticity was observed with a change in temperature when SnCl<sub>4</sub> was used as the metal halide whereas the use of ZnCl<sub>2</sub> as the complexing agent influenced the tacticity of the resulting polymethacrylonitrile formed at different temperatures [14]. The tacticities, however, were found to be dependent upon the nature of the metal halide used in complexing the polar monomer and the nature of the complex, i.e., [MMA . . . SnCl<sub>4</sub>] (1:1) or [(MMA)<sub>2</sub> . . . SnCl<sub>4</sub>] (2:1). These effects were also noticed in the copolymerization of styrene-methyl methacrylate in the presence of various Lewis acids [15, 16]. Thus, the 1:1 MMA . . . metal halide complex resulted in a copolymer of higher coisotacticity than the 2:1 complex when ZnCl<sub>2</sub> or SnCl<sub>4</sub> was used as the metal halide in complexing MMA. In general, ZnCl<sub>2</sub> or AlCl<sub>3</sub> resulted in a more coisotactic polymer in comparison to SnCl<sub>4</sub> irrespective of the nature of the complex formed. The control of the tacticities of the products could be attributed to the structure of the charge transfer complex. In the present case when the amount of ethylaluminum sesquichloride has been varied widely (AN/AlEt<sub>1.5</sub>Cl<sub>1.5</sub> mole ratio 2 and 18), the cotactic configurations were unchanged. This could be attributed to the formation of only one type of complex irrespective of the amount of AlEt<sub>1.5</sub>Cl<sub>1.5</sub> used:







**Fig. 2.** NMR spectra of random  $\alpha$ -methylstyrene-acrylonitrile copolymers prepared with free radical catalysts. Copolymer composition: MS/AN (mole ratio) (A) 66:34, (B) 56:44, (C) 45:55.

Figure 2 (A, B, C) presents the NMR spectra of random  $\alpha$ -methylstyrene-acrylonitrile copolymers. The phenyl protons in all these polymers appear in the range 2.80-3.35  $\tau$  and a slight shift towards a lower field is observed with an increase in the acrylonitrile content because of the neighboring AN units. It is of interest to note that in Figs. 2B and 2C when the copolymer contains more alternating sequences the phenyl protons appear as two broad peaks.

The methylene protons of  $\alpha$ -methylstyrene and both the methylene and methine protons of acrylonitrile appear together at 7.7-8.72, 7.4-8.6, and 7.25-8.55  $\tau$  in Figs. 2A, 2B, and 2C, respectively. In the alternating  $\alpha$ -MS-AN copolymer (Fig. 1) no corresponding absorption was observed at a field lower than 7.4  $\tau$ . The absorption at a lower field in Fig. 2C is due to the methine protons present in successive acrylonitrile units.

The methyl protons of the  $\alpha$ -methylstyrene units appear in the range 8.55-9.50  $\tau$ . In general, the absorptions appear as three peaks. In Fig. 2A

( $\alpha$ -MS/AN = 66/34 analyzed from elemental analyses and NMR measurements) the peaks are at 8.80, 9.05, and 9.32  $\tau$ . The peak at the highest field strength (9.32  $\tau$ ) is due to more of the successive  $\alpha$ -methylstyrene units. However, the MS units are probably not present in longer sequences since in such a case peaks should have been observed at still higher field strengths. It is probable that most of the MS units are present as MS-MS-AN or AN-MS-MS triads. The peak at 8.80  $\tau$  is due to more of the alternating AN-MS-AN triads. The multiplicity arises due to the cotactic configurations. As the AN content increases in Fig. 2B ( $\alpha$ -MS/AN = 56/44) and Fig. 2C ( $\alpha$ -MS/AN = 45/55), all the peaks shift towards lower field strengths, the peaks at 9.1-9.3  $\tau$  gradually diminish in intensity, and the intensity of the peak at 8.75  $\tau$  increases. This is attributed to the increased content of the alternating sequence (AN-MS-AN).

It is also apparent that the spectra in Figs. 2B and 2C, which have approximately equimolar composition, resemble that of the alternating copolymer (Fig. 1). Evidently the equimolar copolymers prepared by conventional free radical catalysts have a predominantly alternating sequence which is expected from the low reactivity ratios ( $r_{MS} = 0.1$ ,  $r_{AN} = 0.06$ ).

