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Determination of the Microstructure of Some Methyl Methacrylate-Butadiene Copolymers by 220 MHz Proton Magnetic Resonance Spectroscopy

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ABSTRACT

Proton magnetic resonance (PMR) spectroscopy at 220 MHz has been used to gain information about the relative proportions of various methyl methacrylate centered triads and pentads in some methyl methacrylate (MMA)-butadiene (BU) copolymers prepared with a free-radical catalyst. The PMR peaks used are the MMA α-methyl peaks recorded using $CDCl_3$ as solvent, and the MMA methoxy peaks recorded using C_5D_5N as solvent. Measured triad and pentad fractions are in good agreement with those calculated from the reactivity ratios $r_1 = 0.17$ and $r_2 = 0.60$, where MMA = Monomer 1. Surprisingly, the α-methyl peaks provide information also about the ratio of cis-1,4- to trans-1,4-butadiene units in the copolymer. Proportions of 1,2-butadiene units are obtained from the relative areas of peaks due to vinyl and vinylene protons.

INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy is now an established and important technique for the determination of the compositions and sequence distributions of copolymers, and several reviews which include details of such applications have appeared [1-3]. However, to date, most emphasis has been placed on the study of copolymers containing vinyl or acrylic monomer units and there have been few studies of diene copolymers, although sequence measurements by PMR spectroscopy have been reported recently for copolymers of butadiene with acrylonitrile [4], methacrylonitrile [5], and α-methyl styrene [6], and of isoprene with methyl methacrylate [7]. Also, NMR has been used to confirm the structure of several alternating diene copolymers (e.g., Refs. 8-12).

This paper describes the use of 220 MHz proton magnetic resonance (PMR) spectroscopy to determine triad and pentad sequences in some methyl methacrylate (MMA)-butadiene (BU) copolymers. Information has also been obtained about the proportions of cis-1,4-, trans-1,4-, and 1,2-butadiene units in the copolymers. The ability to be able to distinguish between cis- and trans-butadiene units in these copolymers by PMR spectroscopy is significant, since this technique cannot be used to distinguish between cis and trans units in pure polybutadienes [13].

EXPERIMENTAL

Random Copolymers

Essentially random copolymers of MMA and BU were prepared by the free-radical polymerization of mixtures of the two monomers under vacuum at 60°C using Analar grade benzene as solvent, and benzoyl peroxide (1 g/liter) as initiator. The required amounts of BU were measured out as vapor at 20°C using a bulb of known volume equipped with a mercury manometer and attached to a vacuum line. They were then distilled from the bulb directly into the reaction ampules which already contained the necessary amounts of degassed MMA, benzene, and initiator. Conversions were limited to 3 wt% and the copolymers were recovered by precipitation in methanol. They were purified by reprecipitation from benzene/methanol, freeze-dried from 5% benzene solutions, and finally dried at 50°C under vacuum. All copolymerizations were carried out at an overall monomer concentration of 5 mole/liter.

Alternating Copolymer

An alternating copolymer (Alt-MB) was prepared by copolymerizing 0.1 mole MMA and 0.1 mole BU under vacuum at room temperature in the presence of 0.05 mole dry zinc chloride and 40 mg of benzoyl peroxide. The MMA was added to the zinc chloride first and stirred to form a homogeneous solution. The BU was then distilled in under vacuum. The polymerization was terminated after 15 min by breaking open the reaction vessel and pouring the contents (with the aid of a little dioxane/chloroform) into an excess of methanol acidified with 50% aq HCl. The copolymer was purified and dried by a method similar to that used for the random copolymers. The yield of copolymer was 0.8 g (5.3% by weight based on the monomers).

PMR Measurements

220 MHz PMR spectra were recorded on a Varian HR 220 spectrometer at ambient temperature using deuterochloroform ($CDCl_3$) and perdeuteropyridine (C_5D_5N) as solvents, and tetramethylsilane (TMS) as the internal reference.

IR spectra of copolymer films cast on rock-salt plates from 2% chloroform solutions were recorded using a Perkin-Elmer 237 Infrared Spectrophotometer.

