Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Patnaik, Birendra , Takahashi, Akio and Gaylord, Norman G.(1970) 'Donor-Acceptor Complexes in Copolymerization. IV. Alternating Tendency in Free Radical Copolymerization. NMR Analyses of Alternating and Random Copolymers', Journal of Macromolecular Science, Part A, 4: 1, 143 — 157

To link to this Article: DOI: 10.1080/00222337008060970

URL: http://dx.doi.org/10.1080/00222337008060970

J. MACROMOL. SCI.–CHEM., A4(1), pp. 143-157, January, 1970

Donor-Acceptor Complexes in Copolymerization. IV. Alternating Tendency in Free Radical Copolymerization. NMR Analyses of Alternating and Random Copolymers

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SUMMARY

An NMR investigation was carried out on variable composition, random and equimolar, alternating copolymers of acrylonitrile (A) with styrene (S), isoprene (I), and butadiene (B). The NMR spectra of the SA copolymers contained peaks at 3 τ (aromatic ring protons), 7.2-7.5 τ (CH protons of A), and 8.1-8.5 τ (CH and CH_2 protons of S and CH_2 protons of A). All NMR peaks of the alternating SA copolymer were shifted to the higher field due to the shielding effect of S. The NMR spectra of the IA copolymers contained peaks at 4.72-4.91 τ (=CH protons of I), 7.27-7.4 τ (CH protons of A), 7.71-7.93 τ (CH_2 protons of I), and 8.35 τ (CH_3 protons of I and CH_2 protons of A). The peaks at 4.72 τ (=CH) and 7.72 τ (CH_2) were assigned to I in the I-A diad and the peaks at 4.91 τ (=CH) and 7.93 τ (CH_2) were assigned to I in the I-I diad. The NMR spectra of the BA copolymers contained peaks at 4.4-4.6 τ (=CH protons of B), 7.2-7.5 τ (CH protons of A), 7.71-7.97 τ (CH_2 protons of B), and 8.0-8.4 τ (CH_2 protons of A). The peaks at 4.42 τ (=CH) and 7.71 τ (CH_2) were assigned to B in the B-A diad and the peaks at 4.6 τ (=CH) and 7.9 τ (CH_2) were assigned to B in the B-B diad. The alternating structure of the copolymers prepared through metal halide-activated complexes was confirmed by NMR analysis. The random copolymers prepared by free radical initiation contain a high concentration of alternating sequences, as anticipated from the values of r_1 and r_2 where r_1(S, I, and B) is 6-10 times higher than r_2 (A).

INTRODUCTION

The tendency to alternation of comonomer units in free radical copolymerization has long been discussed in relation to the monomer reactivity ratio, the formation of a transitory complex between the growing radical end and the incoming monomer, and the polarity of the comonomers.

However, since the alternating structure has been based on the chemical composition of the copolymer obtained from elemental analysis, the actual sequence distribution of monomer units in the copolymer chain could not be determined, with the exception of the copolymerization system in which only alternating copolymer always resulted, irrespective of monomer charge, e.g., styrene-maleic anhydride.

As a result of recent developments in NMR analysis, a number of polymer structures have been successfully determined and it has become possible to determine the distribution of monomers in a copolymer.

In this study an attempt has been made to analyze the sequence distribution of styrene-acrylonitrile, isoprene-acrylonitrile, and butadiene-acrylonitrile in their copolymer backbones, and the results are discussed in relation to the monomer reactivity ratio.

NMR investigation of styrene-acrylonitrile copolymers has been limited to two areas, composition analysis [1, 2] and the calculation of reactivity ratios based on the composition obtained by NMR analysis [3].

NMR investigation of isoprene polymers has been limited to polyisoprene [4-7], isoprene-butadiene [8], and isoprene-isobutylene [9] copolymers. The emphasis in these studies has been on the microstructure and the composition of the polymers.

The configuration, microstructure, and composition of polybutadiene and copolymers of butadiene with isoprene and styrene have been characterized by NMR [10-12]. Although butadiene-acrylonitrile copolymers have not been studied in detail, some information regarding the alternating structure has been reported by Furukawa and Iseda [13].

