Effect of the length of n-alkyl side groups on the microstructure and stereochemistry of methacrylonitrile–alkyl methacrylate copolymers synthesized by free radical polymerization

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The microstructure of free-radical polymerized methacrylonitrile (N)–ethyl methacrylate (E) and N–butyl methacrylate (B) copolymers was studied by ^{13}C n.m.r. spectroscopy, and the results obtained were compared with those of N–methyl methacrylate (M) copolymers synthesized in similar experimental conditions. The distribution of monomer sequences and the stereochemical configuration of N–E and N–B copolymers were slightly different from that of N–M copolymers. The analysis of n.m.r. resonance signals provided a coisotacticity parameter $\sigma_{ij}=\sigma_{ji}=\sigma^*=0.98$ for both N–E and N–B systems, somewhat higher than that of the N–M copolymers ($\sigma^*=0.87$). This result was interpreted on the basis of strong dipolar interactions between the nitrile and carbonyl ester side groups of both kinds of monomeric units. It indicated the selectivity of a meso–meso relative stereochemical configuration for N or n-alkyl methacrylate centred sequences with two neighbouring comonomeric units of the second monomer, independently from the steric hindrance associated with the volume of the side alkyl substituent.

(Keywords: n.m.r. spectroscopy; synthesis; radical polymerization)

INTRODUCTION

High resolution n.m.r. spectroscopy has been proven to be an effective tool for elucidating microstructural features of synthetic polymers[1,2]. For vinyl copolymers, n.m.r. studies provide valuable information on the addition and arrangement of different comonomeric units along the polymer chains (comonomer sequences) and the stereochemistry of the placement of these units along the polymer chain, when one or both repeat units present a pseudoasymmetric centre (cotacticity).

In previous work[3] we described the microstructural analysis of methacrylonitrile (N)–methyl methacrylate (M) copolymers by 75 MHz ^{13}C n.m.r. spectroscopy. The results obtained revealed the existence of some rather strong interactions between the nitrile and carbonyl groups of neighbouring N and M units. In the present work we study the effect of the nature of the carbonyl ester group of the methacrylate on the microstructure and stereoregularity of copolymers prepared with two different n-alkyl methacrylates of increasing n-alkyl group length and N.

EXPERIMENTAL

Reagents

Methacrylonitrile (N), ethyl methacrylate (E) and n-butyl methacrylate (B) (Merck), were purified by washing three times with 5% NaOH aqueous solution and then several times with distilled water. After separation and drying over calcium chloride, the monomers were distilled and stored at low temperature. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol (m.p. = 104°C).

Polymerization

Bulk copolymerization reactions for the N–E and N–B systems were carried out at 60 ± 0.5°C, by taking known amounts of the comonomers and using AIBN as the free radical initiator. The conversion of the monomers to copolymers was restricted to below 5% and the polymers were isolated and purified by repeated solution and precipitation from dimethylformamide and methanol, respectively. The samples were finally dried at 40°C under vacuum to constant weight.

Characterization

N.m.r. spectra (300 MHz, ^1H and 75 MHz, ^{13}C) were

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Table 1 Reactivity ratios and relative reactivities of copolymerization systems based on N (1) and n-alkyl methacrylates (2)

Copolymer system	r_1	r_2	$1/r_1$	$1/r_2$	Ref.
N(1)–M(2)	0.883	0.892	1.132	1.121	3
N(1)–E(2)	0.445	1.030	2.247	0.971	4
N(1)–B(2)	0.432	1.156	2.315	0.865	4

Table 2 Average molar composition and conditional probabilities P_{ij} for the free radical copolymerization of N with E and B at 60°C

N–E system				N–B system			
F_E[a]	f_E[a]	P_{NE}	P_{EN}	F_B[a]	f_B[a]	P_{NB}	P_{BN}
0.904	0.90_6	0.955	0.093	0.902	0.91_6	0.955	0.086
0.826	0.84_2	0.914	0.170	0.785	0.81_1	0.894	0.192
0.632	0.68_9	0.794	0.361	0.582	0.68_0	0.763	0.383
0.527	0.61_1	0.729	0.447	0.452	0.56_5	0.656	0.512
0.320	0.51_6	0.619	0.572	0.348	0.46_4	0.553	0.618
0.201	0.31_2	0.361	0.794	0.186	0.30_5	0.346	0.791

