

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

¹³C-Nuclear Magnetic Resonance Analysis of Some Essentially Random Copolymers of Methyl Methacrylate and Butadiene

J. R. Ebdon^a; S. H. Kandil^{ab}

^a Department of Chemistry, University of Lancaster, Lancaster, England ^b Medical Research Institute, University of Alexandria, Alexandria, Egypt

To cite this Article Ebdon, J. R. and Kandil, S. H.(1980) '¹³C-Nuclear Magnetic Resonance Analysis of Some Essentially Random Copolymers of Methyl Methacrylate and Butadiene', *Journal of Macromolecular Science, Part A*, 14: 3, 409 – 425

To link to this Article: DOI: 10.1080/00222338008056721

URL: <http://dx.doi.org/10.1080/00222338008056721>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

^{13}C -Nuclear Magnetic Resonance Analysis of Some Essentially Random Copolymers of Methyl Methacrylate and Butadiene

J. R. EBDON and S. H. KANDIL*

Department of Chemistry
University of Lancaster,
Lancaster LA1 4YA, England

ABSTRACT

20 MHz ^{13}C -NMR (nuclear magnetic resonance) spectroscopy has been used to determine the relative concentrations of certain methacrylate and butadiene containing monomer sequence fractions in some essentially random free-radical copolymers of methyl methacrylate and butadiene. Several of the results are in good agreement with those obtained in an earlier ^1H -NMR study and confirm, within experimental error, that the copolymerization obeys first-order Markov statistics. The patterns of olefinic carbon resonances reveal that the progressive introduction of methacrylate units into the polymers slightly increases the trans-1,4- to cis-1,4 ratios of the butadiene units relative to that found for a pure polybutadiene prepared under similar conditions.

*Present address: Medical Research Institute, University of Alexandria, Alexandria, Egypt.

INTRODUCTION

Certain features of the monomer sequence distributions of free-radical copolymers of methyl methacrylate (M) with butadiene (B), isoprene, and chloroprene have been determined by 220 MHz proton magnetic resonance spectroscopy [1-3]. In particular, the proton signals from the α -methyl groups of the M units in these copolymers allow M-centered triad fractions to be measured and compared with fractions calculated from reactivity ratios. However, proton signals from the B units appear to provide no sequence information and therefore do not allow a full test of the copolymerization statistics to be made. In this paper, we report an examination of some methyl methacrylate-butadiene copolymers by ^{13}C -nuclear magnetic resonance (^{13}C -NMR). ^{13}C -NMR has been shown to be capable of providing useful information concerning the microstructures of polybutadienes [4-9].

EXPERIMENTAL

Some essentially random copolymers of methyl methacrylate and butadiene (MB-1 - MB-6) were prepared by conventional radical copolymerization. A highly alternating copolymer (MB-A) was prepared with the aid of ZnCl_2 . Details of these preparations and of the isolations of the copolymers have been given elsewhere [1].

The compositions of the copolymers were obtained from integrated 60 MHz proton magnetic resonance spectra recorded on 10% w/v solutions of the copolymers in CDCl_3 [1]. ^{13}C -NMR spectra of the copolymers were recorded also on 10% w/v solutions in CDCl_3 by using a Varian CFT 20 20 MHz spectrometer at ambient probe temperature (ca. 35°C). Other relevant operating parameters were: sweep width, 4000 Hz; acquisition time, 0.51 sec; pulse width, 12 μsec (corresponding to a nuclear tip angle of $\sim 51^\circ$); number of data points used in accumulating the spectra, 4096; number of pulses, $\sim 30\text{K}$. No additional delay between pulses was used, and proton decoupling was accomplished by the usual "white-noise" irradiation technique. For quantitative measurements, the nuclear Overhauser effect was removed by gated decoupling. Peak areas were measured by using the usual cutting and weighing technique, and the deconvolution of overlapped peak components was achieved with the aid of a DuPont 310 curve resolver using generated peaks of Lorentzian shape. Whenever carbon peak areas were used for quantitative measurements, it was previously established that small changes in pulse width and acquisition time or an additional delay between pulses did not affect the relative areas of the relevant peaks. In any case, comparisons were made only between the areas of peaks arising from carbons in similar chemical environments.

TABLE 1. Composition of Copolymers

Copolymer	Methyl methacrylate (mole %)	
	In feed	In copolymer ^a
MB-1	95	80
MB-2	90	72
MB-3	85	62
MB-4	80	58
MB-5	70	51
MB-6	50	40
MB-A	50	46

^a Probable error ± 2 in each case.