The sequence distribution in these copolymers calculated both on the basis of terminal [11] and penultimate [17] models is presented in Table 3. It is evident that there is no difference between the two models as to the AN centered triads because there is no difference in the  $r_{AN}$  and  $r_{AN}'$  values.

The difference is only apparent in Sample 2A where there is a difference in the MS centered triads. Since the cotactic configurations contributed to the multiplicity in the spectrum, it was not possible to obtain evidence for the penultimate effect which is known to exist in the  $\alpha$ -methylstyrene-acrylonitrile system [2]. The results in Table 3 indicate that in Copolymer 2B the MS and AN units are present as individual units to the extent of 85-90% and as expected the probability of cross-propagation is the highest for this sample. This explains why the spectra in Fig. 1 and Fig. 2B are indistinguishable.

An attempt was also made to calculate the coisotacticity probability parameter [11] ( $\sigma$ ) on the basis proposed by Ito et al. [12] for acrylate copolymers. Since the C-CH<sub>3</sub> protons of  $\alpha$ -methylstyrene units were of interest, the three main peaks at X ( $\sim$ 8.75-8.80  $\tau$ ), Y ( $\sim$ 8.95-9.05  $\tau$ ), and Z ( $\sim$ 9.1-9.3  $\tau$ ) were taken into consideration. As presented earlier, the methyl proton resonance in the alternating sequence (AN-MS-AN) has been shown to occur in all the three areas (X, Y, Z) under consideration. Analogous to the spectrum of poly- $\alpha$ -methylstyrene, all the MS-MS-MS

Table 3. Sequence Distribution in  $\alpha$ -Methylstyrene-Acrylonitrile Copolymer

Copolymer model	2A		2B		2C	
	Terminal <sup>a</sup>	Penultimate <sup>b</sup>	Terminal	Penultimate	Terminal	Penultimate
P <sub>MS-AN</sub> <sup>a</sup>	0.526		0.909		0.989	
F <sub>MS-MS-MS</sub>	0.225	0.129	0.008	0.004	0.000	0.000
F <sub>MS-MS-AN</sub>	0.498	0.546	0.166	0.156	0.022	0.020
F <sub>AN-MS-AN</sub>	0.277	0.326	0.826	0.840	0.978	0.980
P <sub>AN-MS</sub> <sup>a</sup>	0.993		0.943		0.649	
F <sub>AN-AN-AN</sub>	0.000	0.000	0.003	0.003	0.122	0.122
F <sub>AN-AN-MS</sub>	0.014	0.014	0.108	0.108	0.457	0.457
F <sub>MS-AN-MS</sub>	0.986	0.986	0.889	0.889	0.421	0.421
P <sub>C</sub> <sup>c</sup>	0.522		0.857		0.642	

<sup>a</sup>P<sub>MS-AN</sub> and P<sub>AN-MS</sub> were calculated on the basis of the terminal model from reactivity ratios  $r_{MS} = 0.1$ ,

$r_{AN} = 0.06$  [3].

<sup>b</sup>Triads on the basis of the penultimate model calculated from reactivity ratios  $r_{MS} = 0.55$ ,  $r_{MS}' = 0.93$ ,  $r_{AN} = r_{AN}' = 0.06$  [2].

<sup>c</sup>Probability of cross propagation  $P_C = P_{MS-AN} \times P_{AN-MS}$ .

sequences are assumed to absorb in the highest field (Z). Assuming that the peak separations are caused only by the nearest neighboring acrylonitrile unit and that the distribution of the methyl proton resonance for any type of triad is constant, the following equations were used in calculating the coisotacticity parameter  $\sigma$ .

$$F_X = \sigma^2 F_{\text{AN-S-AN}}$$

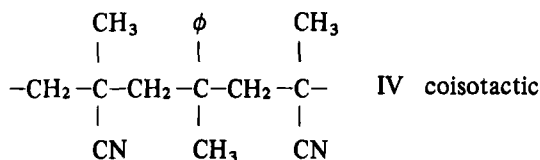
$$F_Y = 2\sigma F_{\text{MS-MS-AN}} + 2\sigma(1 - \sigma)F_{\text{AN-MS-AN}}$$