[a] F and f refer to molar fraction of monomer in the feed and in the copolymer chains, respectively

$P_{ii}=1-P_{ij}$; $P_{jj}=1-P_{ji}$

recorded using a Varian VXR-300 spectrometer. The samples were analysed as 20% (w/v) solution in perdeuterated dimethyl sulfoxide (DMSO-d_6) at 80°C. In order to obtain a quantitative response, the ^{13}C n.m.r. spectra were recorded using a flip angle of 80° (pulse width of 13 μs), a relaxation delay of 5 s and inversed gated decoupling in the acquisition and spectral width of 16K data points. These conditions ensure the complete relaxation of all the ^{13}C nuclei analysed. Relative peak intensities were measured from peak areas calculated by means of the electronic integrator or by triangulation and planimetry.

RESULTS AND DISCUSSION

The free radical copolymerization of N with E and B was carried out in bulk at 60°C under high vacuum. The concentration of the free radical initiator (AIBN) was 0.5×10^{-2} mol l^{-1}. The composition of copolymer samples was determined by ^1H n.m.r. and the corresponding reactivity ratios for both systems were calculated according to linear and non-linear methods[4]. Values of the monomer reactivity ratios for these copolymerization systems are given in *Table 1*, together with those of the N–M system[3]. The values of $1/r_1$ and $1/r_2$ given in *Table 1*, indicate that the relative reactivity of M is similar to that of N for both kinds of growing macroradicals. However, the reactivity of N towards alkyl methacrylate ending radicals is higher than that of E or B monomers towards N ending macroradicals. This behaviour could indicate some kind of specific interactions between N and n-alkyl methacrylate radicals or molecules. The conditional probabilities[5] for the addition of monomers to polymeric chain ends of N–E and N–B systems (P_{ij}, i,j=N, E or N, B) were calculated according to the copolymerization model proposed by Mayo and Lewis[6] and Alfrey and Goldfinger[7], and the corresponding values are given in *Table 2*, being rather similar for both systems as could be expected from the corresponding reactivity ratios.

The conditional probabilities are very useful parameters to determine the statistical distribution and length of monomer sequences along the copolymer chains. In this sense, the statistical analysis of the sequence distribution of monomers has been carried out assuming the validity of the terminal unit model for the addition of monomeric units to copolymer chain ends[6,7]. However, although both comonomeric units present a pseudoasymmetric centre (the quaternary carbon atom), with respect to the stereochemical configuration of copolymer sequences, it has been assumed that the tacticity may be described according to Bernoullian statistics, with the isotacticity and coisotacticity parameters σ_{ii}, σ_{jj}, σ_{ij} and σ_{ji} as defined by Bovey[8,9] and Coleman[10], where σ_{ij} is the probability of generating a *meso* diad between an i-ended growing radical and the incoming j monomer. Traditionally it has been considered that the parameters σ_{ii} and σ_{jj} are practically equal to the isotacticity parameters for the free radical homopolymerization of the corresponding monomers, whereas the coisotacticity parameters σ_{ij} and σ_{ji} have the same value[11,12], i.e. $\sigma_{ij}=\sigma_{ji}=\sigma^*$.

Regarding the isotacticity parameters of the free radical homopolymerization of E and B, we have determined values of $\sigma_{EE}=0.19$ and $\sigma_{BB}=0.17$ from the ^{13}C n.m.r. spectrum of the corresponding poly(ethyl methacrylate) and poly(n-butyl methacrylate) synthesized under the same experimental conditions of the copolymers. The isotacticity parameter for the free radical polymerization of N was determined previously[3], giving a value of $\sigma_{NN}=0.37$, somewhat higher than those of the n-alkyl methacrylates.