EXPERIMENTAL

Styrene-Acrylonitrile Copolymers

The random copolymers were prepared in bulk at 60°C using benzoyl peroxide as the initiator. The reaction was stopped in all cases at less than 8% conversion.

The 1:1 alternating copolymer was prepared by the procedure of Gaylord and Antropiusova [14]. A solution containing styrene, acrylonitrile, and benzoyl peroxide was inserted by means of a hypodermic syringe through a self-sealing rubber cap into a reaction flask which contained anhydrous zinc chloride, and was flushed with nitrogen and kept at 25°C. The reaction mixture was stirred in a nitrogen atmosphere until approximately 5% monomer conversion was obtained, and the reaction was then terminated by the addition of acetone containing hydroquinone. The acetone solution of the reaction product was poured into a large amount of methanol to precipitate the copolymer.

The copolymers were dissolved in chloroform or dimethyl sulfoxide, reprecipitated into methanol, and dried at 40°C in vacuo to constant weight. The chemical composition was calculated from the nitrogen analysis.

The NMR spectra of the free radical-initiated samples (Fig. 1) were examined in $CDCl_3$ or dimethyl sulfoxide-d_6 (DMSO-d_6) at 31°C, and the alternating copolymers were examined in $CDCl_3$ at 70°C at 100 Mc.

Diene-Acrylonitrile Copolymers

Copolymers containing isoprene and acrylonitrile in 47/53 and 42/58 mole ratios were prepared from 35/65 and 10/90 monomer charges in bulk at 50 ± 5°C using t-butyl peroxypivalate as the radical initiator. The reactions were terminated at less than 10% monomer conversion and the copolymers were precipitated into methanol. A copolymer containing butadiene and acrylonitrile in a 43/57 mole ratio was similarly prepared from a 10/90 monomer charge.

The other random diene-acrylonitrile copolymers were prepared in emulsion according to the method described in Ref. [15].

The 1:1 diene-acrylonitrile alternating copolymers were prepared according to the procedure of Gaylord and Takahashi [16], which involves substantially the same technique as in the preparation of the 1:1 styrene-acrylonitrile alternating copolymer using zinc chloride or ethylaluminum sesquichloride as complexing agent. The reactions were carried out both in the presence and in the absence of t-butyl peroxypivalate at 50 ± 5°C and were terminated at less than 5% monomer conversion. Although the resulting copolymer composition is always equimolar, independent of monomer charge, the reaction was generally carried out with monomer charges containing more acrylonitrile than diene.