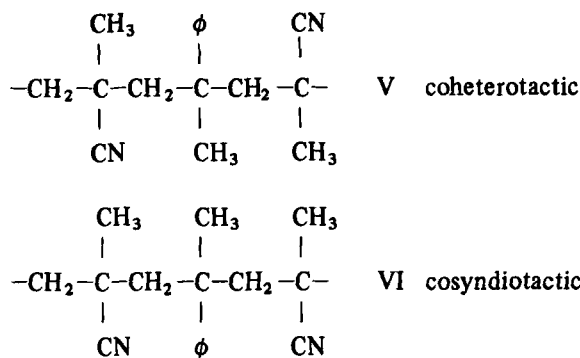
$$F_Z = F_{\text{MS-MS-MS}} + 2(1 - \sigma) F_{\text{MS-MS-AN}} + (1 - \sigma)^2 F_{\text{AN-MS-AN}}$$

The value of  $\sigma$  was estimated to be  $0.85 \pm 0.1$ , indicating a high probability of coisotactic placement of the MS and AN units which would be attributed to the interaction of the methyl group with the nitrile group. This high coisotacticity is also manifested in the polymerization of the  $[\text{MS}^+ \cdot \text{AN} \cdot \cdot \cdot \text{AlEt}_{1.5}\text{Cl}_{1.5}]$  complex, as shown earlier in Table 2.

#### $\alpha$ -Methylstyrene–Methacrylonitrile Copolymer (MS-MAN)

Figure 3 presents the NMR spectra of alternating and random MS-MAN copolymers of equimolar composition. Figure 3A presents the NMR spectrum of the alternating copolymer. The aromatic protons appear in the range 2.4-3.2  $\tau$ . The backbone methylene protons (belonging to both  $\alpha$ -methylstyrene and methacrylonitrile units) overlap with the C-CH<sub>3</sub> protons resonance of methacrylonitrile units and appear together in the range 7.6-8.9  $\tau$ . The multiplicities observed in the region 8.5-8.9  $\tau$  could be due to the contribution of the cotactic configurations. The significant characteristic is the appearance of the  $\alpha$ -methyl protons of the MS units in several peaks in the range 8.9-9.8  $\tau$ . The peaks at X (8.90-9.15  $\tau$ ), Y (9.15-9.60  $\tau$ ), and Z (9.60-9.85  $\tau$ ) are assigned to the coisotactic (IV), coheterotactic (V), and cosyndiotactic (VI) configurations.





The cotactic configurations are assigned by analogy to that of the MS-AN copolymer (I-III), i.e., the coisotactic configuration represents the  $\alpha$ -methyl group of the MS unit to be between the two nitrile groups of the neighboring MAN units and is thus assigned to the lowest field strength. These cotactic configurations are estimated to be present in the ratio X:Y:Z = 38:39:23, indicating the copolymer to be a random copolymer but having a slight preference for the coisotactic placement over the cosyndiotactic placement. This would reasonably be expected because of the interaction of the  $\text{CH}_3$  groups with the nitrile groups. This would also appear to be correct when considering the fact that in poly- $\alpha$ -methylstyrene, the syndiotactic configuration (the same as IV but CN is substituted by  $\phi$ ) is much more strongly favored over the isotactic configuration [10].

Figure 3B presents the NMR spectrum of the random copolymer of 1:1 MS-MAN composition. The peak positions and shapes are similar to those of the alternating copolymer but the fine structure is lacking. The broadening of the peaks is due to the contributions of the other sequences although the alternating sequence appears to be the major one ( $F_{\text{MAN-MS-MAN}} = 0.718$ ,  $F_{\text{MS-MAN-MS}} = 0.658$ ) as estimated from their reactivity ratios [3]:  $r_{\text{MS}} = 0.12$ ,  $r_{\text{MAN}} = 0.35$ . Thus the NMR spectra indicate that the random equimolar  $\alpha$ -methylstyrene-methacrylonitrile copolymers do not have as high an alternating tendency as observed in the  $\alpha$ -methylstyrene-acrylonitrile copolymers.

