Compositional sequence determination of acrylonitrile–butyl acrylate copolymers by ^{13}C n.m.r. spectroscopy

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Acrylonitrile–butyl acrylate (A/B) copolymers of different monomer compositions were prepared by bulk polymerization using a free radical initiator. Copolymer compositions were determined by elemental analyses and comonomer reactivity ratios were determined using a non-linear least squares errors-in-variables model. Terminal and penultimate reactivity ratios were calculated using the observed monomer triad sequence distribution determined from $^{13}C\{^1H\}$ n.m.r. spectra. The triad sequence distribution was used to calculate diad concentrations, conditional probability parameters, number-average sequence lengths and block character of the copolymers. The observed triad sequence concentrations determined from $^{13}C\{^1H\}$ n.m.r. spectra agreed well with those calculated from reactivity ratios.

(Keywords: copolymers; monomer structure; spectroscopy)

INTRODUCTION

In our earlier publications, we reported the microstructures of acrylonitrile–alkyl methacrylate[1–3], acrylonitrile–methyl acrylate[4] and acrylonitrile–ethyl acrylate[5] copolymers by ^{13}C n.m.r. spectroscopy. Perusal of the literature showed that no work has been reported on the sequence determination of acrylonitrile–butyl acrylate (A/B) copolymers. As a continuation of our earlier work, in this paper we report the reactivity ratios for A/B copolymers using the errors-in-variables (EVM) computer program written by O'Driscoll *et al.*[6]. The primary structure factors, including monomer composition, diad/triad sequence distribution, conditional probabilities, number-average sequence lengths and block character of A/B copolymers, have been determined on the basis of $^{13}C\{^1H\}$ n.m.r. analyses.

EXPERIMENTAL

Acrylonitrile and butyl acrylate monomers were vacuum distilled and stored below 5°C. Benzoyl peroxide (0.5 w/v%) was mixed with the monomers at different molar feed ratios and polymerization was carried out at 70°C. The conversion was kept at 5–10% by controlling the time of polymerization and precipitating the copolymers in an excess of methanol.

Elemental analyses

The C, H and N analyses were done on a Perkin-Elmer 240 C Elemental Analyzer. The copolymer composition was calculated from the percentage of nitrogen in the copolymers.

N.m.r. analyses

^{1}H n.m.r. and $^{13}C\{^1H\}$ n.m.r. spectra were recorded on a Bruker WH-400 spectrometer operating at 400 and 100 MHz, respectively. The detailed conditions of operation are as follows: temperature of the probe, 25°C; reference, centre peak of $CDCl_3$ assigned as 77.0 ppm; spectral width, 27 777 Hz; pulse repetition time, 5 s. The details of recording the spectra and Lorentzian shape curve fitting have been described elsewhere[1,2]. The copolymer samples were examined as 5 wt% solutions for ^{1}H n.m.r. and 15–20 wt% for $^{13}C\{^1H\}$ n.m.r. spectra. The χ^2 values for various computer-fitted resonance signals were always taken as less than one.

RESULTS AND DISCUSSION

Reactivity ratios determination

The composition of the A/B copolymers was determined from the nitrogen content of the copolymers. *Table 1* shows the comonomer mole fractions in the feed and in the copolymers along with the nitrogen content in the copolymers. The variation of copolymer composition obtained from the copolymer equation using the terminal model reactivity ratios ($r_A = 0.65$ and $r_B = 0.84$) along with the experimental points for A/B copolymerization is shown in *Figure 1*. The experimental points are in good agreement with the theoretical curve, indicating that the reactivity ratios obtained from the C, H and N analyses are more reliable. The copolymer composition data were used to calculate the terminal model reactivity ratios using the non-linear least square errors-in-variables method (EVM). The EVM program requires a knowledge of the measurement errors for both dependent and independent variables. It was estimated that the error in the measurement of the comonomer

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Table 1 Copolymer composition and molecular weight data for acrylonitrile–butyl acrylate (A/B) copolymers

Sample no.	f_A[a]	f_B[a]	Nitrogen (%)	F_A[b]	F_B[b]	Conversion (%)
1	0.20	0.80	2.61	0.21	0.79	8.0
2	0.40	0.60	5.46	0.39	0.61	6.0
3	0.50	0.50	6.53	0.44	0.56	6.0
4	0.60	0.40	8.96	0.55	0.45	5.0
5	0.80	0.20	16.05	0.79	0.21	7.0
6	0.90	0.10	19.67	0.88	0.12	8.5