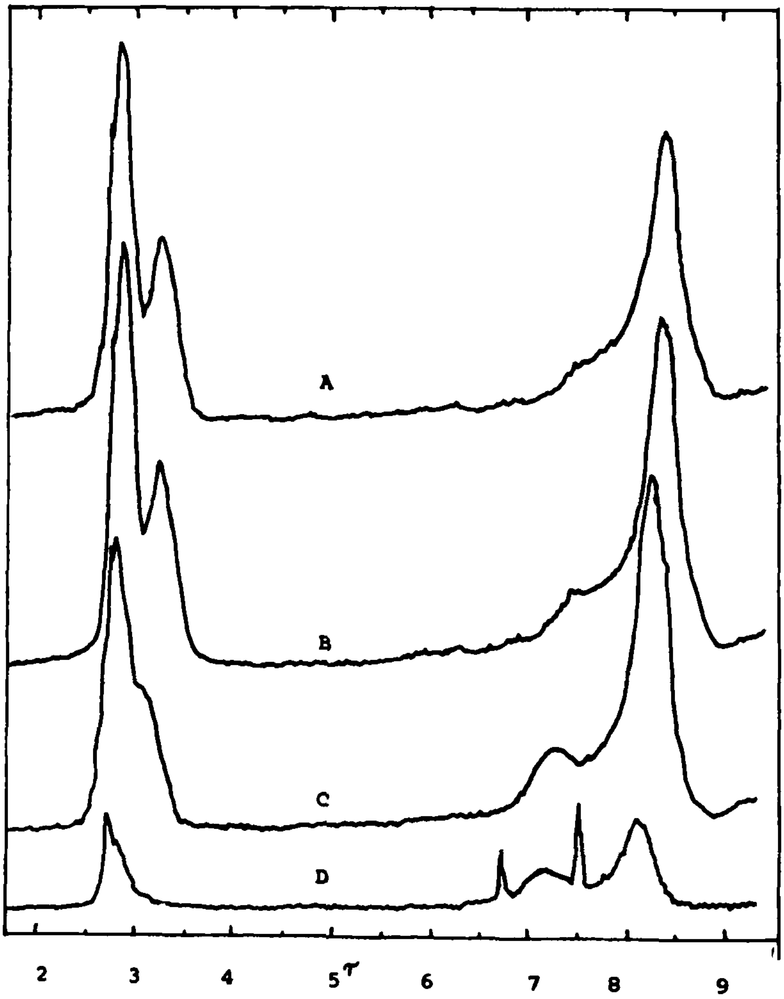


Fig. 1. NMR spectra of styrene-acrylonitrile copolymers prepared with free radical catalysts. Copolymer composition S/AN (mole ratio): (A) 71/29; (B) 65/35; (C) 45/55; (D) 30/70.

The copolymers were dissolved in chloroform, reprecipitated into methanol, and dried at 40°C in vacuo to constant weight.

RESULTS AND DISCUSSION

As shown in Table 1, both r_1 (styrene, isoprene, or butadiene) and r_2 (acrylonitrile) are very small and hence suggest that there would be a strong alternating tendency for M_1 and M_2 in the three comonomer systems. Further, since r_1 is considerably higher than r_2, M_1 would tend to be present in longer blocks, in addition to the alternating tendency of M_1 and M_2. Therefore, if the copolymers obtained at low conversion of monomers are analyzed as containing less than 50 mole % of acrylonitrile, the acrylonitrile (A) unit of the copolymer must be surrounded by M_1, i.e., styrene (S), isoprene (I), or butadiene (B), to give an $-M_1M_1AM_1-$ sequence. If the copolymer contains more than 50 mole % of M_2, then A–A–A blocks result.

Table 1. Reactivity Ratios

M_1-M_2	r_1	r_2	Ref.
Styrene-acrylonitrile	0.37-0.52	0.03-0.06	[17-19]
Isoprene-acrylonitrile	0.29-0.45	0.03-0.05	[20]
Butadiene-acrylonitrile	0.28-0.46	0.0 -0.05	[20]

Therefore, the alternating tendency of A in the copolymer containing less than 50 mole % of A would be very high when compared with that in the copolymer containing more than 50 mole % of A, while the exact opposite would be the case for M_1, although the block tendency would be high for M_1 such as S, I, and B monomers. Therefore, if the copolymers are analyzed as 1:1 molar compositions, they should have alternating monomer sequences, irrespective of whether they are prepared by the conventional free radical system or the metal halide-complexed system.

These postulates based on the reactivity ratios should be readily demonstrated by NMR investigation of the copolymers containing varying ratios of monomers, and the results may be compared with those from the alternating copolymers obtained from the metal halide systems [13, 14, 16, 21, 22]. In fact, this should be a most effective physical method to prove the alternating structure of the copolymer whose composition is indicated, by the chemical analysis and by the nature of the copolymerization reaction, to be a 1:1 copolymer, irrespective of monomer charge ratio.

Styrene-Acrylonitrile (SA) Copolymer

The NMR spectra of the SA copolymers of different composition, prepared by the conventional free radical catalysts, are presented in Fig. 1. In general, the peaks appear in three areas of the spectrum. The peak at ~3 τ is obviously due to the aromatic ring protons. The peak at ~7.2-7.5 τ is due to the methine of A and is due to the fact that in polyacrylonitrile the methine proton appears at a lower field than the methylene protons. The area under this peak decreases as the A content in the copolymer decreases. In addition, the area under this peak (Fig. 1C and Fig. 2) corresponds to only one proton. The peak at the highest field strength (~8.1-8.5 τ) is assigned to the methylene protons of A and the methine and methylene protons of S.