On the other hand, the coisotacticity parameter σ^* may be determined from the analysis of spectra of several copolymer samples with different composition. In view of the spectra recorded, we were interested in the analysis of the resonance signals assigned to the pseudoasymmetric quaternary carbon and the carbonyl group of methacrylate centred sequences. Unfortunately the nitrile group resonance signal is not sensitive to the composition or the stereochemistry of sequences and the α-CH_3 groups of the repeat units overlap with the resonance signals of the carbon atoms of the n-alkyl ester residue. Therefore it is not possible to analyse resonance signals of N centred sequences.

The quaternary carbon resonance signals of E units in the spectra of N–E copolymers (*Figure 1*) are similar to those of B units in the spectra of N–B copolymers (*Figure 2*). In both cases this carbon atom gives three peaks whose intensities change drastically with the copolymer composition. Comparison with resonance signals of these carbon atoms in the spectra of poly(ethyl methacrylate)[13] and poly(n-butyl methacrylate)[13,14], suggests that they correspond to E and B centred triads, independently of the chemical composition (EEE, EEN or NEE and NEN) and (BBB, BBN or NBB and NBN), but with the relative stereochemical configuration: syndiotactic triads, *rr*, $\delta=44.60$, 44.55 ppm; heterotactic triads, *mr*+*rm*, $\delta=44.95$, 45.00 ppm and isotactic traids, *mm*, $\delta=45.30$, 45.35 ppm. The chemical shifts of these signals are similar for both systems and very close to those of the quaternary carbon of M units in the spectra of N–M copolymers[3]. It is interesting to stress here that the chemical shift of these resonance signals does not change with the average composition of the copolymer samples analysed. Therefore, these signals correspond to n-alkyl methacrylate centred triads with the relative stereochemical configuration above indicated, independently of the composition of the sequence. This

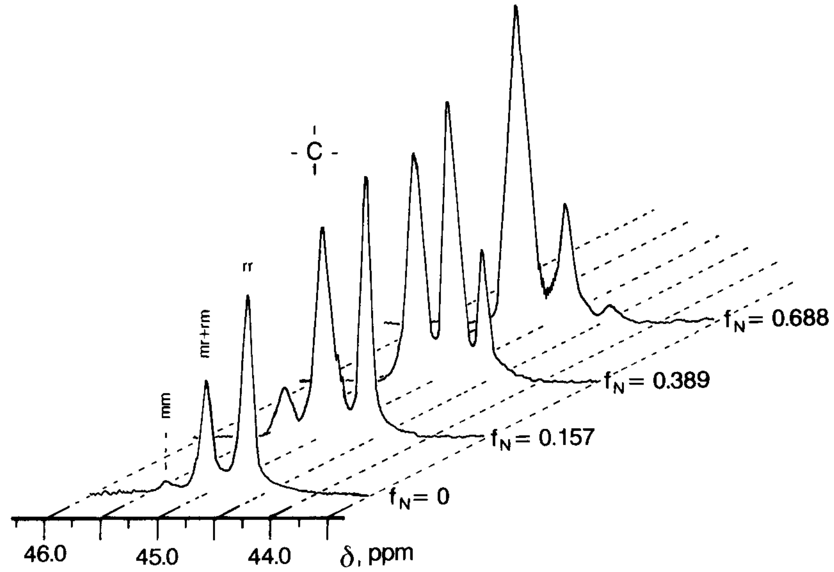

Figure 1 Expanded ^{13}C n.m.r. signals of the quaternary carbon of E units in N–E copolymers

