Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Polymers. Part II.† Determination of Monomer Sequence Distribution in Butadiene–Acrylonitrile Copolymer

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Noise-decoupled carbon-13 n.m.r. spectra of a range of butadiene (B)–acrylonitrile (A) copolymers confirm the ' short-run ' alternation of acrylonitrile units in otherwise block butadiene. Direct measurements of individual peaks representing B-centred triads (BBB, ABB, ABA) can be made using the vinyl absorptions which, over a 10 p.p.m. range, show two peaks each for ABA, ABB, and BBA, together with one broad peak for BBB. The populations were plotted and extrapolated over the range 0—50 mole % acrylonitrile. Block acrylonitrile appears to be absent and essentially all the acrylonitrile exists in alternation (BAB). Deshielding effects on the vinyl carbon atoms due to nitrile groups and double bonds were quantitatively measured for each function at several distances; the results confirm the assignments. The methylene absorption indicates that the block butadiene units are linked predominantly in *trans,trans*-diads.

NATURAL abundance pulsed Fourier transform noise-decoupled carbon-13 n.m.r., which is rapidly becoming the single most useful diagnostic tool in the study of the microstructures of macromolecules, has been applied successfully to the characterization of vinyl polymers,[1,2] including acrylonitrile,[3,4] butadiene,[5] and the related copolymer, styrene–acrylonitrile.[6] We have now applied this technique for the first time to commercial butadiene–acrylonitrile copolymers.

A previous study [7] of butadiene (B)–acrylonitrile (A) copolymers containing 26—46% acrylonitrile by proton n.m.r. has demonstrated that the acrylonitrile units occur almost entirely in alternation with butadiene units as is expected from the widely differing monomer reactivity ratios ($r_A = 0{\cdot}03$; $r_B = 0{\cdot}18$); agreement was reached between the experimentally measured and the statistically calculated diads.[7] Small amounts only of AA diads are predicted at compositions up to 50% acrylonitrile. Styrene–acrylonitrile copolymers were likewise found to be highly alternating; a 40% acrylonitrile sample showed virtually all of the acrylonitrile as SAS units.[6]

RESULTS AND DISCUSSION

Six commercial samples of emulsion butadiene–acrylonitrile copolymers of nominal acrylonitrile composition 28, 33, 34, 36, 40, and 41 mole % have now been shown by carbon-13 n.m.r. to contain the acrylonitrile residues mainly in BAB triads, and we give quantitative data concerning their triad composition. A further sample, prepared by Furukawa and his co-workers using an alkylaluminium halide catalyst, was already known from proton n.m.r. and i.r. data to be fully alternating (with the butadiene units linked *trans*-1,4 predominantly),[8] and this is confirmed.

The n.m.r. spectrum in Figure 1(a) shows the undecoupled signals of the 41% acrylonitrile sample. Figure 1(b) shows the simplification of these same signals by the noise-decoupling technique and the

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† Part I, B. Ibrahim, A. R. Katritzky, A. Smith, and D. E. Weiss, preceding paper.

[1] V. D. Mochel, *J. Macromol. Sci.*, 1972, C8(2), 289.

[2] F. A. Bovey, ' High Resolution NMR of Macromolecules,' Academic Press, New York, 1972, p. 226.

[3] J. Schaefer, *Macromolecules*, 1971, **4**, 105.

[4] Y. Inoue and A. Nishioka, *Polymer Journal*, 1972, **3**, 149.

[5] M. W. Duch and P. M. Grant, *Macromolecules*, 1970, **3**, 165.

[6] J. Schaefer, *Macromolecules*, 1971, **4**, 107.

[7] D. F. Kates and H. B. Evans, Amer. Chem. Soc. (Div. Org. Coatings and Plastic Chem.), 1970, 1214. *Cf.* also T. Suzuki, Y. Takegami, J. Furukawa, E. Kobayashi, and Y. Arai, *Polymer J.*, 1973, **4**, 657.

[8] J. Furukawa, Y. Iseda, K. Haga, and N. Kataoka, *J. Polymer Sci.*, *Part A*-1, *Polymer Chem.*, 1970, **8**, 1147.

accompanying gain in signal-to-noise ratio by the resulting nuclear Overhauser effect. The samples were observed at probe temperature in $CDCl_3$ except for two (34 and 36%), which were studied at elevated temperature in pentachloroethane as solvent [Figure 2(a)]. Chemical shifts in the two solvents were very similar. No gain in sensitivity was observed at the elevated temperatures. Figure 2(b) shows the carbon-13 n.m.r. signals of the 50% fully alternating sample.