Sample 1D in Fig. 1 (S/AN = 30/70) was run in DMSO-d_6 and the peaks centered at 6.75 and 7.5 τ are due to the water absorbed in the solvent and the hydrogen atoms remaining in dimethyl sulfoxide-d_6 (DMSO-d_6).

It would appear that in all of these samples the aromatic protons appear in two peaks due to the ortho and meta-para protons. The aromatic protons have shifted to a lower magnetic field as compared to polystyrene because of the A units in the backbone, and as the A content increases, the aromatic protons shift downfield.

In Fig. 1A the α-methine proton of A absorbs at a higher field than the corresponding proton in polyacrylonitrile because of the shielding provided by the neighboring S units. In Fig. 1A the α-methine proton peak is broadened because of partial overlapping of the other backbone protons due to both S and A. As the A content increases, the peak takes a more definite shape, as in Fig. 1C and D, and its position approaches the absorption observed in polyacrylonitrile, indicating the presence of more A-A diads (Fig. 1D). It would appear that the α-methine proton absorption of A is more broadened in Fig. 1D (S/A = 30/70) than in Fig. 1C (S/A = 45/55). Similar effects are also observed with the methylene proton absorption in all the samples.

Figure 2 illustrates the NMR spectra of SA 1:1 alternating copolymers prepared by complexation with $ZnCl_2$ both spontaneously (Fig. 2A) and catalyzed by a free radical catalyst (Fig. 2B). Both spectra run at 100 Mc in $CDCl_3$ at 70°C are identical. In these spectra there are three principal areas of sharp absorption. The aromatic ring protons appear as two peaks around 3 τ. The α-methine proton of A appears as a single peak around 7.35 τ, and the other backbone protons are centered around 8.33 τ. The

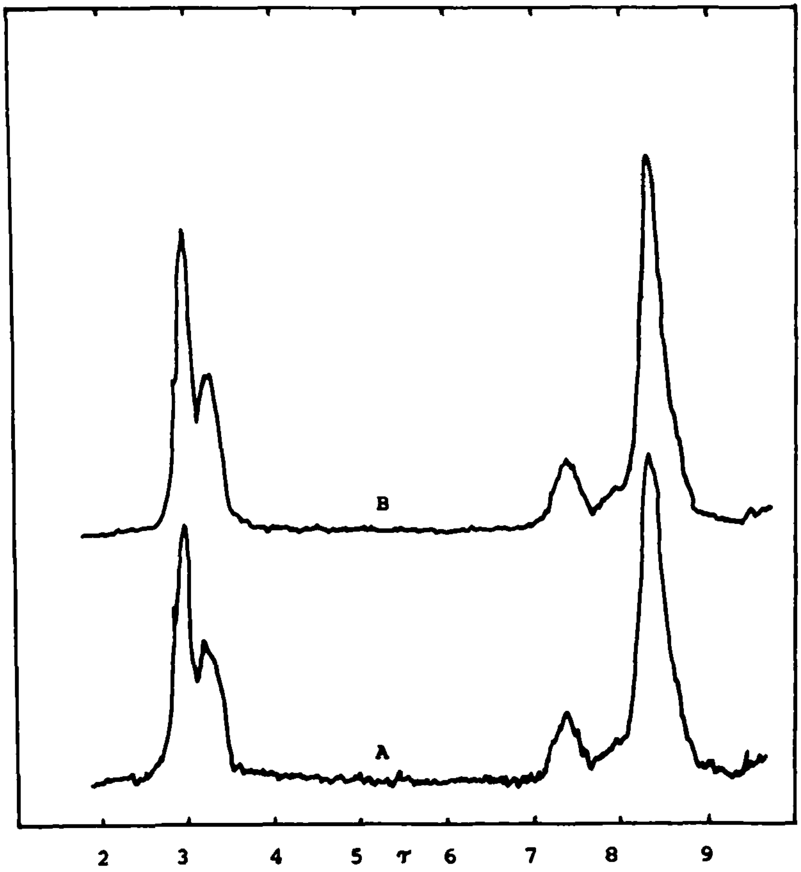


Fig. 2. NMR spectra of 1:1 alternating styrene-acrylonitrile copolymer prepared by complexation with $ZnCl_2$. (A) Spontaneous; (B) benzoyl peroxide catalysis.