[a] Mole fractions of monomers in the feed
[b] Mole fractions of monomers in the copolymers

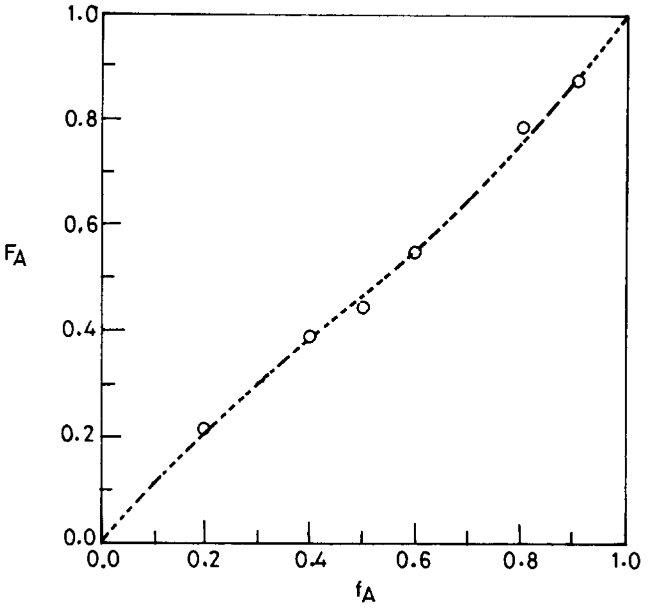

Figure 1 Variation of copolymer composition obtained from the copolymer equation (– – –) using terminal model reactivity ratios ($r_A = 0.65$, $r_B = 0.84$) along with the experimental points (–○–) for A/B copolymers

composition in the copolymer (using the elemental analyses) and in the feed was 1%. The initial estimates of the reactivity ratios were carried out by the method of Kelen and Tüdos[7]. The values of the reactivity ratios obtained from the Kelen–Tüdos plot are $r_A = 0.80$ and $r_B = 0.99$. These values are then fed into the computer program to calculate the exact values of the reactivity ratios. The reported[8–10] values of the reactivity ratios vary in the range 0.71–1.0 for acrylonitrile and 1.0–1.52 for butyl acrylate, depending on the method of polymerization. In the present case, the reactivity ratios obtained from the Kelen–Tüdos method lie in the range of the reported values and the EVM program gave the values of $r_A = 0.65 \pm 0.04$ and $r_B = 0.84 \pm 0.03$. The 95% posterior probability contour (*PPC*) for the A/B comonomer pair is shown in *Figure 2*. The value of $r_A \times r_B \cong 0.55$ indicates that it is not possible to specify whether the A/B comonomer pair polymerizes in random or alternate fashion.

^{1}H n.m.r. studies

The assignments of different resonance signals in the ^{1}H n.m.r. spectra of the A/B copolymers have been carried out by comparing the spectra of the copolymers with those of the homopolymers. In the case of polyacrylonitrile (PAN), the methylene ($-CH_2$) proton signal appeared around $\delta = 2.10$ ppm and the methine ($-CH$) proton signal appeared around $\delta = 3.40$ ppm. In the case of polybutyl acrylate (PBA), the methyl ($-CH_3$) protons appeared around $\delta = 0.91$–0.96 ppm and the $-\beta CH_2$, $-\alpha CH$ and $-OCH_2$ proton signals appeared around $\delta = 1.8$–2.0, 2.2–2.4 and 4.0 ppm, respectively. The resonance signals around $\delta = 1.30$–1.42 and 1.50–1.65 ppm can be assigned to C3 and C2 protons. To the best of our knowledge, these assignments in the ^{1}H n.m.r. spectra of A/B copolymers have not yet been reported. In the case of the A/B copolymer, $(-CH_3)_B$ and $(-OCH_2)_B$ protons appeared around $\delta = 1.0$ and 4.10 ppm, respectively. The broad signal around $\delta = 2.4$–3.4 ppm can be attributed to the $-\alpha CH$ proton