Absorption peaks are found in three regions: the sp^2-hybridized ' vinyl ' carbons around 130·95 p.p.m., the sp^3-hybridized ' methylene ' and ' methine ' carbons near 33·73 p.p.m., and the sp-hybridized ' cyanide ' carbons at 122·78 p.p.m. downfield from Me_4Si.

Vinyl Absorption.—The vinyl carbons are the most sensitive to the environment: they are identified in spectra (a)—(f) of Figure 3 and assigned in Figure 4. Examination of the vinyl regions reveals that in general seven absorptions occur (designated peaks I—VII); two sets of three peaks with one broad ' singlet ' occurring between them (Table 1). The fully alternating 50 : 50 copolymer sample shows only two peaks which correspond in position to the centre peaks of the two sets of three. These peaks, II and VI, must therefore represent the two vinyl carbons T and U (see Figure 4) in a BAB triad. The assignment of II to T and VI to U follows from their relative distance from the nearest CN group. In the spectra of all the other samples peaks II and VI are accompanied by a satellite on each side. These ' triplets,' *i.e.* I,II,III and V,VI,VII, resemble each other in each sample. We therefore assign the satellite peaks (I,III) and (V,VII) to special cases of the corresponding parent peaks (II) and (VI), respectively. Further, these satellites decrease in intensity relative to the parent peak with increasing acrylonitrile content and they are thus attributed to ABB and BBA triads. An ABA triad will show only two different vinyl carbon environments (T and U) whereas replacement of one A unit for a B unit to give ABB and BBA triads results in four new vinyl carbon environments (V,W,X,Y), each of the same population (see Figure 4). Peak IV in the vinyl absorption, which decreases to a nominal 5% at 40% acrylonitrile, must be due to the BBB triad (carbon Z). These assignments are consistent with the expected deshielding effects by the double bond (db) and nitrile group (CN) as listed at the top of Table 1.

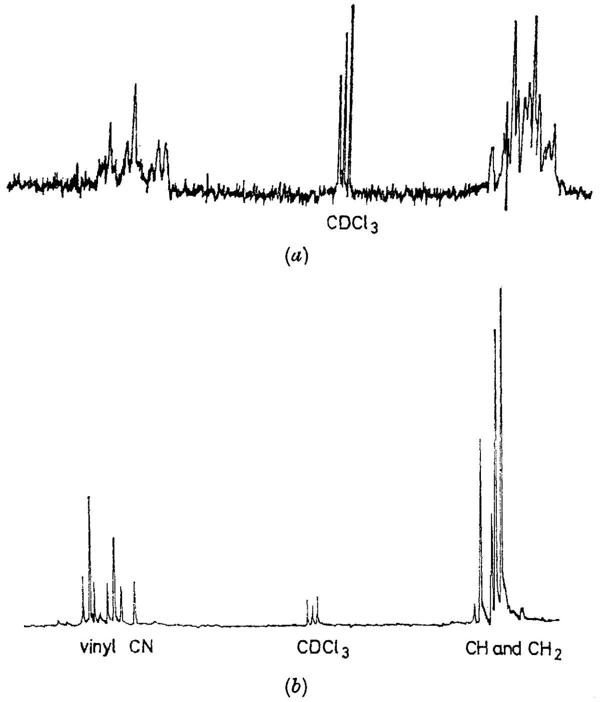

FIGURE 1 (*a*) Carbon-13 n.m.r. spectrum (25·2 MHz) of 41% acrylonitrile sample in $CDCl_3$ with external D_2O lock, 98,000 transients; (b) noise-decoupled carbon-13 spectrum of the same sample, 108,000 transients