SA copolymer prepared using ethylaluminum sesquichloride also exhibits an identical spectrum.

The copolymers prepared by complexation with metal halides are considered to be alternating equimolar copolymers [14, 21]. The splitting in the phenyl resonance (Fig. 2A and B) might be considered as due to the diamagnetic shift of the ortho proton arising from successive styrene units. However, it is generally understood that this is also due to all other environmental groups [23]. Similar splitting of the phenyl resonance has

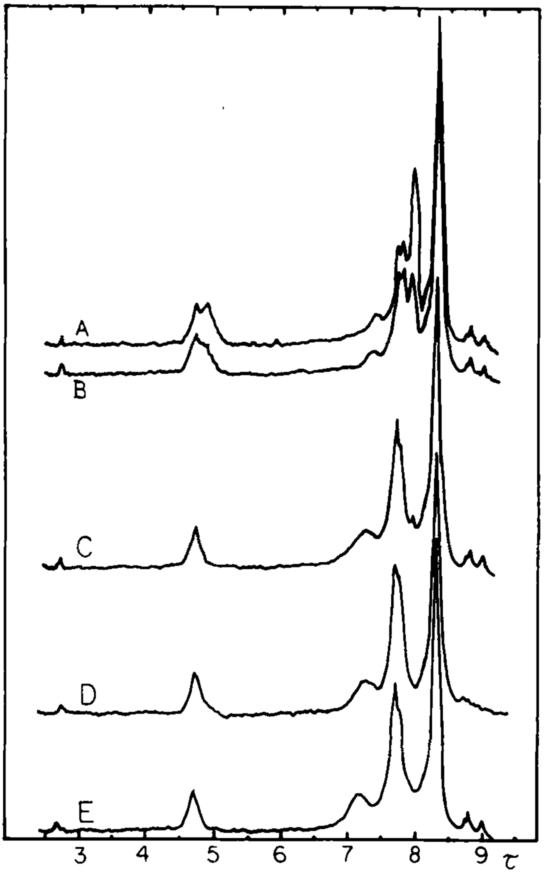


Fig. 3. NMR spectra of isoprene-acrylonitrile copolymers. (A, B, C, E) Prepared with free radical catalysts; (D) prepared in the presence of $ZnCl_2$ or $Et_{1.5}AlCl_{1.5}$. Copolymer composition I/AN (mole ratio): (A) 73/27; (B) 64/36; (C) 53/47; (D) 50/50; (E) 42/58.

also been observed in 1:1 styrene-methyl methacrylate alternating copolymers [21].

It is also apparent that the spectra in Fig. 2 resemble the spectrum in Fig. 1C which has an approximately 1:1 (S/A = 45/55) composition. It is of interest to note that equimolar SA copolymers prepared by conventional radical copolymerization exhibit infrared spectra, differential thermal analysis, and X-ray patterns which are indistinguishable from the corresponding copolymers prepared through complexation with $AlEt_{1.5}Cl_{1.5}$ [21].

The 1:1 SA copolymer prepared by the conventional free radical catalyst apparently has a predominantly alternating structure. This is supported by the reactivity ratios and the probabilities of the sequence distribution based on the radical effect indicates a 75-80% alternating sequence.