RESULTS AND DISCUSSION

PMR Spectra

The complete PMR spectra in $CDCl_3$ for the alternating copolymer and for the random copolymer prepared from an equimolar feed (MB 6) are shown in Fig. 1. The peaks at around 5 δ (ppm relative to TMS) may be assigned to the $-CH=$ and $CH_2=$ protons in 1,4- and 1,2-BU units; that at 3.7 δ to the MMA methoxy protons; those between 2.7 and 1.4 δ to the BU and MMA methine and methylene protons, and those between 1.4 and 0.8 δ to the MMA α-methyl protons. The prominent peak at 2.0 δ in the spectrum of the random copolymer (MB 6) arises from the adjacent methylene groups in BU dyads. The absence of this peak in the spectrum of the copolymer prepared in the presence of zinc chloride confirms its alternating structure.

Reactivity Ratios

Mole fractions of MMA in the copolymers (x) were obtained from the PMR spectra using the relationship:

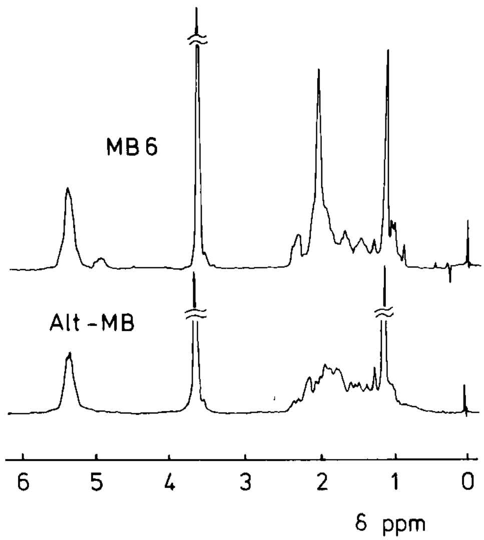

FIG. 1. Complete PMR spectra of copolymer MB6 and alternating copolymer in $CDCl_3$.

$$x = 6A_{OMe}/(3A_{total} - 2A_{OMe})$$

where A_{OMe} is the area of the MMA methoxy signal and A_{total} is the total proton peak area. Peak areas were measured by the technique of tracing, cutting, and weighing. Copolymer and feed compositions are shown in Table 1. Substitution of these figures into the Fineman and Ross equation [14] gives the reactivity ratios $r_1 = 0.17 \pm 0.02$ and r_2 and 0.60 ± 0.10, where MMA = Monomer 1. These values are close to those of Johnston and Harwood [15] for copolymers prepared in bulk at 55°C ($r_1 = 0.18$, $r_2 = 0.73$). The linearity of the Fineman and Ross plot indicates that for this copolymer system, the terminal model of Mayo and Lewis [16] is quite adequate, and that any penultimate group effects must be negligibly small. Thus sequence calculations based on these reactivity ratios can be considered to be reliable.

Proportion of 1,4- and 1,2-Diene Units

The relative amounts of 1,4- and 1,2-diene units in the copolymers can be estimated from the areas of the CH_2= and —CH= proton peaks

TABLE 1. Copolymer Compositions

Copolymer	MMA in feed (mole %)	MMA in copolymer (mole %)
MB 1	95	80
MB 2	90	72
MB 3	85	62
MB 4	80	58
MB 5	70	51
MB 6	50	40
Alt-MB	50	46

(A_{CH2} and A_{CH}) at around 4.9 and 5.4 δ, respectively, using the relationship:

$$\% \text{ 1,2-units} = 200\, A_{CH2}/(2A_{CH} + A_{CH2})$$

For the random copolymers, the proportion of 1,2- units is 10 ± 2% in all cases, whereas for the alternating copolymer there appear to be no 1,2-units. Thus, for the random copolymers, the 1,2- to 1,4-unit ratio is not influenced by the amount of MMA present.