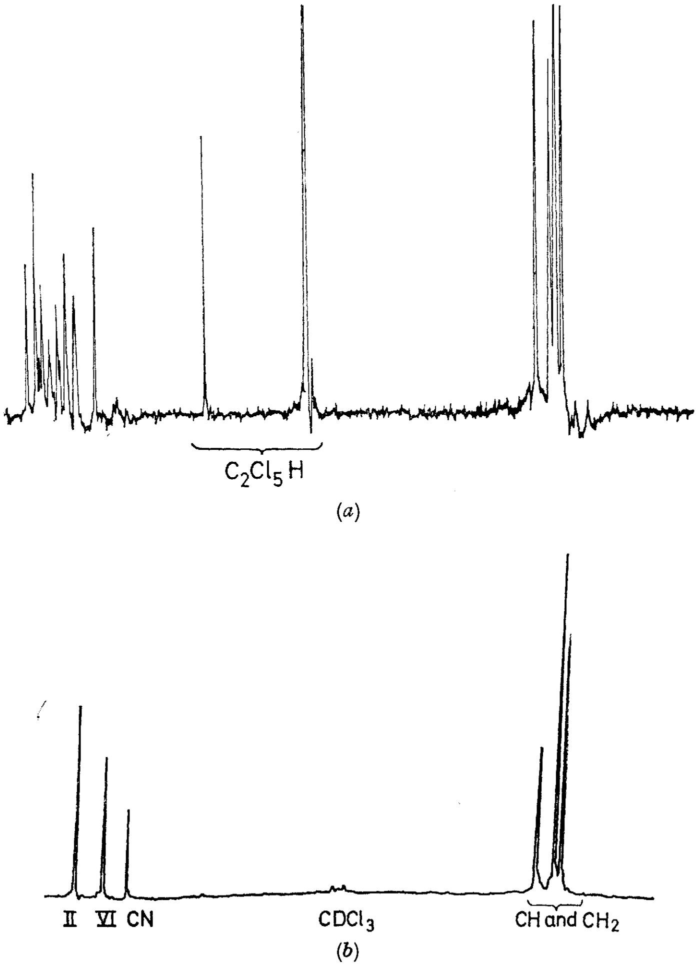

FIGURE 2 (a) Noise-decoupled carbon-13 n.m.r. spectrum (25·2 MHz) of 36% acrylonitrile sample in C_2Cl_5H with external D_2O lock; (b) noise-decoupled carbon-13 n.m.r. spectrum (25·2 MHz) of 50% acrylonitrile fully alternating sample in $CDCl_3$, external D_2O lock

Indeed such deshielding effects of a cyano-group or a double bond on a vinyl carbon [relative to the chemical

TABLE 1

Peak positions [a] and peak intensities [b] for vinyl absorption

Environment:[c]	CN(2) db(4)		CN(2) CN(4)		CN(3) db(3)		db(3) db(4)		CN(4) db(3)		CN(3) CN(3)		CN(3) db(4)	
Peak no.:	I		II		III		IV		V		VI		VII	
Carbon:	V		T		W		Z		X		U		Y	
Triad:	ABB		ABA		ABB		BBB		BBA		ABA		BBA	
Sample [d]	Posn.	Int.	Posn.	Int.	Posn.	Int.	Posn.	Int.	Posn.	Int.	Posn.	Int.	Posn.	Int.
28	135·4	8	133·7	6	132·7	8	131·2	21	129·5	10	127·8	9	126·0	10
33	135·4	7	133·7	10	132·7	10	131·3	12	129·5	9	127·8	10	126·1	9
34	135·7 [e]	11	134·1	13	132·9 [e]	9	131·7 [e]	9	130·0	8	128·3 [e]	9	126·7 [e]	7
36	135·6 [e]	9	133·9 [e]	11	132·9 [e]	9	131·5 [e]	8	129·9 [e]	7	128·2 [e]	11	126·6 [e]	9
40	135·4	6	133·7	15	132·7	7	131·2	5	129·5	6	127·7	14	126·0	7
41	135·5	8	133·7	15	132·7	5	131·3	5	129·5	7	127·8	14	126·1	5
50			133·7	29							127·8	21		

[a] Recorded in p.p.m. downfield from Me_4Si at 25·2 MHz. [b] Reported as % normalized absorption (see text for precise definition). [c] Number in brackets indicates distance (no. of carbons) of functional group from the vinyl carbon under consideration. [d] Mole % acrylonitrile. [e] These samples were run in C_2Cl_5H at 90°.