RESULTS AND DISCUSSION

The compositions of the copolymers obtained from the proton magnetic resonance spectra (by comparing the areas of the MMA methoxyl proton peaks with the total proton peak areas) are listed in Table 1 together with the compositions of the feeds from which they were prepared. Substitution of these compositions into the Fineman and Ross equation [10] gives the reactivity ratios $r_M = 0.17 \pm 0.02$ and $r_B = 0.60 \pm 0.10$. The proton spectra also show that of the butadiene units in the copolymers, ca. 10% are in the 1,2-configuration, the remainder being 1,4 units, and that these proportions do not depend on the copolymer composition [1].

The complete ^{13}C -NMR spectra for copolymers MB-A and MB-5 are shown in Fig. 1. Of particular interest are the peaks arising from (a) the α -methyl, quaternary and carbonyl carbons of the M units (15-22, 44-47, and 176-179 ppm relative to TMS, respectively), (b) the olefinic carbons of the butadiene units (110-142 ppm), and (c) the various methylene carbons (principally 22-44 ppm). All of these peaks show splittings characteristic of the effects of monomer sequence distribution and/or monomer unit configuration. The information concerning the microstructures of the copolymers that may be obtained from these carbon peaks is discussed below.

MMA α -Methyl, Quaternary, and Carbonyl Carbon Peaks

Expansions of the α -methyl signals for copolymers MB-A, MB-5, MB-2 and for a sample of poly(methyl methacrylate) (PMMA) prepared

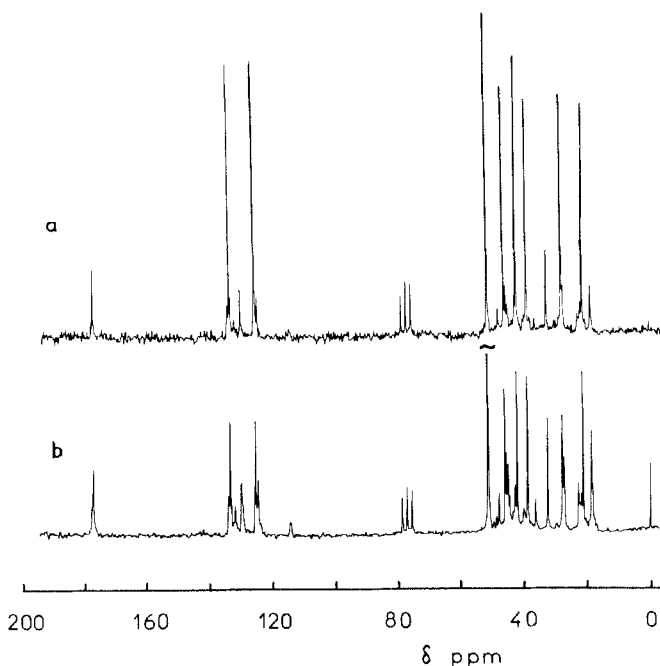


FIG. 1. Complete 20 MHz ^{13}C -NMR spectra of copolymers: (a) MB-A; (b) MB-5.

under conditions similar to those used in the copolymerizations are shown in Fig. 2. The shaded peaks (22.8 ppm) are butadiene methylene resonances. The overall pattern of the α -methyl signals and the way in which this pattern is influenced by the copolymer composition is analogous to the behavior of the α -methyl proton signals [1]. Thus the highly alternating copolymer (MB-A) exhibits one major α -methyl signal (G) at 21.2 ppm characteristic of MMA units in BMB triads. (Here and subsequently the unit within a sequence giving rise to the signal in question is underlined.) This signal is a major component also in the α -methyl peaks of random copolymers relatively rich in butadiene (MB-4, MB-5, and MB-6). Poly(methyl methacrylate) shows only two α -methyl signals (A and F) characteristic of syndiotactic and heterotactic $\overline{\text{MMM}}$ triads, respectively. A third small signal arising from the isotactic $\overline{\text{MMM}}$ triads which would be expected at ~ 21.0 ppm is apparently masked by the baseline noise. The α -methyl signal from syndiotactic $\overline{\text{MMM}}$ triads in the copolymers is split into three components (A, B, and $\overline{\text{C}}$) at 16.7, 17.2, and 17.7 ppm, respectively; this splitting is attributed to next-nearest-neighbor effects and the components are assigned, in order of increasing chemical shift, to the pentads $\overline{\text{MMMM}}$, $\overline{\text{BMMMM}}$ (and $\overline{\text{MMMMB}}$), and