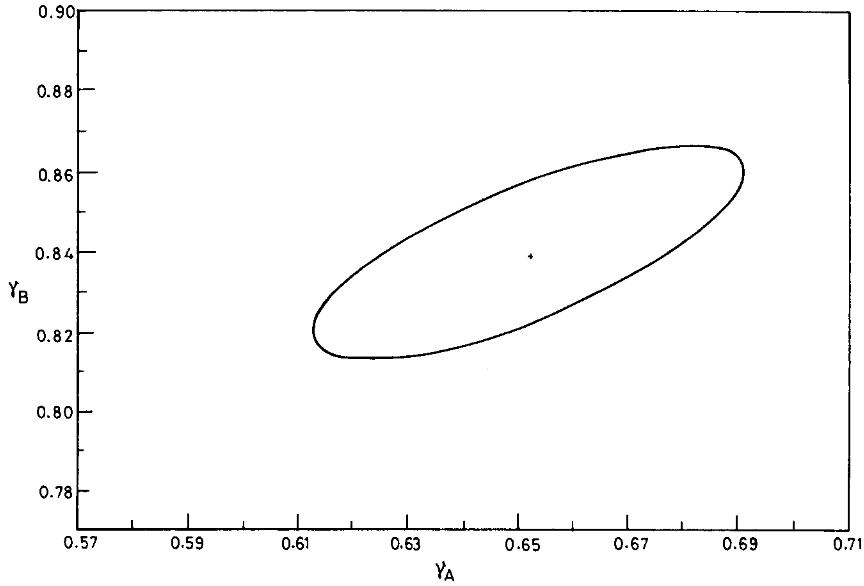

Figure 2 The 95% posterior probability contour (PPC) for an acrylonitrile–butyl acrylate comonomer pair. The (+) point represents the best estimated values of r_A and r_B

of both monomeric units. The other broad signal at 1.2–2.3 ppm can be assigned to $(C2)_B$, $(C3)_B$, $(\beta CH_2)_B$ and $(\beta CH_2)_A$ protons. The resonance signals around $\delta = 3.7$ ppm can be assigned to water molecules adsorbed by the DMSO-d_6 solvent. The ^1H n.m.r. spectrum of the A/B copolymers is very complex and various resonance signals from different monomeric units overlap with each other. Therefore, ^1H n.m.r. spectra could not be used for the determination of the monomer content in the copolymers. Elemental analysis was considered to be an accurate method for the determination of copolymer composition.

^{13}C *n.m.r. studies*

The $^{13}C\{^1H\}$ n.m.r. spectrum of the A/B copolymer (A = 55.0 mol%) recorded in a mixture of $CDCl_3$ and DMSO-d_6 at room temperature is shown in *Figure 3*. The various resonance signals have been assigned by comparing the copolymer spectrum with n.m.r. spectra of homopolymers. In the case of PAN, $-CH_2$ and $-CH$ carbons appeared around $\delta = 33.4$ ppm and 27.8–28.1 ppm, respectively. The nitrile (–CN) carbon in PAN appeared as a multiplet in the region $\delta = 118.2$–120.8 ppm. Kamide *et al.*[11] have evaluated the pentad tacticity of R–PAN using high-magnetic-field n.m.r. In the case of PBA, the resonance signals around $\delta = 64.2$ and 174.2 ppm can be assigned to $-OCH_2$ and $>C{=}O$ carbons, respectively. The $-\alpha CH$ and $-\beta CH_2$ in PBA appeared around $\delta = 41.3$ and 34.4–36.3 ppm. The sharp resonance singlets around $\delta = 30.5$, 18.9 and 13.5 ppm can be attributed to C2, C3 and $(-CH_3)$ carbons, respectively. In the A/B copolymer, the resonance signals around $\delta = 13.4$, 18.7, 30.1 and 64.4 ppm can be assigned to $(-CH_3)_B$, $(C3)_B$, $(C2)_B$ and $(O{-}CH_2)_B$ carbons of butyl acrylate monomer. The resonance signals around $\delta = 26.8$–28.2 and 33.4–35.1 ppm can be attributed to $(-\alpha CH)_A$ and $(-\beta CH_2)_A$ carbons, respectively, but could not be used for the sequence analysis because of poor resolution. The $(-CH_2)_B$ and $(-CH)_B$ carbons overlapped with the solvent DMSO-d_6 signals ($\delta = 38.8$–42.0 ppm) and, therefore, could not be used for the analysis of B-centred sequences. The carbonyl carbon in the A/B copolymer appeared as a multiplet around $\delta = 172.6$–174.2 ppm, indicating that the splitting of the $>C{=}O$ signal is due to its sensitivity towards the compositional sequences. The nitrile carbon of the A unit appeared as a well resolved multiplet around $\delta = 119.2$–121.2 ppm, showing its sensitivity towards different monomer placements. In the case of the A/B copolymer, a shift occurs in the position of various functional groups of A and B units compared to that in homopolymers; this is due to the change in the nature of adjacent monomeric units in the copolymer, which changes the chemical shifts of A- and B-centred triads.