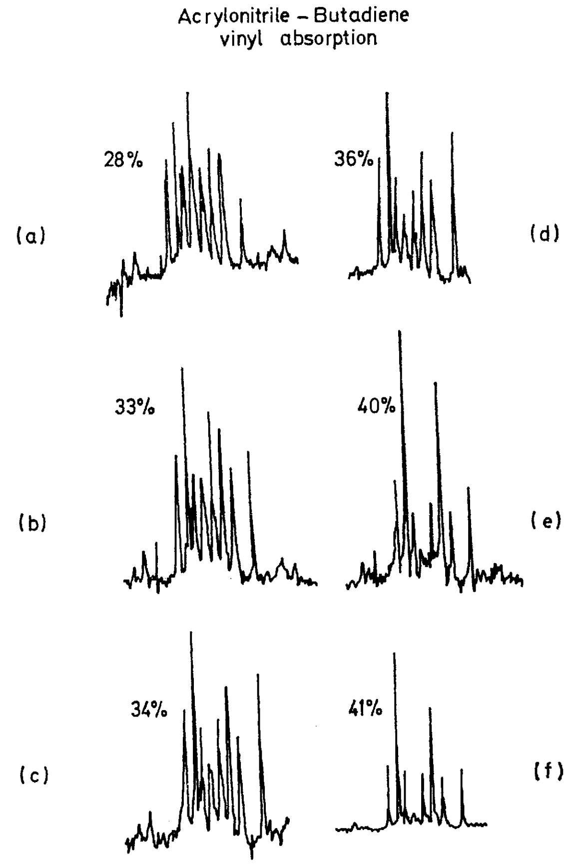

FIGURE 3 Noise-decoupled carbon-13 n.m.r. spectra of vinyl carbons for the 28% (a), 33% (b), 34% (c), 36% (d), 40% (e), and 41% (f) acrylonitrile samples of butadiene–acrylonitrile copolymer

shifts (131·2 p.p.m.) of the vinyl carbons for *trans,trans*-diads in *trans*-1,4-polybutadiene [9]] can be quantized as follows (in p.p.m.):

No. of carbon atoms away	2	3	4
Cyano-group	+7·9	−1·9	−5·3
Double bond		+3·6	−3·6

Use of these increments gives calculated chemical shifts which are in good agreement with those determined (Table 2).*

Small satellite peaks at each side of the vinyl absorptions at 142·1 and 118·2 p.p.m. are due to the small amount of 1,2-linked polybutadiene indicated present in these copolymers by Kates and Evans.[7] Their assignment is confirmed from a spectrum of 95% 1,2-poly-

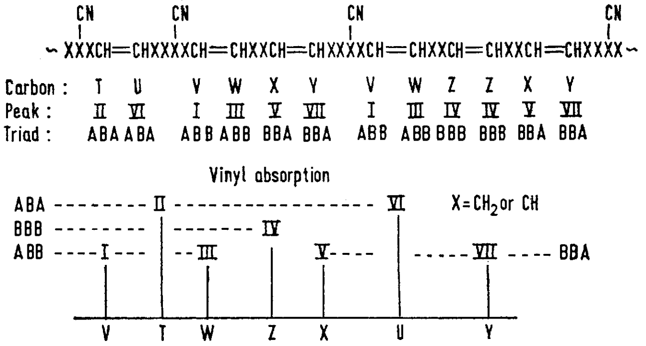

FIGURE 4 Composite of the butadiene–acrylonitrile chain showing the environments giving rise to seven types of vinyl carbon. A graphic representation of the vinyl absorption drawn to horizontal scale shows peak assignments. Carbon designations (letter), peaks (no.), and associated triads are indicated

TABLE 2

Observed and calculated [a] frequencies for peaks I—VII

Carbon	Peak	Obs. freq. (p.p.m.)	Calc. freq. (p.p.m.)
V	I	135·5	135·5
T	II	133·7	133·8
W	III	132·7	132·5
Z	IV	131·2	131·2
X	V	129·5	129·5
U	VI	127·8	127·5
Y	VII	125·9	125·8

[a] By summing the chemical shifts measured for the functional group neighbours (environment) and adding the sum to 131·2 (peak IV).

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* The method adopted requires five parameters to calculate seven shifts. An alternative calculation using four parameters for six shifts involves considering the effect only of the nitrile, two and three carbon atoms away with no intervening unsaturation (to give +4·3, −5·4), and three and four carbon atoms away with one intervening double bond (to give +1·3, −1·7). The four parameters are established by the frequencies of U, W, X, and Y, with only one cyano-substituent. The predicted shifts for T and U are +2·6 and −4·1 p.p.m., relative to Z, close to the observed shifts of +2·6 and −3·7 p.p.m., respectively.

butadiene by Mochel[10] showing peaks at *ca.* 142·9 and 114·1 p.p.m. Further, a sample of polybutadiene formed by n-butyl-lithium catalysis[10] was found to be 10·5% 1,2- and 89·5% 1,4-linked, suggesting that this may be typical of block polybutadiene.