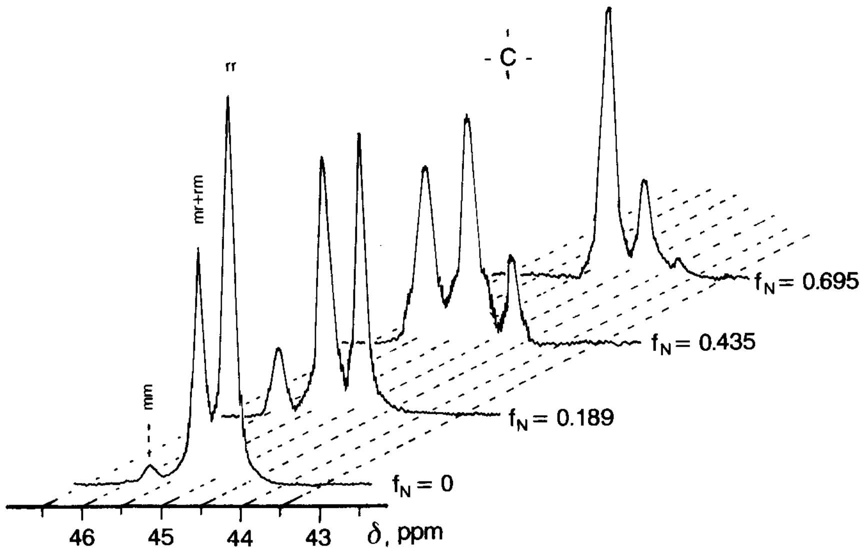

Figure 2 Expanded ^{13}C n.m.r. signals of the quaternary carbon of B units in N–B copolymers

characteristic has been schematically explained in detail for N–M copolymers[3]. According to this assignment the methacrylate central unit in sequences of triads presents a stereochemical configuration predominantly syndiotactic for copolymers rich in the corresponding alkyl methacrylate, and a predominantly *meso* or isotactic configuration for copolymers rich in N, which permits the determination of the coisotacticity parameter for the formation of alternating diads σ_{ij} or σ_{ji}.

If the copolymerization process follows the classical copolymerization model of Mayo and Lewis[6], i.e. the addition of monomers to polymeric growing chain ends fits first-order Markov statistics and the stereochemical configuration of comonomeric units can be described by Bernoullian statistics, according to well known statistical relations we can derive expressions that relate the coisotacticity parameter $\sigma^* = \sigma_{12} = \sigma_{21}$ with the concentration of *mm* and *rr* alkyl methacrylate centred triads, giving the equations:

$$\sigma^* = \frac{2[(mm)^{1/2} - P_{11}\sigma_{11}]}{P_{12}+P_{21}}$$

and

$$1-\sigma^* = \frac{2[(rr)^{1/2} - P_{11}(1-\sigma_{11})]}{P_{12}+P_{21}}$$

where *mm* and *rr* are the molar fractions of isotactic and syndiotactic alkyl methacrylate centred triads, P_{11}, P_{12} and P_{21} the conditional probabilities for the addition of monomers 1 and 2 (1, 2 = E or B and N) to polymeric growing chains, and σ_{11} the isotacticity parameter of the homopolymerization of the corresponding alkyl methacrylate. Although these equations can be applied to all the compositions, the best values are obtained for intermediate compositions avoiding the use of data corresponding to extreme molar fractions of the monomers. The application of these equations to the *mm* and *rr* data obtained from the analysis of the quaternary resonance signals of copolymers prepared with different compositions gives a value of σ^* per composition analysed, from which it is possible to consider an average value. The results obtained for the E–N and B–N systems are very similar, giving an average value of $\sigma^* = 0.98$. It is noteworthy that this coisotacticity parameter is even slightly higher than that reported[3] for the free radical copolymerization of the N–M system.

Experimental and calculated values of the molar fraction of tactic methacrylate centred triads for copolymer samples of both systems are summarized in *Table 3*. The experimental values have been determined from the integrated intensities of the three resonance signals assigned in *Figures 1* and *2*, whereas the calculated values have been determined by the sum of the contribution of E or B centred sequences with the stereochemical configuration mentioned above, according to Bernoullian statistics[1] with the values of σ_{11}, σ_{22} and σ^* described above. The good agreement of experimental and calculated values over the whole composition range supports the validity of the copolymerization model considered for the microstructural analysis of these systems.

Table 3 Distribution of the stereochemical configuration of methacrylate centred sequences along the copolymer chains for N–E and N–B copolymers