Isoprene-Acrylonitrile (IA) Copolymer

The NMR spectra of the IA copolymers are presented in Fig. 3. The peaks centered around 4.75 τ are due to the olefinic protons in the I unit. The peak at 7.35 τ is ascribed to the methine proton of the A unit. The peaks around 7.7-7.95 τ are due to the chain methylene protons belonging to the I unit. The methyl protons of I along with the methylene protons of A are observed at the highest field strength at about 8.35 τ. This has been arrived at from measurement of relative peak areas and comparison with a BA copolymer. In the NMR spectra, however, no 3,4-polyisoprene could be detected. This suggests that the I units are almost exclusively present in 1,4 configuration. In polyisoprenes, the cis- and trans-1,4 configurations can be differentiated from the methyl proton resonance. In these copolymers the methyl protons appear in a single peak, and it is assumed that the I units are present in all trans structure by analogy with the almost exclusively trans structure present in the corresponding BA copolymers.

In Fig. 3, spectra A, B, C, and E represent the IA copolymers of different compositons whereas the spectrum in Fig. 3D is that of the 1:1 alternating copolymer. It would appear that, whereas in the spectrum in Fig. 3D the peaks are all sharp and do not exhibit multiplicity, the random copolymers prepared by a free radical catalyst exhibit either broad peaks or multiplicity in the peaks. This is due to the different sequence distributions. In the case of 1:1 IA alternating copolymer the olefinic protons appear at 4.72 $\tau$and the methine proton of A appears at 7.27 τ. The assignment of the methine proton of A is based on the lower-field absorption of the methine proton compared to the methylene proton in polyacrylonitrile and the relative peak area measurement. The peak at 7.72 τ is assigned to the methylene protons of isoprene units present in the isoprene-acrylonitrile diad. The peak at 8.32 τ is assigned to the methyl protons of the I units and the methylene protons of the A units.

In addition to the alternating IA sequence, other sequences such as A-I-I and I-I-I should be present in the sample in Fig. 3A which has a 73/27 I/A composition. The olefinic proton appears as three peaks at 4.72, 4.80, and 4.91 τ. These peaks are assigned essentially to the A-I-A,

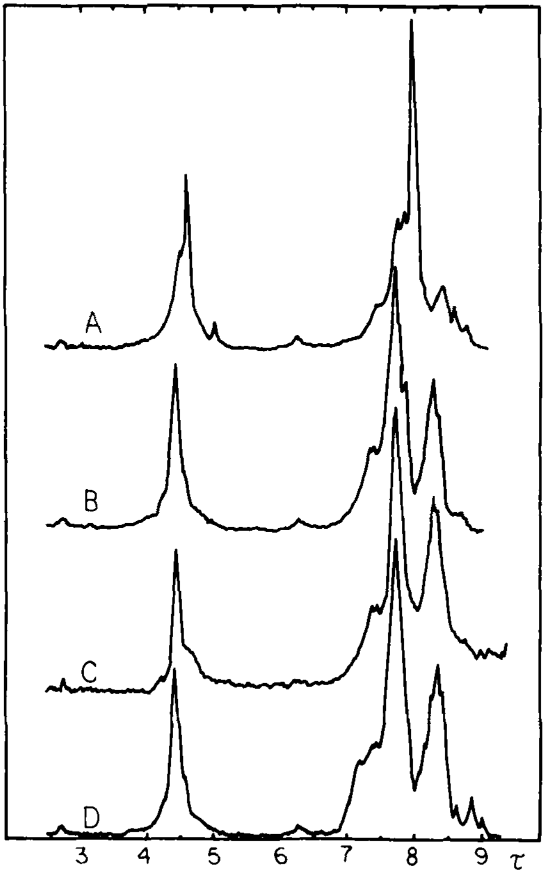


Fig. 4. NMR spectra of butadiene-acrylonitrile copolymers. (A, B, D) Prepared with free radical catalysts; (C) prepared in the presence of $ZnCl_2$ or $Et_{1.5}AlCl_{1.5}$. Copolymer composition B/AN (mole ratio): (A) 78/22; (B) 54/46; (C) 50/50; (D) 43/57.

A-I-I, and I-I-I sequences, although contributions by the different cotactic configurations cannot be ruled out.

The peak at 4.80 τ in Fig. 3B is more intense because of the presence of a greater number of A-I-I sequences. As the A content in the copolymers increases, the peaks at 4.80 and 4.91 τ become less intense and almost disappear.