sp^3-*Hybridized Carbon Absorption.*—The four peaks (VIII—XI) (Table 3) are assigned as follows. In the spectrum of the 50% alternating sample [Figure 2(b)], peak IX is not present; IX is accordingly assigned to carbons C, arising from block butadiene (Figure 5). Of the normalized intensities of peaks I—VII in Table 1, the similarity of the intensity of peak IV in Table 1 to the percent absorption of IX in Table 3 supports this assignment. Previous work by Furukawa[9] has shown that signals due to the block *trans,trans*-diads in polybutadiene occur at 33·7 p.p.m., in good agreement with our value of 33·6 p.p.m. We conclude that block butadiene in butadiene–acrylonitrile copolymers exists mainly in *trans,trans*-diads. The highest field peak (XI; 31·2 p.p.m.) is assigned to carbons A which are attached only to sp^3-hybridized carbon. Carbons D and B are each attached to one sp^2-hybridized and one sp^3-hybridized carbon, but B is γ to the cyano-group and is thus assigned to peak X (36·3 p.p.m.), with D, which is β to the cyano-group, assigned to VIII (32·5 p.p.m.).

TABLE 3

Peak positions[a] and peak intensities[b] for aliphatic, cyano, and solvent absorption

Region:	Cyano	Methylene and methine								Solvent[c,d]	
Peak no.:		VIII		IX		X		XI			
Carbon:	CN	D		C		B + E		A		$CDCl_3$	C_2Cl_5H
Sample	Posn.	Posn.	Int.	Posn.	Int.	Posn.	Int.	Posn.	Int.	Posn.	Posn.
28	122·8	36·3	17	33·6	30	32·5	29	31·2	22	†	
33	122·8	36·3	16	33·7	20	32·3	36	31·2	28	78·3	
34	122·7[f]	36·7[f]	17	33·9[f]	18	32·7[f]	35	31·5[f]	30		81·5
36	122·6[f]	36·7[f]	17	33·9[f]	23	32·7[f]	34	31·5[f]	26		81·3
40	122·7	36·3	19	33·5	15	32·5	36	31·2	30	78·3	
41	122·8	36·4	20	33·7	12	32·5	34	31·3	34	78·3	
50	122·7	36·2	25			32·5	47	31·2	28	†	

† Not assigned.
[a] Recorded in p.p.m. downfield from Me_4Si at 25·2 MHz. [b] Reported as % absorption. [c] Position of the centre peak of the C–D triplet in $CDCl_3$. [d] Position of the $CHCl_2$ peak in pentachloroethane. [e] Mole % acrylonitrile. [f] These samples were run in C_2Cl_5H at 90°.

The intensities of the sp^3-hybridized carbon peaks cannot in general be treated qualitatively owing to considerable overlap of triads (*i.e.* D = ABB, ABA, A = ABB, BBA, BAB). However, in the 50% sample the intensity of D is nearly identical with that of A, as predicted.

Cyano-carbon Absorption.—The CN carbon resonance is a sharp singlet in all samples observed [spectra (a)—(f) in Figure 3]. There is no broadening and diminished intensity which could result from ^{14}N quadrupole coupling. This is consistent with previous observations.[3,4,6] Lack of multiplicity in the CN signal is not due to lack of sensitivity, since both CN and CH signals in the spectrum of polyacrylonitrile are clearly split into three peaks representing tactic triads.[3,4] Also, in styrene–acrylonitrile with high acrylonitrile content (98 and 92 mole %), there is multiplicity in these signals due to monomer sequence distribution (MSD) triads.[6] Therefore, we believe that the CN signal observed is due only to the BAB triad and no block AAA or significant amounts of AAB occur. It should follow that the percentage of BAB is the same as that of acrylonitrile in all samples studied. The spectrum in Figure 6 shows the effect of tris(acetylacetonato)chromium(III) on the 36% sample. This reagent is known to reduce the relaxation times for carbon nuclei and thus undermines the Overhauser effect in noise-decoupled n.m.r. spectra. While the vinyl and methylene carbons remain relatively unaffected (probably owing to their inaccessibility), T_1 both for the solvent signals and for the CN carbon (expected to be complex) is shortened. The enhanced CN signal is now a doublet, which indicates the sensitivity of the CN carbon to its environment. With chromium now complexed with CN groups, the frequency of the CN carbon becomes more sensitive to neighbouring CN groups and thus distinguished B*A*BA from B*A*BB. The two nearly equal peaks are expected, as in the 36%