The carbonyl carbon ($>C{=}O$) and nitrile carbon

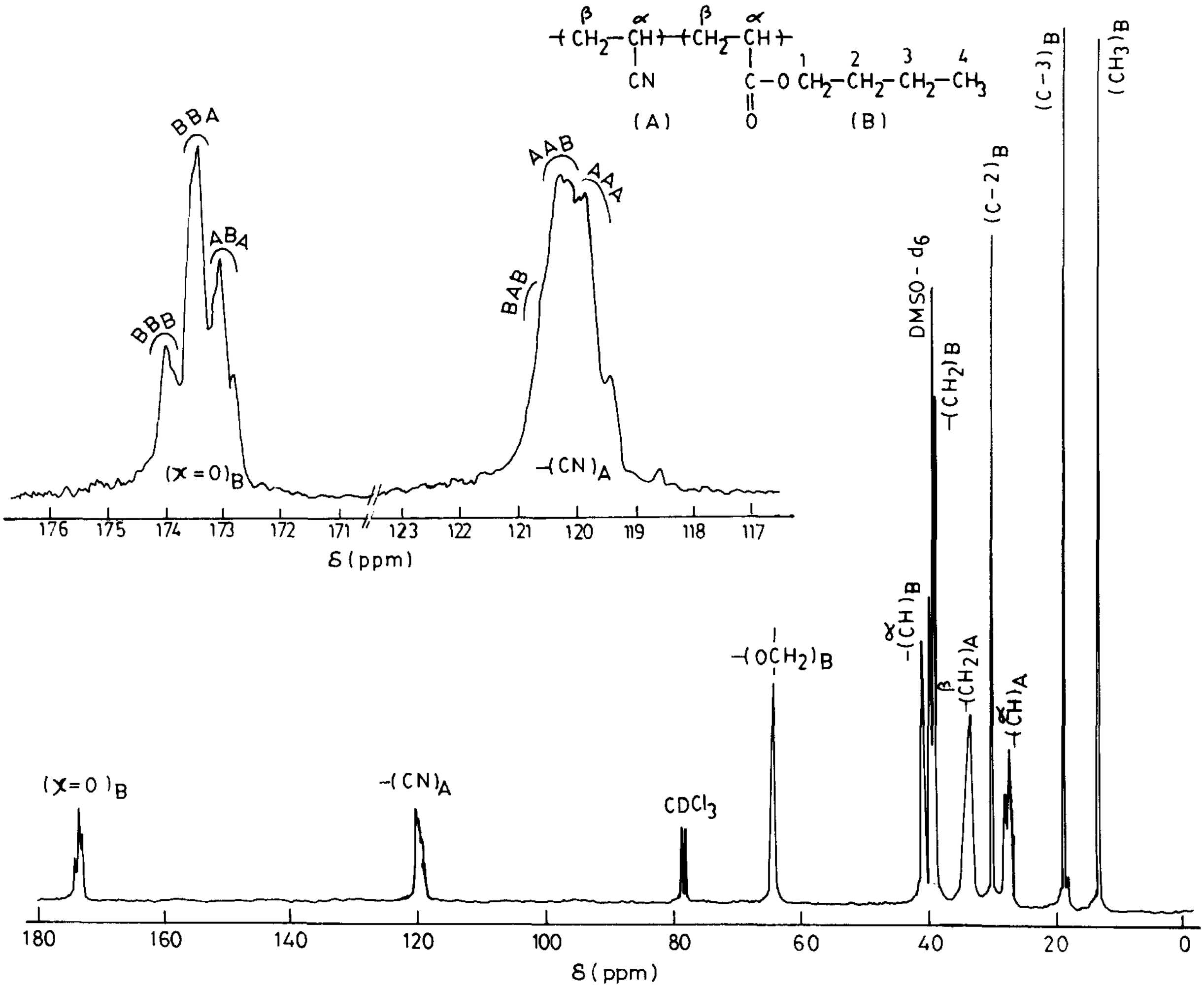

Figure 3 $^{13}C\{^1H\}$ n.m.r. spectrum of the A/B copolymer (A = 55.0 mol%) along with the expanded carbonyl carbon ($>C{=}O$) and nitrile carbon (–CN) in mixture of $CDCl_3$ and DMSO-d_6 at room temperature

(–CN) expansion of the A/B copolymer (A = 55.0 mol%) are shown in *Figure 3*. PBA shows a singlet centred around $\delta = 174.2$ ppm. As the concentration of acrylonitrile in the copolymer increases, signals characteristic of PBA decrease, whereas a set of signals centred around $\delta = 173.5$ ppm start appearing. These signals, with a further increase in the acrylonitrile content, increase to a maximum and then decrease, whereas a third new set of resonance signals appears at around $\delta = 173.0$ ppm. The three sets of signals whose intensities change with copolymer composition can be assigned to the carbonyl carbon of a central B unit in BBB, ABB (BBA) and ABA triad sequences from low to high field. The assignment of signals was done on the basis of electronic interactions. In the case of the B-centred triad, addition of an A unit in BBB triads causes the upfield shift in the position of BBA (by $\simeq 0.70$ ppm) and ABA (by $\simeq 0.50$ ppm). This is due to the increase in electron density at the carbonyl carbon of the central B unit which can be due to the diamagnetic shielding effect from the anisotropy of immediate –CN neighbours. The change in chemical shift due to the monomer placements is larger than the cotacticity within the polymer chain. Since three sets of peaks were observed in the case of carbonyl carbon and were assigned as BBB, BBA and ABA from low to high field as explained earlier. There was no possibility of scrambling of the signals due to the compositional and cotacticity sequences. Concentrations of various