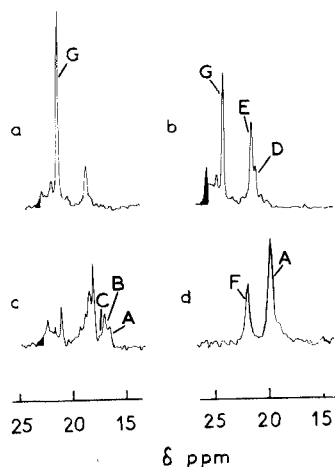


FIG. 2. α -methyl carbon signals for copolymers: (a) MB-A; (b) MB-5; (c) MB-2; (d) PMMA.

BMMMB containing, at their centers, syndiotactic MMM triads. A similar, but less well resolved, pentad effect is exhibited in the α -methyl proton resonances [1]. The two peaks (D and E) at 18.2 and 18.6 ppm which are particularly prominent in the spectra of copolymers MB-3, MB-4, and MB-5 are together assigned to BMM and MMB triads containing racemic MM dyads. Again, the splitting is believed to arise from a next-nearest-neighbor effect with the component at 18.2 ppm being a measure of MMBB (and BMMB) sequences and that at 18.6 ppm being a measure of BMMB sequences. The equivalent peaks from BMM and MMB triads containing meso MM dyads arise between 21.8 and 22.5 ppm but are not well resolved in any of the spectra.

Expansions of the quaternary carbon signals for copolymers MB-A, MB-5, MB-2 and for the poly(methyl methacrylate) are shown in Fig. 3. At least five components are discernible in the quaternary carbon signals of the copolymers. In poly(methyl methacrylate), the three components (H, I, and J) at 44.7, 45.1, and 45.4 ppm are assigned to syndiotactic, heterotactic, and isotactic MMM triads, respectively, while the prominent component at 46.2 ppm (K) in the signals from the copolymers is assigned to BMB triads. The remaining peaks must arise from BMM and MMB triads but are not well enough resolved to allow positive assignments to be made.

Figure 4 shows expansions of the methyl methacrylate carbonyl carbon signals for copolymers MB-A and MB-2 and for the poly(methyl methacrylate). The assignments of the poly(methyl methacrylate) resonances are well known [11], and can be used to measure the

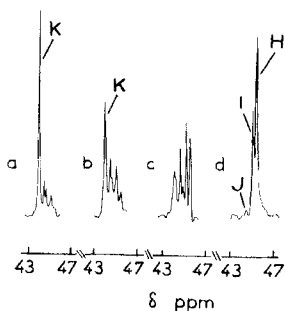


FIG. 3. Quaternary carbon signals for copolymers: (a) MB-A; (b) MB-5; (c) MB-2; (d) PMMA.

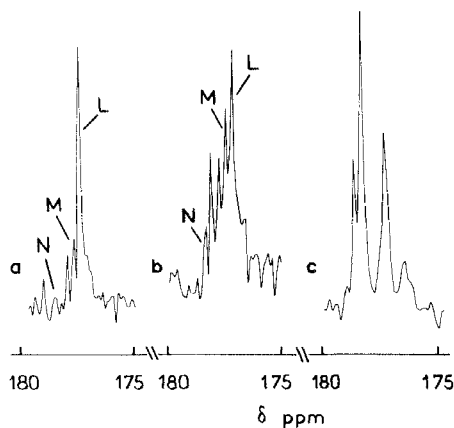


FIG. 4. Carbonyl carbon signals for copolymers: (a) MB-A; (b) MB-2; (c) PMMA.

relative amounts of configurational pentads. The introduction of butadiene leads to new carbonyl resonances (L, M, and N) at 177.1, 177.4 and 178.3 ppm. Of these new resonances, only that at 177.1 ppm can be assigned with any certainty (to $\underline{\text{BMB}}$ triads) as this is the largest component in the spectrum of MB-A and in the spectra of the random copolymers relatively rich in butadiene (MB-4, MB-5, and MB-6).