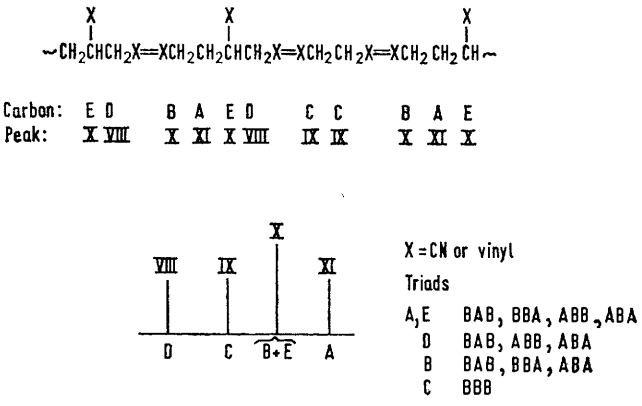

FIGURE 5 Composite of the butadiene–acrylonitrile chain showing the environments giving rise to four types of methylene carbon. A graphic representation of the aliphatic absorption drawn to horizontal scale shows peak assignments. Carbon designations (letter), peaks (no.), and associated triads are indicated

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[9] J. Furukawa, E. Kobayashi, T. Kawagae, N. Katsuki, and M. Imanari, *Polymer Letters*, 1973, **11**, 239.

[10] V. D. Mochel, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1972, **10**, 1009.

sample the populations of B*A*B and A*B*B + B*B*A (Figure 5) are nearly equal.

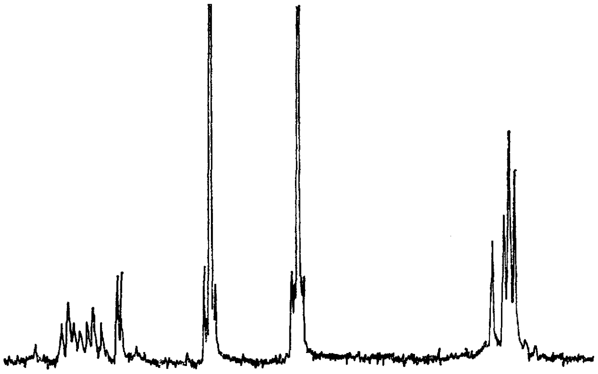

FIGURE 6 Noise-decoupled carbon-13 n.m.r. spectrum of 36% acrylonitrile sample in C_2Cl_5H with $Cr(acac)_3$, external D_2O lock

Copolymer Sequence.—Multiplicity in the individual peaks I—VII reflects different pentad environments. Peak intensities of I—VII are given in Table 1. Each individual intensity is expressed as the percent of the total vinyl absorption, normalized to account for the composition of the particular copolymer, *i.e.* the total vinyl absorption adds up in the case of each copolymer to the percent butadiene content.

For a particular type of carbon, peaks within these absorptions can be compared with one another reasonably accurately (the nuclear Overhauser effect being nearly the same for all regardless of detailed environment).[3,4]

This assumption, and the overall self-consistency can be tested in various ways. The population ABB is equal to the population BBA; also the number of T carbons is equal to the number of W carbons, and similarly for X and Y. Hence intensities of peaks I, III, V, and VII should all be equal. This can be seen to be approximately true from Table 1.

To determine the populations of the B-centred triads we group the normalized peaks in Table 1 together in the following way. Peaks II and VI clearly represent ABA, peaks I, III, V, and VII together represent the total ABB and BBA population, and peak IV alone represents BBB. These B-centred triad populations are tabulated in Table 4 and plotted in Figure 7, the percent acrylonitrile curve representing essentially the population of BAB. Thus, all four populations of triads existing in butadiene–acrylonitrile for the samples examined are clearly shown.

TABLE 4

Normalized B-centred triads [a]

	% Acrylonitrile						
Triad peaks	28	33	34	36	40	41	50
ABA II,VI	15	20	22	22	29	29	50
ABB I,III	16	17	20	18	13	13	0
BBA V,VII	20	18	15	16	13	12	0
BBB IV	21	12	9	8	5	5	0
BBB IX	22	13	12	15	9	7	0
I—VII Total	72	67	66	64	60	59	50

[a] Reported as % population of the total copolymer composition.