Table 2 Calculated and observed fractions of A- and B-centred triads in A/B copolymers

			Triad concentrations[a]		
Sample no.	A mole fraction (in copolymer)	Triad	Obs.	Calc. (Alfrey–Mayo model)	Calc. (Harwood penultimate model)
1	0.21	AAA	0.04	0.02	0.03
		AAB	0.29	0.24	0.26
		BAB	0.67	0.74	0.71
		BBB	0.61	0.59	0.63
		BBA	0.33	0.35	0.32
		ABA	0.06	0.06	0.05
2	0.39	AAA	0.06	0.09	0.14
		AAB	0.44	0.42	0.42
		BAB	0.50	0.49	0.44
		BBB	0.32	0.31	0.33
		BBA	0.49	0.49	0.46
		ABA	0.20	0.19	0.21
3	0.44	AAA	0.20	0.16	0.24
		AAB	0.49	0.48	0.45
		BAB	0.31	0.36	0.31
		BBB	0.24	0.21	0.23
		BBA	0.50	0.50	0.46
		ABA	0.26	0.29	0.31
4	0.55	AAA	0.31	0.25	0.35
		AAB	0.52	0.50	0.45
		BAB	0.17	0.25	0.20
		BBB	0.13	0.13	0.14
		BBA	0.47	0.46	0.43
		ABA	0.40	0.41	0.43
5	0.79	AAA	0.57	0.52	0.63
		AAB	0.39	0.40	0.32
		BAB	0.04	0.08	0.05
		BBB	0.04	0.03	0.03
		BBA	0.31	0.29	0.26
		ABA	0.65	0.68	0.71
6	0.88	AAA	0.78	0.73	0.81
		AAB	0.20	0.25	0.17
		BAB	0.02	0.02	0.02
		BBB	0.01	0.01	0.01
		BBA	0.17	0.16	0.14
		ABA	0.82	0.83	0.85

[a] Standard deviation is ±0.04

B-centred triads can be calculated from the relative areas of the resonance signals. These triad concentrations are the normalized areas of the respective resonance signals. The relaxation times for the carbons of the same functionalities in different comonomers and configurational sequences have been found to be of the same value, within the experimental errors of T_1 measurements. Spin-lattice relaxation (T_1) measurements for acrylonitrile–methyl methacrylate copolymer systems have been reported by Gerken and Ritchey.[12] Therefore, we have assumed that the areas of the respective resonance signals in the $^{13}C\{^1H\}$ n.m.r. spectra of the A/B copolymers correspond to concentrations of various A- and B-centred triads.