### Styrene-Methacrylonitrile Copolymer (S-MAN)

The NMR spectra of styrene-methacrylonitrile copolymers of varying compositions have been reported recently by Harwood et al. [18]. The

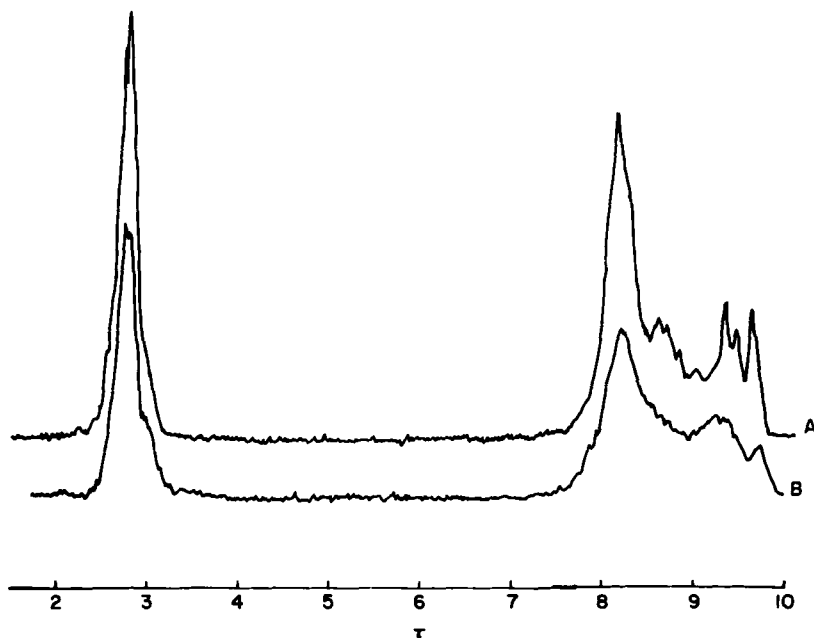


Fig. 3. NMR spectra of 1:1  $\alpha$ -methylstyrene-methacrylonitrile copolymers. (A) Alternating copolymer prepared by complexation with  $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ . (B) Random copolymer prepared with free radical catalyst.

methine proton (styrene) resonance was broken down and assigned to various styrene centered triads. In a similar manner the methyl proton (methacrylonitrile) resonance was broken down and assigned to various methacrylonitrile centered triads. The assignments were supported by matching the observed and calculated triad fractions. Evidence has also been provided for the pentad configurations.

The influence of the cotactic configurations on the NMR spectra of copolymers is well known. The alternating copolymer provides conclusive evidence for these effects. Figure 4A represents the NMR spectrum of the aliphatic protons of an alternating styrene-methacrylonitrile copolymer. The copolymer analysis indicates 48 mole % from elemental analysis and 50 mole % MAN from NMR analysis. The aliphatic protons appear in three general areas. The peak at 6.60-7.05  $\tau$  is assigned to the methine proton of styrene units. The broad single peak at 7.9-8.6  $\tau$  is assigned to the methylene protons belonging to both styrene and methacrylonitrile units. The peaks in the range 8.55-9.60  $\tau$  are assigned to the C-CH<sub>3</sub> protons of the methacrylonitrile

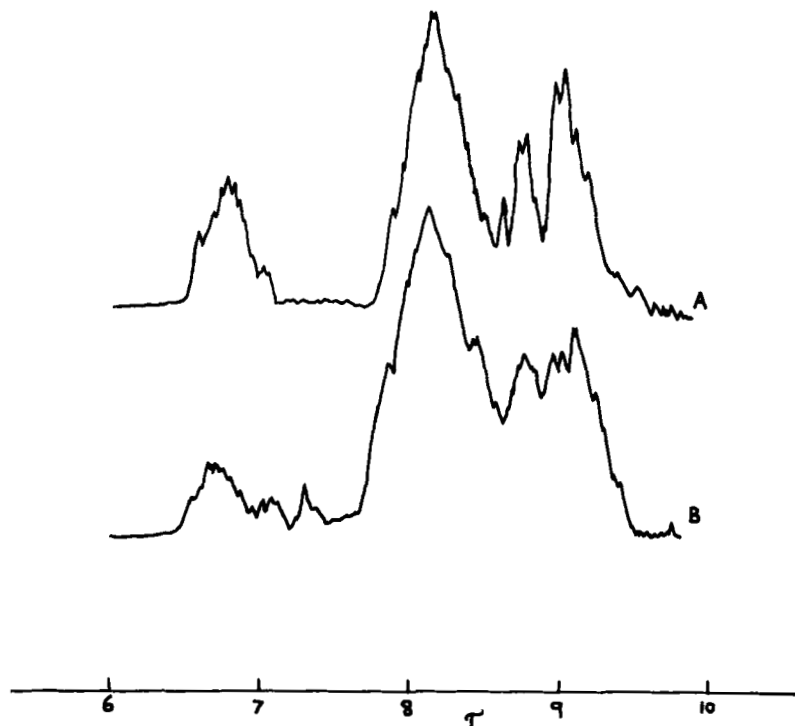
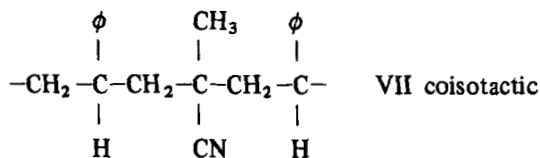
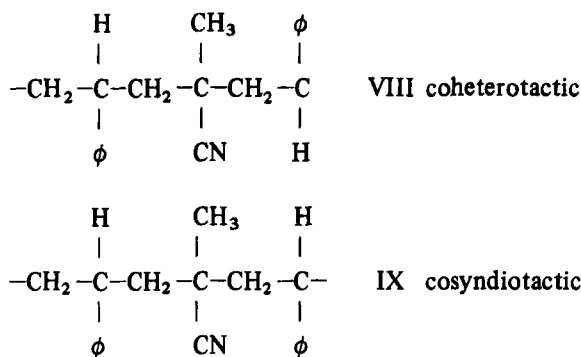