Thus, the α -methyl, quaternary, and carbonyl resonances can all be used to give information about certain M-centered sequences. Tables 2 and 3 compare sequence fractions determined from the areas of these peaks with those calculated from the

TABLE 2. M-Centered Triad Fractions from Reactivity Ratios, Carbonyl Carbon Peaks, Quaternary Carbon Peaks, and α -Methyl Carbon Peaks

Copolymer	Triad fractions (mole %) ^a											
	From r values			Quaternary C			α -Methyl C			Carbonyl C		
	BMB	MMB	MMM	BMB	MMB	MMM	BMB	MMB	MMM	BMB	MMB	MMM
MB-1	5	34	61	7	22	71	5	33	62	17		
MB-2	14	47	39	16	39	45	12	57	31	25		
MB-3	25	50	25	18	49	33	19	53	28	32		
MB-4	34	49	17	28	51	21	29	59	12	34		
MB-5	51	41	8	40	44	16	46	49	5	47		
MB-6	73	25	2	59	36	5	67	30	3	78		
MB-A	100 ^b	0 ^b	0 ^b	67	33	0	68	32	0	79		

^a Probable error ± 2 in each case except for those calculated from r values.

^b Theoretical values for completely alternating copolymer.

TABLE 3. M-Centered Pentad Fractions from Reactivity Ratios and from α -Methyl Carbon Peaks

Copolymer	Pentad fractions (mole %)										
	From r values					From α -Methyl C ^a					
	<u>B</u> <u>M</u> <u>M</u> <u>M</u> <u>B</u>	<u>B</u> <u>M</u> <u>M</u> <u>M</u> <u>M</u>	<u>M</u> <u>M</u> <u>M</u> <u>M</u> <u>M</u>	<u>B</u> <u>M</u> <u>M</u> <u>M</u> <u>B</u>	<u>M</u> <u>M</u> <u>M</u> <u>M</u> <u>B</u>	<u>B</u> <u>M</u> <u>M</u> <u>M</u> <u>M</u>	<u>B</u> <u>M</u> <u>M</u> <u>M</u> <u>M</u>	<u>M</u> <u>M</u> <u>M</u> <u>M</u> <u>M</u>	<u>B</u> <u>M</u> <u>M</u> <u>M</u> <u>B</u>	<u>B</u> <u>M</u> <u>M</u> <u>M</u> <u>B</u>	<u>M</u> <u>M</u> <u>M</u> <u>M</u> <u>B</u>
MB-1	3	21	37	8	26	8	23	32	11	22	22
MB-2	6	18	15	18	29	5	16	10	22	35	35
MB-3	6	13	6	25	25	10	12	6	22	31	31
MB-4	6	8	3	28	21	5	5	2	32	29	29
MB-5	4	3	1	29	12	3	2	0	34	15	15
MB-6	1.5	0.5	0	21	4	-	-	-	26	4	4

^a Probable error ± 2 in each case.

reactivity ratios using a modified version of the Harwood program [12]. For the copolymers, the total fractions of MMM triads have been determined from the syndiotactic MMM carbon resonances on assuming that the relative proportions of syndiotactic, heterotactic, and isotactic MMM triads in the copolymers are the same as that in the poly(methyl methacrylate), i. e., that the probability of meso placement P_m is 0.25, and thus that the areas of the syndiotactic MMM peaks represent 56% of the contribution from all MMM triads. It is assumed also for those sequences involving butadiene units (e. g., MMB, BMB, etc.) that the peaks being measured are those arising from sequences in which the butadiene units are in the predominant 1,4-configuration. Thus the measured peak areas may be subject to some error because of the uncertainty in the positions of resonances arising from M-centered sequences containing 1,2-units and also because it is not known whether the 1,2-units are distributed randomly among the butadiene units in the copolymer. However these errors are not likely to be large because of the low concentrations of 1,2-units in the copolymers and will be comparable with the errors in the calculated sequence fractions arising from the probable errors in the reactivity ratios. As can be seen from Tables 2 and 3, despite the uncertainties, the measured M-centered sequence fractions are in reasonable agreement with those calculated from the reactivity ratios.

Butadiene Olefinic Carbon Peaks

Expansions of the olefinic carbon peaks for copolymers MB-A and MB-5 and for a sample of polybutadiene prepared under conditions similar to those used for the copolymer preparations are shown in Fig. 5. The assignments of the olefinic carbon peaks for polybutadiene containing cis-1,4-, trans-1,4-, and 1,2-units have been discussed by Elgert et al. [9], who have shown that many of the observed chemical shifts can be rationalized with the aid of a set of empirical shift parameters similar to those used to describe the spectra of simple alkanes and alkenes [13, 14]. Comparison of the spectrum of the polybutadiene with the data of Elgert et al. leads to the assignments for the olefinic carbon peaks given in Table 4. In Table 4, C denotes a cis-1,4-unit, T a trans-1,4-unit, and V a 1,2-unit. The superscripts 2 and 3 denote the particular carbon atom under consideration in cis- and trans-units. The superscript 2 appears before the symbol to which it refers and the superscript 3 appears behind the symbol to which it refers. The particular unit being considered within a sequence is underlined. Thus, $\underline{\text{CT}^3\text{V}}$ denotes the underlined carbon atom in sequences of the type I. Brackets are used in the nomenclature system to denote situations where two or more units have similar effects upon a particular chemical shift, e. g., $\text{V}^2\overline{\text{CC}}$, $\text{V}^2\overline{\text{CT}}$, and $\text{V}^2\overline{\text{CV}}$ have similar chemical shifts and together are denoted as $\text{V}^2\overline{\text{C}}(\text{C}, \text{T}, \text{V})$.