	N–E copolymers			N–B copolymers		
		Triad molar fraction			Triad molar fraction	
Tactic sequence	f_N (copol.)	Expt.	Calc.[a]	f_N (copol.)	Expt.	Calc.[a]
mm		0.05_3	0.071		0.06_7	0.058
mr+*rm*	0.09_4	0.38_7	0.390	0.08_4	0.38_1	0.365
rr		0.56_0	0.539		0.55_2	0.577
mm		0.10_6	0.105		0.11_6	0.109
mr+*rm*	0.15_7	0.41_0	0.438	0.18_9	0.42_4	0.443
rr		0.48_4	0.456		0.46_0	0.448
mm		0.33_6	0.299		0.21_4	0.225
mr+*rm*	0.38_9	0.45_8	0.496	0.32_0	0.51_0	0.499
rr		0.20_6	0.205		0.27_6	0.276
mm		0.42_4	0.415		0.50_7	0.454
mr+*rm*	0.48_4	0.45_3	0.459	0.53_6	0.39_4	0.439
rr		0.12_3	0.127		0.09_9	0.106
mm		0.68_2	0.668		0.70_2	0.657
mr+*rm*	0.68_8	0.28_2	0.298	0.69_5	0.25_0	0.307
rr		0.03_6	0.033		0.04_8	0.036

[a] The calculated values have been determined with the copolymerization parameters indicated in the text

Figures 3 and *4* show the expanded resonance signals of the carbonyl ester groups of E and B units for copolymer samples with different average composition. The resonances of these carbon atoms give rise to eight peaks whose intensities change drastically with the copolymer composition. As in the case of the pseudoasymmetric quaternary carbon, the chemical shift of these signals is independent of the composition of the copolymer samples. Therefore, the splitting is associated with the stereochemical configuration of methacrylate centred pentads as indicated in *Figures 3* and *4*, on the basis of equivalent signals of the respective homopolymers. *Tables 4* and *5* show the values of molar fraction and tacticity of methacrylate centred pentads for several N–E and N–B copolymer samples prepared with different compositions. The variation of the intensity of peaks with composition presents the same trend observed for the quaternary carbon resonances, which verifies a predominant *racemic* or syndiotactic character for methacrylate-rich copolymers, increasing gradually the relative concentration of *meso* arrangement of E and B centred sequences as the mole fraction of N in the copolymer increases.

In order to verify the reliability of the assignments suggested above and the models considered for the treatment of these copolymerization systems, the variation of the mole fraction of alkyl methacrylate centred triads as a function of the molar fraction of N monomer in the copolymer chains is shown in *Figures 5* and *6*. The solid symbols correspond to data derived from the carbonyl ester resonances and the open symbols to data obtained from the quaternary carbon resonances. The lines are the statistical prediction on the basis of the terminal model for the addition of monomers to growing chain ends, with a stereochemical configuration according to Bernoullian statistics, with the

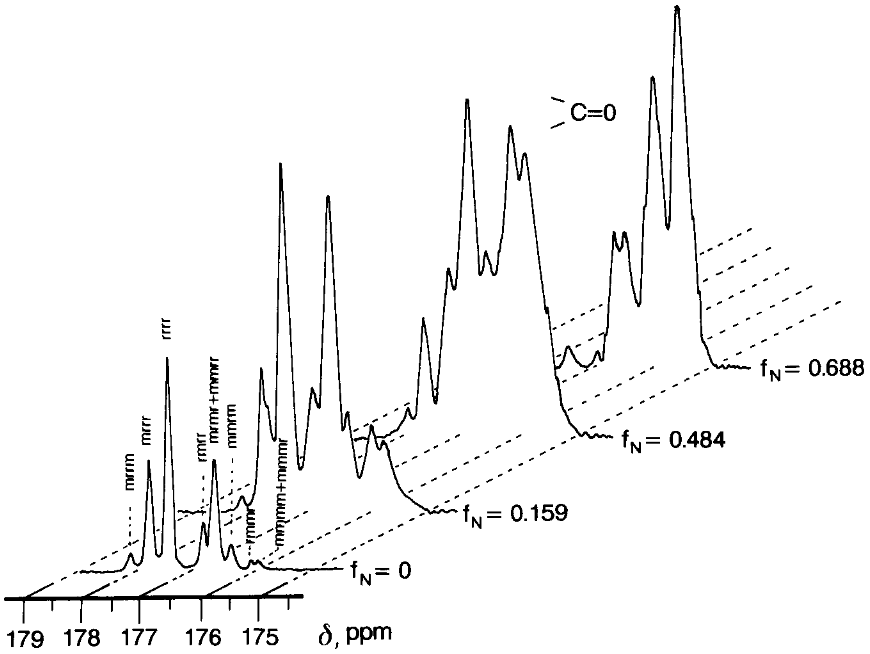

Figure 3 Expanded ^{13}C n.m.r. pattern of the carbonyl carbon resonances of E centred sequences in N–E copolymers