The peak at 7.4 τ in Fig. 3A is assigned to the methine proton of A.

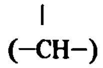
The intensity of the peak increases and the peak shifts toward the lower field approaching that of polyacrylonitrile with the increase in the A content, which is expected due to the deshielding effect and the increased A-A diad content.

The peaks at 7.71-7.93 τ are assigned to the methylene protons of the I units only. This appears as three distinct peaks in Fig. 3A and B depending on the sequence distribution. The peak at 7.93 τ is assigned to the methylene units present in I-I diads. The peaks at 7.72 and 7.78 τ are assigned to the methylene protons of I in A-I-A and A-I-I sequences. As the A content increases, the intensity of the 7.93 τ peak decreases and ultimately disappears. The methylene protons of I in the alternating 1:1 copolymer (Fig. 3D) show a small shoulder at 7.78 τ. The spectrum of this sample when run at 70°C (not shown in the figure) showed three peaks at 7.72, 7.77, and 7.82 τ. This is possible due to the contributions by the cotactic configurations of the I and A units. The close spacings could be attributed to the flexible nature of the copolymer chain.

It would appear that the spectra in Fig. 3C and D are almost identical except for a shoulder at 7.93 τ in Fig. 3C due to the I-I diad. The sample of Fig. 3C analyzes for an almost equimolar composition, and its spectrum indicates that it has a very high content of 1:1 alternating sequences.

Butadiene-Acrylonitrile (BA) Copolymer

The NMR spectra of the BA copolymers are presented in Fig. 4. There are four principal areas of absorption. The peaks at 4.4-4.6 τ are assigned to the olefinic protons in the 1,4 configuration of B. The olefinic protons ($=CH_2$) in 1,2 configuration appear at 5.0 τ. The peaks around 7.2-7.5 τ are due to the methine proton of A, which was arrived at from the relative peak position in polyacrylonitrile and the peak area. The peaks at 7.7-8.0 τ are assigned to the methylene protons of the B units, supplemented by the chain methine protons



$$(-\overset{|}{C}H-)$$

present in the 1,2 configuration of the B unit. The peaks at 8.0-8.4 τ are assigned to the methylene protons of the A units. The B units are essentially present in 1,4-trans structure. The infrared spectrum indicates that the trans content is more than 90%, the remainder being due to 1,2- and 1,4-cis configurations [16].

Samples A, B, and D in Fig. 4 were obtained with a free radical catalyst, whereas sample C is an alternating 1:1 copolymer. In sample C the olefinic protons appear at 4.42 τ, the methine proton of the A unit around 7.4 τ, the methylene proton of the B unit at 7.71 τ, and the methylene proton of the A unit at 8.3 τ.

Since the sample in Fig. 4A has a 78/22 B/A composition, it is expected from the reactivity ratios that B-B-B sequences would be present to a considerable extent, in addition to other sequences such as B-A-B and B-B-A. Thus, the main peak appears at 4.62 τ and is due to the presence of butadiene blocks, while the shoulder at 4.5 τ is possibly due to B-B-A sequences. When the B/A compositon is changed to 66/34 (spectrum not shown), the olefinic protons appear as three peaks at 4.42, 4.52, and 4.59 τ which are due to the contributions by all the possible sequences complemented by the possible cotactic configurations contributed by the alternating sequences. In the spectra of the samples of Fig. 4B and D, with B/A compositions of 54/46 and 43/57, respectively, the olefinic protons appear predominantly at 4.42 τ with a shoulder at 4.5 τ. It appears that the predominant sequence is the alternating sequence, accompanied by some B-B-A sequences. The B-B-B sequence is almost absent.

The methine proton of A appears at 7.5 τ in A and gradually shifts to lower fields with increase in the A content. It is of interest to note that in Fig. 4B, C, and D the peak position is at ~7.37 τ, which also shows that most of the A units are present in B-A-B sequences. A peak appears at 7.2 τ in Fig. 4D, possibly due to the B-A-A sequences resulting from the presence of higher A content.