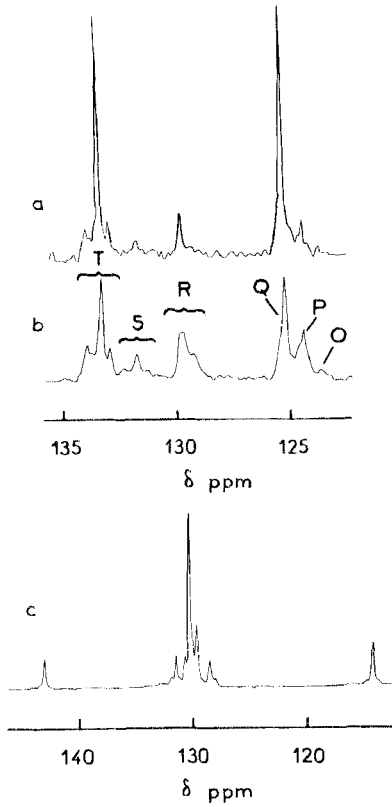
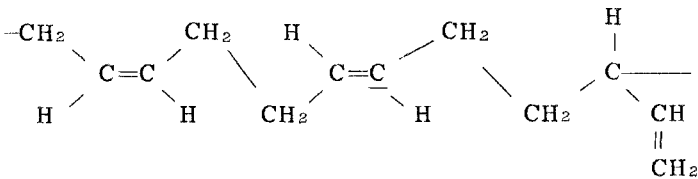


FIG. 5. Olefinic carbon signals for copolymers: (a) MB-A; (b) MB-5; (c) polybutadiene.



I

The introduction of methyl methacrylate units into the polymer leads to new butadiene olefinic carbon resonances between 123 and 126 ppm and between 131 and 135 ppm. In the alternating copolymer, MB-A, the olefinic resonances are largely confined to two large peaks, one at 125.6 ppm and the other at 133.6 ppm. Since in copolymer MB-A,

TABLE 4. Assignments of Polybutadiene Olefinic Carbon Signals (Fig. 5c)

Chemical shift relative to TMS (ppm)	Assignment
114.2	Olefinic methylene in V units
127.9	$\text{V}^2\text{C}(\text{C}, \text{T}, \text{V})$
128.4	$\text{V}^2\text{T}(\text{C}, \text{T}, \text{V})$
129.5	$(\text{C}, \text{T})^2\text{C}(\text{C}, \text{T}, \text{V})$
130.0	Principally $(\text{C}, \text{T})^2\text{T}(\text{C}, \text{T}, \text{V})$
130.6	$\text{VC}^3\text{V} + \text{VT}^3(\text{C}, \text{T})$
131.3	$(\text{C}, \text{T})\text{T}^3\text{V}$
131.8	VT^3V