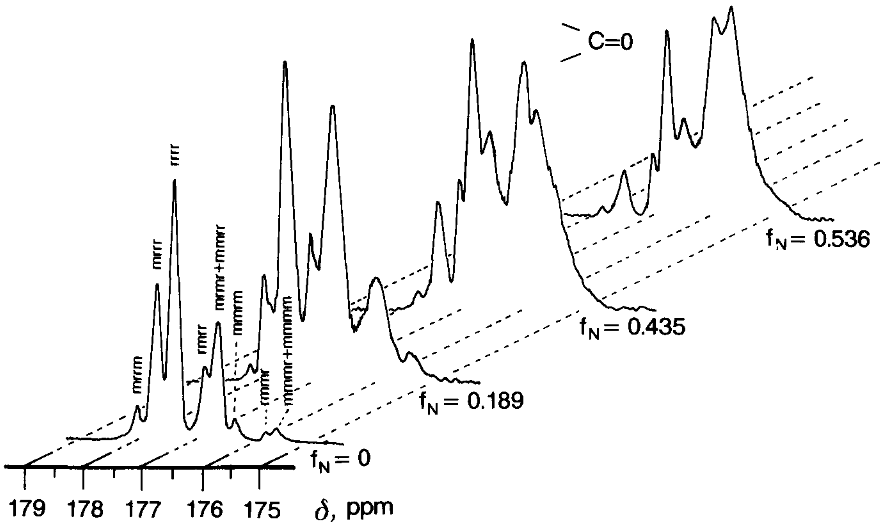

Figure 4 Expanded ^{13}C n.m.r. pattern of the carbonyl carbon resonances of B centred sequences in N–B copolymers

Table 4 Tacticity of E centred pentads in N–E copolymers

Resonance δ (ppm)	Signal sequence	Pentad molar fraction				
		$f_N=0.094$	$f_N=0.157$	$f_N=0.389$	$f_N=0.484$	$f_N=0.688$
178.10	*mrrm*	0.03_1	0.01_3	0.00_8	0.00_0	0.00_0
177.65	*mrrr*	0.18_1	0.11_9	0.03_3	0.02_1	0.00_0
177.45	*rrrr*	0.37_3	0.29_3	0.12_5	0.08_5	0.02_3
176.90	*rmrr*	0.06_9	0.11_4	0.12_6	0.11_4	0.01_8
176.65	*mrmr*+*mmrr*	0.21_5	0.26_5	0.25_3	0.23_7	0.13_3
176.35	*mmrm*	0.06_2	0.06_0	0.14_3	0.13_2	0.13_3
175.95	*rmmr*	0.04_2	0.07_3	0.17_1	0.21_6	0.31_2
175.60	*mmmr*+*mmmm*	0.02_7	0.06_3	0.14_1	0.19_5	0.38_1

Table 5 Tacticity of B centred pentads in N–B copolymers

Resonance δ (ppm)	Signal sequence	Pentad molar fraction				
		$f_N=0.084$	$f_N=0.189$	$f_N=0.320$	$f_N=0.435$	$f_N=0.536$
178.10	*mrrm*	0.04_6	0.01_4	0.00_0	0.00_0	0.00_0
177.90	*mrrr*	0.18_5	0.09_7	0.04_8	0.01_4	0.01_0
177.50	*rrrr*	0.36_1	0.30_4	0.18_5	0.09_3	0.05_5
177.00	*rmrr*	0.10_5	0.14_0	0.13_2	0.11_8	0.07_7
176.70	*mmrr*+*mrmr*	0.21_2	0.26_2	0.24_6	0.23_3	0.23_0
176.50	*mmrm*	0.03_7	0.06_3	0.16_6	0.15_6	0.12_1
175.90	*rmmr*	0.04_3	0.09_9	0.15_6	0.21_8	0.24_7
175.70	*mmmr*+*mmmm*	0.00_9	0.01_9	0.06_6	0.17_0	0.26_1

parameters reported above. The excellent agreement between experimental and predicted results supports the treatment used in the present work.