Fig. 4. NMR spectra of 1:1 styrene-methacrylonitrile copolymers. (A) Alternating copolymer prepared by complexation with  $AlEt_{1.5}Cl_{1.5}$ . (B) Random copolymer prepared with free radical catalyst.

units. These assignments are based on the relative peak area measurements and order of absorption. The significant feature is that the C-CH<sub>3</sub> proton resonance appears in three distinct peaks which are centered at 8.65  $\tau$  (X), 8.80  $\tau$  (Y), and 9.0  $\tau$  (Z) which are assigned to the cosyndiotactic (IX), coheterotactic (VIII), and coisotactic (VII) configurations, respectively.





The  $\text{CH}_3$  protons in the coisotactic configuration (VII) are expected to appear at the highest field strength. These cotactic configurations are estimated to be present in the ratio  $\text{X}:\text{Y}:\text{Z} = 6:27:67$ , indicating the copolymer has a high coisotactic configuration and a very low cosyndiotactic configuration. This is expected because of the strong steric repulsion in the cosyndiotactic configuration (IX). This is also in accordance with the relative cotactic configurations observed in the alternating MS-AN copolymer in which the Configuration III (corresponding to IX in S-MAN copolymer) is present to a low extent and Configuration I (corresponding to VII in S-MAN copolymer) is present to a very high extent. The observed splitting of the peaks is due to the configurations of the remote units, e.g. pentads.

In contrast, Fig. 4B presents the aliphatic protons in the NMR spectrum of a random 50:50 S-MAN copolymer. The methine proton resonance appears in the range 6.45-7.45  $\tau$  in which essentially three separate peaks are observed. This, however, does not correspond to the resonance expected from elemental analysis, an observation similar to that made by Harwood et al. [18]. The  $\text{C}-\text{CH}_3$  proton resonance of methacrylonitrile units appears in the range 8.5-9.5  $\tau$  which is also partly overlapped by the methylene proton resonance. The several signals observed could be due to the pentad configurations. The resonance at 8.5-8.8 and 8.8-9.5  $\tau$  had been assigned to the MAN-MAN-S and S-MAN-S triads, respectively. However, as shown in Fig. 4A, the alternating copolymer having S-MAN-S triads only exhibited methyl proton resonance in the entire range 8.55-9.60  $\tau$  in which the configurational effect was prominent. Thus the appearance of several signals for the methyl protons in Fig. 4B is not only due to the pentads but also due to the cotactic configurations.

It would appear that the methyl proton resonance of the random



copolymer is relatively not as sharp as that for the alternating copolymer although there is some general resemblance. The general resemblance would be due to the presence of the alternating sequence to a major extent ( $F_{S-MAN-S} = 0.630$ ,  $F_{MAN-S-MAN} = 0.730$ ), as expected from the reactivity ratios [18]:  $r_S = 0.17$ ,  $r_{MAN} = 0.26$ . Thus, here again the NMR spectra reveals that the random equimolar S-MAN copolymers do not have the high alternating tendency observed in the  $\alpha$ -methylstyrene-acrylonitrile copolymers.

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