the butadiene units are apparently almost exclusively in the trans-1,4 configuration [1] and are expected to be flanked by pairs of methacrylate units (M) the following assignments are reasonable: 125.6 ppm, M^2TM ; 133.6 ppm, MT^3M . By analogy with the relative positions of the V^2TV and V^2CV resonances and of the VT^3V and VC^3V resonances, the M^2CM resonance would be expected to occur about 0.5 ppm to higher field than the M^2TM resonance, while the MC^3M resonance would be expected to occur about 1 ppm to higher field than the MT^3M resonance. In the spectra of copolymers MB-1 - MB-6, which contain cis-1,4-butadiene units as well as trans-1,4 units, distinct new olefinic resonances are observed at 124.7 and at 132.0 ppm, i. e., upfield from the M^2TM and MT^3M resonances by 0.9 and 1.6 ppm, respectively. In view of the discussion above, it seems reasonable to assign these new resonances to M^2CM and MC^3M . However, the spectra of copolymers MB-1 - MB-4 show that the peak at 124.7 ppm must contain contributions from sequences other than M^2CM , since in these spectra this peak is disproportionately large when compared with that from M^2TM , yet there is evidence of only a slight change in the cis/trans ratio of the butadiene units in the copolymers as the methacrylate content is increased (see later). Since the relative size of the peak at 134.7 ppm grows as the methacrylate content of the copolymer is increased (from MB-4 to MB-1) it is reasonable to suggest that the sequence responsible is the MM^2TM sequence, i. e., that the ^2T resonance is sensitive to a next-nearest-neighbor effect. The component of the M^2TM resonance at 125.6 ppm would thus be assigned to $(\text{C}, \text{T})\text{M}^2\text{TM}$. By analogy, the $(\text{C}, \text{T})\text{M}^2\text{CM}$ and MM^2CM resonances would be expected to be separated also by 0.9 ppm and thus for the MM^2CM resonance to appear at 123.8 ppm. In fact, a

small peak is visible in this position in the spectra of all the random copolymers. It is interesting to note also that for the random copolymers, there seem to be no distinct resonances for the M^2TC and M^2TT sequences nor for the M^2CC and M^2CT sequences. Thus for copolymer MB-6, where such sequences should be dominant, a pattern of 2T and 2C peaks very similar to that for MB-A is observed. Therefore it may be concluded that the 2T and 2C resonances are not sensitive to the nature of the immediately succeeding unit in the sequence and the following final assignments for the 2T and 2C peaks may be made: 125.6 ppm (peak Q), $(C,T)M^2T(C,T,\bar{V},M)$; 124.7 ppm (peak P), $(C,T)M^2C(C,T,\bar{V},M)$ and $MM^2T(C,T,\bar{V},M)$; 123.8 ppm (peak O), $MM^2C(C,T,\bar{V},M)$. The total area of the above three peaks thus provides an effective measure of the fraction of MB dyads in the copolymer.

The main T^3 and C^3 resonances in the random copolymers at 133.6 and 132.0 ppm, respectively, are also associated with some minor resonances which may arise from next-nearest-neighbor effects. Thus, the main T^3 resonance is associated with peaks at 134.2, 134.0, and 133.2 ppm, while the main C^3 resonance is associated with peaks at 132.5 and 131.6 ppm. It is proposed therefore that the total area of the peaks from 134.2 to 133.2 ppm (group T) is effectively a measure of BM dyads in which the B unit is in a trans-1,4 configuration while those from 132.5 to 131.6 ppm (group S) are effectively a measure of BM dyads in which the B unit is in a cis-1,4 configuration. The peaks at 130.1 and 129.5 ppm (group R) which predominate in the spectrum of the polybutadiene and which are evident also in the spectra of the random copolymers relatively rich in butadiene (MB-5 and MB-6) are effectively a measure of BB dyads; the former of BB dyads in which one or both of the B units have a trans-1,4 configuration, and the latter of BB dyads in which one or both of the B units have a cis-1,4 configuration. Table 5 compares the fractions of MB, BB, and BM dyads obtained from the areas of the olefinic carbon peaks with those calculated from the reactivity ratios.

Methylene Carbon Peaks

Figure 6 shows expansions of the methylene regions for copolymers MB-A and MB-4 and for the polybutadiene. The assignments of the methylene resonances for polybutadienes containing units with a mixture of configurations have been discussed most recently by Hoffman et al. [7] and by Suman and Werstler [8]. Of the two sets of assignments, those of Suman and Werstler are the most self-consistent and for this reason have been adopted here as a basis for the assignment of the methylene resonances in the copolymers. Just as the introduction of methacrylate units would be expected to give rise to a pattern of olefinic resonances from 1,4-butadiene units similar to that produced by the introduction of 1,2-butadiene units, so the pattern of methylene resonances produced by the introduction of

TABLE 5. Dyad Fractions from Butadiene Olefinic Resonances and from Reactivity Ratios^a

Copolymer	Dyad fraction (mole %)											
	From r values					From olefinic C						
	BM	BB	MB	BM	BB	MB	BM	BB	Trans	Cis	BM (%) ^b	BB (%) ^b
MB-1	49	2	49	48	2	50	48	2	80	20	-	-
MB-2	48	4	48	47	2	51	47	2	76	24	-	-
MB-3	48	4	48	54	4	42	54	4	69	31	62	38
MB-4	48	4	48	46	7	47	46	7	76	24	65	35
MB-5	44	12	44	45	12	43	45	12	71	29	64	36
MB-6	38	24	38	41	18	41	41	18	72	28	65	35
MB-A	-	-	-	50	4	46	50	4	87	13	-	-

^aDyad fractions are normalized only over those dyads containing B units in cis- or trans-1,4 configurations. Dyads containing 1,2 units are ignored. Thus it is assumed that 1,2 and 1,4 configurations are randomly distributed among the butadiene units in the copolymers. Probable error of ± 2 is associated with each measured dyad fraction.