Finally, it is clear from the microstructural analysis of N–E and N–B copolymer systems, that the coisotacticity parameter σ^* increases with increasing number of carbon atoms in the alkyl ester residue. This seems to indicate some specific interactions between the nitrile and carbonyl groups of two neighbouring units. This could be explained in terms of polar effects (e values) of the corresponding monomers, since as it has been reported by Cameron *et al.*[15], the values of e for E and B are negative and lower than that for N. Effectively, if we consider a value of $e=0.68$ for N[16], according to the reactivity ratios quoted in *Table 1* and considering the equation:

$$e_i = e_N \pm (-\ln r_N r_i)^{1/2}$$

we obtain values of $e_E=-0.20$ and $e_B=-0.15$, in the range of those reported by Cameron *et al.*[15] ($e_E=-0.25$ and $e_B=-0.30$), whereas the values of the parameter Q are in the range of 0.75–0.86 for all four monomers considered[16]. Therefore, the introduction of n-alkyl side substituents of increasing length gives rise to a modification of the polar character of the corresponding acrylic derivatives, favouring the dipolar interactions with the nitrile group of N molecules, rather than an effect on the steric hindrance.

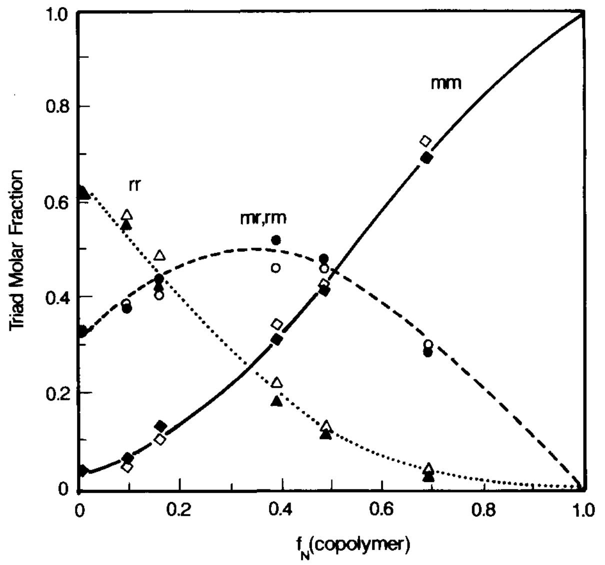

Figure 5 Variation of the molar fraction of E centred triads as a function of N molar fraction in the copolymer samples. Solid symbols correspond to data obtained from the carbonyl carbon signals; open symbols correspond to data from quaternary carbon; lines are the theoretical diagrams with the statistical parameters indicated in the text

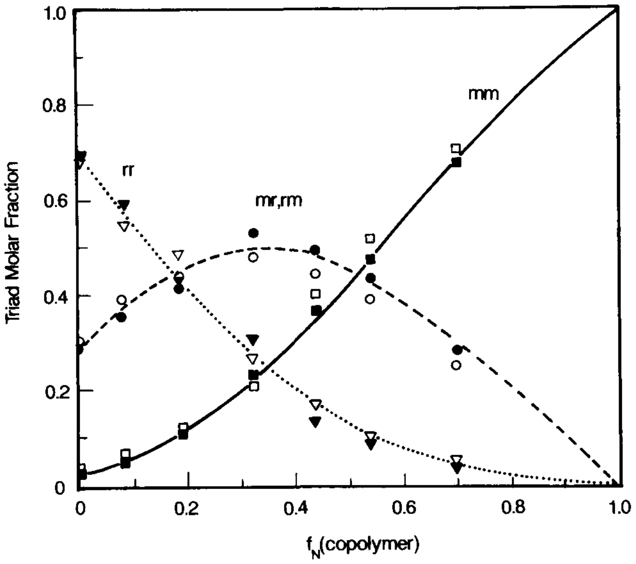

Figure 6 Variation of the molar fraction of B centred triads as a function of N molar fraction in the copolymer samples. Symbols and lines have the same meaning as in *Figure 5*

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