Assuming the Alfrey–Mayo model (first-order Markov terminal model)[13] to be valid at any moment of the reaction for these low-conversion copolymers, the mole fraction (F) of A- and B-centred triads can be predicted. *Table 2* contains the compositional information concerning the various B-centred triads using the terminal model reactivity ratios ($r_A = 0.65 \pm 0.04$ and $r_B = 0.84 \pm 0.03$)[4].

Similar compositional information regarding the A-centred triad can be made using the –CN carbon resonance region. A multiplet around $\delta = 119.2$–121.2 ppm is split into three envelopes. The chemical shift difference within the resonance signals and the splitting pattern show its sensitivity towards monomer sequences and cotacticity in the nitrile resonance. The increase in concentration of the A unit in the copolymer increases the most upfield signal of the nitrile group centred around $\delta = 119.7$ ppm, while the downfield signal around $\delta = 120.8$ ppm decreases. On the basis of the compositional variation in the intensities of A-centred triads, the most upfield resonance signal is assigned to the AAA triad and the most downfield to the BAB triad. The addition of butyl acrylate to the AAA-centred triad causes the downfield shift in the position of AAB (by $\simeq 0.50$ ppm) and BAB (by $\simeq 0.60$ ppm) due to the deshielding effect of the carbonyl group in butyl acrylate.

A-centred triads along with those calculated using the Alfrey–Mayo model are given in *Table 2. Figures 4a* and *4b* show the plots of normalized A- and B-centred triad concentrations *versus* the mole fractions of acrylonitrile and butyl acrylate in feed, respectively. The increase in the concentration of acrylonitrile in the copolymers increases the fraction of the AAA triad while it decreases the fraction of the BAB triad. The fraction of the AAB triad first increases with the increase in concentration of acrylonitrile, passes through a maximum value and then starts decreasing. The maximum fractions of AAB and BBA triads are obtained at 0.60 and 0.55 mole fractions of the respective monomers. On the basis of the triad resonance assignments described earlier, penultimate reactivity ratios were evaluated for A/B copolymers from the triad fractions determined from carbonyl and nitrile resonances of the $^{13}C\{^1H\}$ n.m.r. spectra[4]. The penultimate reactivity ratios have been determined from the slopes of the plots of individual triad ratios [(AAA/AAB), (AAB/BAB)] and [(BBB/BBA), (BBA/ABA)] *versus* f_B/f_A, respectively. The values of the penultimate reactivity ratios obtained are $r_{AA} = 1.05$, $r_{BA} = 0.74$, $r_{BB} = 0.99$ and $r_{AB} = 0.73$. Using these values, the triad sequence distribution was obtained by Harwood's program[14] and is given in *Table 2*. The uncertainty in the values of triad compositional sequences obtained from n.m.r. spectra and reactivity ratios is ± 0.04.

In earlier publications the sequence and cotacticity have been reported in acrylonitrile–alkyl methacrylate copolymers[1–3]. In the present case of A/B copolymers, the cotacticity could not be observed in the carbonyl carbon and nitrile carbon resonance signals even at 100 MHz ^{13}C n.m.r. spectra. Substitution of the α-methyl group in alkyl methacrylate by a hydrogen atom causes a drastic change in the ^{13}C n.m.r. spectrum with respect to the carbonyl and nitrile resonance signals, which are cotacticity sensitive in alkyl methacrylate copolymers.