The methylene protons of the B units appear in the region 7.70-7.97 τ. In Fig. 4A, the major peak appears at 7.97 τ due to the extensive B blocks. The small peaks at 7.77 and 7.85 τ are due to the other sequences. When the A content increases to 34 mole % (not shown), the intensity of the peak at 7.97 τ decreases and it shifts to lower field strength to 7.90 τ, while correspondingly the other peaks increase in intensity and shift to 7.71 and 7.78 τ, respectively. In Fig. 4B the predominant peak is at 7.71 τ accompanied by a small peak at 7.87 τ, due to the B-A-B and B-B-B diads, respectively. In Fig. 4D, where the B content of the sample is lower, the exclusive absorption is at 7.70 τ, which indicates the absence of B blocks as in the alternating copolymer (Fig. 4C).

The methylene protons of A units appear at 8.2-8.4 τ. In Fig. 4A the peak appears at 8.4 τ. As the A content increases, the intensity of this peak increases and the peak shifts to lower wavelengths.

In Fig. 4D, where the A content of the sample is higher, the methylene proton appears as several peaks due to the presence of different sequences.

Table 2. Sequence Distribution in BA Copolymers

	A/B mole ratio		Calculated					Found
Copolymer	Charge	Found	P_{BA}[a]	F_{ABA}	P_{AB}[b]	F_{BAB}	P_C[c]	F'_{ABA}
A	15/85	22/78	0.369	0.137	0.990	0.980	0.365	0.134
E	31/69	34/66	0.599	0.359	0.974	0.949	0.583	0.368
B	65/35	46/54	0.861	0.742	0.900	0.810	0.775	0.773
D	90/10	57/43	0.968	0.937	0.647	0.419	0.626	0.844

[a] Calculated assuming $r_B = 0.3$ [20].
[b] Calculated assuming $r_A = 0.03$ [20].
[c] Probability of cross-propagation $P_{BA} \times P_{AB}$.

It was also observed that when the spectrum of the alternating copolymer of Fig. 4C was run at higher temperatures all the peaks corresponding to the different protons appeared as several peaks although they were more closely spaced as compared to copolymers such as styrene-methyl methacrylate and α-methylstyrene-methyl acrylate. These are due to the various cotactic configurations, and the close spacings are possibly due to the flexible nature of the polymer.

It was again noted that the NMR spectra of 1:1 copolymer samples prepared with free radical catalysts are not readily distinguishable from that of the alternating copolymer. This suggests the predominantly alternating sequences present in the free radical copolymers. This is plausible since each of the reactivity ratios is less than unity and the reactivity ratio of B monomer is at least six times higher than that of A monomer.

For further confirmation of the predominantly alternating structure of the essentially 1:1 free radical copolymers, the sequence distribution of several BA copolymers was calculated using Bovey's equation [24] and the results were compared with the values obtained from the NMR spectra. Since the B units in the copolymer were found to be present to more than 90% in trans-1,4 structure, the effect of cotactic configurations of the B units on the NMR spectra was neglected. The peak at 7.71 τ, assigned to the methylene protons of butadiene in the A-B-A triad, was sharp and distinguishable and was used for the calculation.

The results shown in Table 2 indicate that more than 90% of the A units in the copolymer are surrounded individually by B units at low A monomer compositions, whereas the same percentage of B units are surrounded by A units at high A monomer compositions. As expected, the probability for cross-propagation is highest at the monomer charge which leads to a 1:1 copolymer composition. Since the peak at 7.71 τ is assigned to the methylene protons of the B unit in the A-B-A triad, the area of this peak (F'_{ABA}) should match the calculated F_{ABA}.

As shown in Table 2, the results are in fairly good agreement. Some small deviations were noted for the values obtained from the copolymer having a high A monomer content. This might be due to the presence of cotactic configurations and/or the penultimate effect, which would affect either the F_{ABA} or the F'_{ABA} value.

Since F'_{ABA} for sample B in Table 2 closely matches the calculated F_{ABA} and F_{BAB} values, a predominantly alternating structure is indicated.

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Accepted by editor June 26, 1969
Received for publication July 29, 1969