^bPercentage of BM and BB dyads containing B units of the particular configuration (the B unit under consideration is underlined).

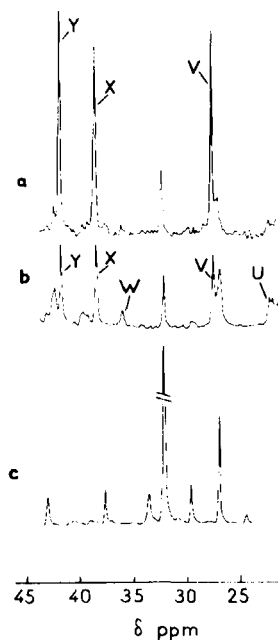


FIG. 6. Methylene carbon signals for copolymers: (a) MB-A; (b) MB-4; (c) polybutadiene.

methacrylate units would similarly be expected to resemble the pattern produced by 1,2-units. The assignments of the methylene resonances for the polybutadiene are given in Table 6. The system of nomenclature is similar to that used before; the superscripts 1 and 4 are used to indicate the particular methylene group in cis- and trans- units being referred to. The peaks at 39.5 and 43.5 ppm arise from backbone methine carbons of 1,2- units in \underline{VV} and $\underline{CV} + \underline{TV}$ dyads respectively.

As can be seen from Table 6, the effect on a \underline{T}^1 resonance of the replacement of a neighboring cis or trans unit by a vinyl unit is to move the resonance upfield by 2.5 ppm (from 32.7 to 30.2 ppm). Such a replacement has a similar effect upon a \underline{C}^1 resonance (moved from 27.5 to 25.0 ppm). Thus the replacement of a neighboring cis or trans unit by an MMA unit might be expected to produce comparable upfield shifts of \underline{T}^1 and \underline{C}^1 resonances. For the random copolymers, two new methylene resonances are visible to high field at 28.0 (V) and 22.7 ppm (U), i. e., 4.7 and 4.8 ppm upfield from the \underline{T}^1 (C,T) and \underline{C}^1 (C,T) resonances, respectively. These new resonances are assigned to $\underline{T}^1\text{M}$ and $\underline{C}^1\text{M}$. In the spectrum of the alternating copolymer, the component at 28.0 ppm ($\underline{T}^1\text{M}$), is, as expected, the major one.

TABLE 6. Assignments of the Methylene Resonances in Polybutadiene (Fig. 6)

Chemical shift relative to TMS (ppm)	Assignment
25.0	$\underline{\text{C}^1\text{V}}$
27.5	$\underline{\text{C}^1(\text{C}, \text{T})}$
30.2	$\underline{\text{T}^1\text{V}}$
32.7	$\underline{\text{T}^1(\text{C}, \text{T})} + \underline{\text{V}^1\text{C}}$
34.2	$(\text{C}, \text{T})\underline{\text{V}}$
38.2	$\text{V}^1\underline{\text{T}}$
40.0	(Backbone methine in V sequences)
41.1	$\underline{\text{VV}}$
43.5	(Backbone methine in isolated V units)

TABLE 7. M-Centered Triad Fractions from Butadiene Methylene Peaks and Reactivity Ratios

Copolymer	Triad fractions (%) ^a			
	From r values		From methylene C	
	MMB	BMB	MMB	BMB
MB-1	78	22	71	29
MB-2	62	38	69	31
MB-3	50	50	48	52
MB-4	35	65	43	57
MB-5	29	71	22	78
MB-6	15	85	17	83

^aTriad fractions are normalized to $[\text{MMB}] + [\text{BMB}] = 100\%$. Probable error of ± 2 associated with each measured fraction.