The conditional probabilities $P_{B/A}$ and $P_{A/B}$ have been calculated from the results of composition with respect

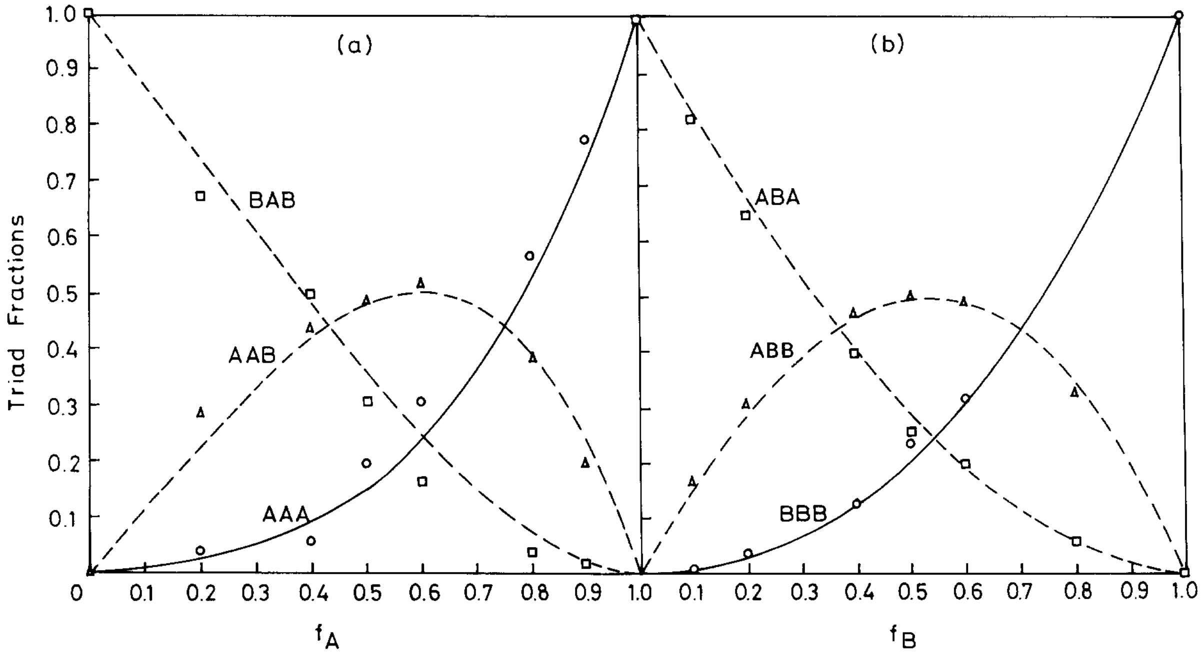

Figure 4 Plots of (a) A- and (b) B-centred triad fractions *versus* the feed in mole fractions of A and B monomers, respectively

Table 3 Copolymerization parameters of A/B copolymers determined by ^{13}C n.m.r. spectroscopy

Sample no.	A mole fraction (in copolymer)	$P_{B/A}$	$P_{A/B}$	$\bar{N}_A$	$\bar{N}_B$	r_A	r_B
1	0.21	0.81	0.23	1.23	4.35	0.93	0.83
2	0.39	0.72	0.44	1.39	2.27	0.58	0.85
3	0.44	0.55	0.51	1.81	1.96	0.81	0.96
4	0.55	0.43	0.63	2.32	1.59	0.88	0.88
5	0.79	0.23	0.81	4.35	1.23	0.83	0.94
6	0.88	0.12	0.90	8.33	1.11	0.81	1.00

to various A- and B-centred triads[4]. The value of $P_{B/A}$ decreases from 0.81 to 0.12 with the decrease in the content of butyl acrylate in the copolymer, while the value of $P_{A/B}$ increases from 0.23 to 0.90 with the increase in concentration of acrylonitrile in the copolymer. The terminal model reactivity ratios (r_A and r_B) have been calculated for individual copolymers. The reactivity ratios calculated from the EVM program are $r_A = 0.65 \pm 0.04$, $r_B = 0.84 \pm 0.03$ and from triad compositions are $r_A = 0.80$, $r_B = 0.91$. The number-average sequence lengths ($\bar{N}_A$ and $\bar{N}_B$), the reciprocal of conditional probabilities, were also obtained. The value of $\bar{N}_A$ increases from 1.23 to 8.33 as the concentration of acrylonitrile in the copolymer increases while the value of $\bar{N}_B$ decreases from 4.35 to 1.11 with the decrease in the concentration of butyl acrylate in the copolymer. *Table 3* shows the copolymerization parameters of A/B copolymers for various monomer feed ratios.

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