Over the short range of composition studied, the ABA triad rises steadily, to become equal to BAB at the 50% composition level. In the 28% sample, where BAB is nearly twice ABA, it is apparent that only short runs of alternation occur. That is, every A unit has two B neighbours but most of those B neighbours do not have an additional A neighbour. Thus, in a large block of B units, short sequences of alternating A units appear; hence the high ABB population.

Further, as the percent acrylonitrile, and therefore the percent BAB triad, increases, the populations of ABA and BAB increase at nearly the same rate, BBB quickly decreases, and ABB decreases more slowly. The population of ABB drops very quickly at 40% acrylonitrile after block butadiene is nearly exhausted and ABA increases dramatically (nearly doubling) to bring the copolymer up to full alternation.

In summary, as expected from reactivity ratios, the butadiene prefers to react with itself rather than with acrylonitrile and thus as acrylonitrile is added the resulting copolymer appears at the start as block butadiene containing short sequences of alternating acrylonitrile units; later, the copolymer (at 40% ACN)

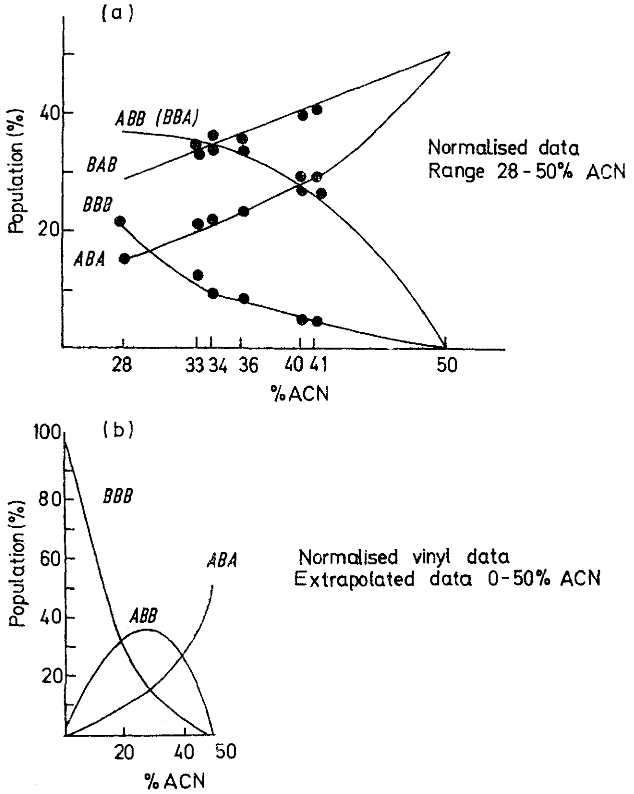

FIGURE 7 (a) Plot of percent population *vs.* percent acrylonitrile composition in butadiene–acrylonitrile copolymer for the four triads ABA, BBA(ABB), BBB, BAB; (b) plot extrapolated to 0% acrylonitrile may be visualized as blocks of butadiene averaging 2—3 units occurring between longer blocks of alternating copolymer, averaging 7—8 units (*i.e.* islands of B units uniformly distributed in an alternating sequence).

Multiplicity in the vinyl ABB absorptions could give quantitative information on tetrads such as ABBB and ABBA and minor peaks to high field of the methylene absorption may yield more information about the block butadiene structure which has been confirmed in this study to be mostly of *trans,trans*-diads.

EXPERIMENTAL

Samples.—These were B.P. Breon 1041 (41% ACN), Butakon 3003 (34% ACN), B.P. Breon 1042 (36% ACN), British Geon 1001 (40% ACN), B.P. Breon 1043 (28% ACN), and British Geon 1002 (33% ACN). Butakon is manufactured by Revertex Ltd., the remainder by B.P. Chemicals International Ltd. All samples were prepared by free-radical methods.

Spectroscopy.—The proton noise-decoupled Fourier transform carbon-13 n.m.r. spectra were obtained on a Varian XL-100 instrument; 12 mm tubes containing about 50 mg of polymer in 2·5 ml of $CDCl_3$ were used with a 5 mm tube containing D_2O fixed down the centre of each larger tube for an external lock. In the case of two samples (34 and 36%), pentachloroethane was used as solvent with an external D_2O lock. These samples were run at 90° (uncalibrated). Chemical shifts are expressed in p.p.m. downfield from Me_4Si in $CDCl_3$ solvent.

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