Additional methylene resonances in the spectra of the random copolymers arise at 36.5, 39.0, and 42.3 ppm (W, X, and Y); these are assigned to $\overline{M^1C}$, $(C,T)\overline{M}$, and $M^1\overline{T}$, respectively. For the copolymers relatively rich in MMA, the $M^1\overline{T}$ peak is clearly associated with additional peaks at around 43 ppm. These additional peaks are believed to arise from a next-nearest-neighbor effect and are assigned to sequences of the type $MM^1\overline{T}$. The peak at 42.3 ppm can thus be more fully assigned to $(C,T)\overline{M^1T}$ (where the $VM^1\overline{T}$ resonance arises is not clear). A next-nearest-neighbor effect is probably responsible also for the relatively high intensity of the methylene peak at 27.5 ppm in the random copolymers; in addition to $\overline{C^1}(C,T)$, this peak is believed to contain a contribution from $\overline{T^1}MM$ [the peak at 28.0 ppm is thus more fully assigned to $\overline{T^1}M(C,\overline{T})$]. The relative areas of the peaks at 42.3 and at around 43 ppm have been used to measure the relative proportions of BMB and MMB triads (assuming that the cis- and trans-1,4 configurations are randomly distributed among the butadiene units in the copolymers). These relative proportions are compared with those calculated from the measured reactivity ratios in Table 7.

CONCLUSIONS

The various M-centered and B-containing triad and dyad fractions that have been obtained from the ^{13}C -NMR spectra are in reasonable agreement with those calculated from the experimentally determined binary reactivity ratios. Thus the ^{13}C -NMR results support the conclusion reached from the earlier proton NMR study [1], namely, that the copolymerization obeys simple first-order Markov statistics. The results support also the contention that the overall tacticity of the methacrylate sequences is unaffected by the introduction of butadiene comonomer units and follows simple Bernoullian trial statistics as in conventional atactic methyl methacrylate homopolymers.

Perhaps the most interesting result is that the average configuration of the butadiene units is influenced to a slight extent by the presence of the methacrylate units; the proportion of trans-1,4-butadiene units in BM dyads is, on average, slightly higher than the proportion in BB dyads. This effect is similar in kind (but not in extent) to that reported for butadiene-acrylonitrile copolymers where IR analysis has indicated that acrylonitrile-rich copolymers contain proportionately more butadiene units in trans-1,4 configurations than those rich in butadiene [14]. The origin of this type of effect is not known but may be the result either of a more favorable interaction between the butadienyl radical and the incoming methacrylate unit when the butadienyl radical is in the trans/1,4 configuration or of unfavorable steric interaction in BM dyads containing butadiene units in cis-1,4 and 1,2 configurations. In a system of competing reactions

involving small activation energies such as copolymerization propagation steps, even quite small differences in interaction energies could significantly affect the activation energy differences and hence demonstrably affect the overall balance of the reactions.

ACKNOWLEDGMENT

We thank the British Council and Fylde College, University of Lancaster for financial support for S. H. K. during the period of this research.

REFERENCES

- [1] J. R. Ebdon, *J. Macromol. Sci.-Chem.*, **A8**, 417 (1974).
- [2] J. C. Bevington and J. R. Ebdon, *Makromol. Chem.*, **153**, 173 (1972).
- [3] J. R. Ebdon, *Polymer*, **15**, 782 (1974).
- [4] K.-F. Elgert, B. Stützel, P. Frenzel, H.-J. Cantow and R. Streck, *Makromol. Chem.*, **170**, 257 (1973).
- [5] Y. Tanaka and K. Hatada, *J. Polym. Sci. Polym. Letters Ed.*, **11**, 569 (1973).
- [6] J. Furukawa, E. Kobayashi, N. Katsuki, and T. Kawagoe, *Makromol. Chem.*, **175**, 237 (1974).
- [7] W. Hoffman, P. Kuzay, and W. Kimmer, *Plaste u. Kaut.*, **21**, 423 (1974).
- [8] P. T. Suman and D. D. Werstler, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 1963 (1975).
- [9] K.-F. Elgert, G. Quack, and B. Stützel, *Polymer*, **16**, 154 (1975).
- [10] M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
- [11] Y. Inoue, A. Nishioka, and R. Chujō, *Polym. J.*, **4**, 535 (1971).
- [12] H. J. Harwood, N. W. Johnston, and H. Piotrowski, *J. Polym. Sci. C*, **25**, 23 (1968).
- [13] L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971).
- [14] D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971).
- [15] Q.-T. Pham, J. Vialle, and J. Guillot, *Proceedings of the 2nd European Symposium on Polymer Spectroscopy, Milan, 1971*, C. Tosi and G. Zerbi, Eds., Consiglio Nazionale delle Ricerche, Rome, 1973, p. 42.

Accepted by editor February 16, 1979

Received for publication February 20, 1979