MMA α-Methyl Peaks in $CDCl_3$ Solvent

Figure 2 depicts the PMR peaks arising from the MMA α-methyl protons for four of the random copolymers, for the alternating copolymer, and for a sample of free-radical polymethyl methacrylate prepared at 60°C. As can be seen from the figure, the peaks can be divided into three main regions (A, B, and C). The relative areas of these three regions were measured for each polymer, and the results are given in Table 2. For polymethyl methacrylate, it is well known that Regions A, B, and C arise from MMA units at the center of isotactic, heterotactic, and syndiotactic triads, respectively [17]. For the copolymers, the way in which the relative areas of the three regions change with copolymer composition suggests that Region A is largely associated with MMA units at the center of BMB triads (where M = MMA and B = BU), that Region B is largely

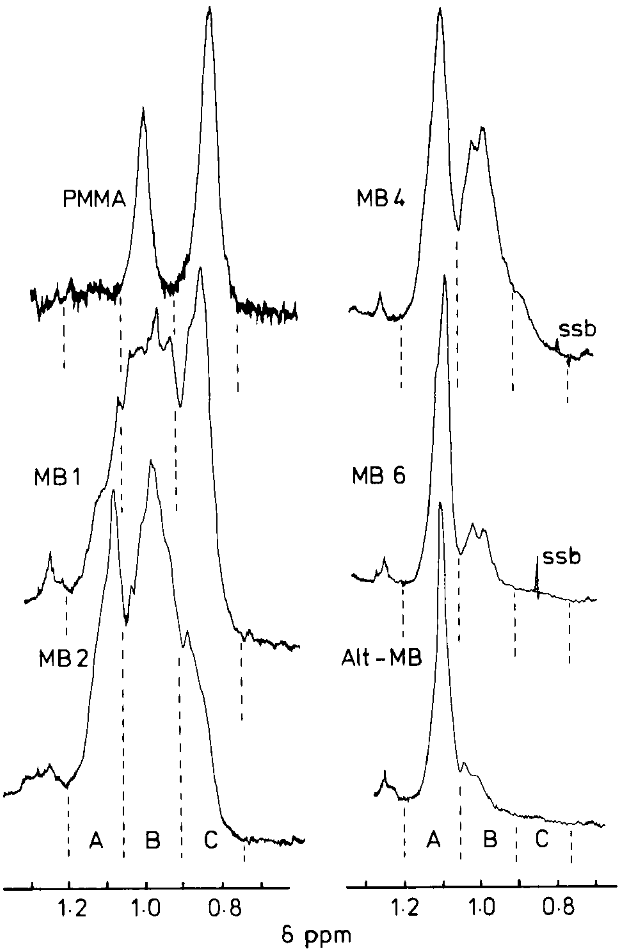

FIG. 2. MMA α-methyl peaks in $CDCl_3$.

associated with MMA units at the center of MMB and BMM triads, and that Region C represents the syndiotactic MMM triads (as in polymethyl methacrylate). However, triad fractions calculated on the basis of these peak identifications differ markedly from those calculated from the reactivity ratios. Much better agreement between measured and calculated triad fractions is obtained if it is assumed 1) that Region A corresponds to isotactic MMM triads + BMB triads + BMM and MMB triads containing an MM dyad with a meso configuration,

TABLE 2. Relative Areas of α-Methyl Peaks in Regions A, B, and C

Polymer	A (%)	B (%)	C (%)
PMMA	6	36	58
MB 1	20	44	36
MB 2	34	48	18
MB 3	38	48	14
MB 4	47	46	7
MB 5	55	38	7
MB 6	75	21	4
Alt-MB	81	15	4

2) that Region B corresponds to heterotactic MMM triads + BMM and MMB triads containing an MM dyad with a racemic configuration, and 3) that Region C corresponds to syndiotactic MMM triads. The extent of the agreement between measured and calculated fractions can be seen in Table 3. The calculated fractions were obtained from the reactivity ratios using a version of the computer program described by Harwood et al. [18]; they are corrected for the effects of finite conversion. To calculate the proportion of BMM and MMB in which the dyad is in the meso configuration, a value of Pm (probability of meso placement) of 0.25 was used. This value of Pm is consistent with the observed tacticity of the polymethyl methacrylate sample. Also, it has been assumed that the tacticity of the MMM triads is the same in the copolymers as it is in the homopolymer. This is a reasonable assumption, since in free-radical homopolymerizations of MMA the tacticity closely obeys Bernoullian statistics and thus would not be expected to be affected by the introduction of comonomer units.

For the random copolymers containing the larger amounts of methyl methacrylate (MB 1, 2, 3, and 4), Region C of the α-methyl peaks is composed of two overlapped peaks centered at 0.89 and 0.85 δ, respectively. The areas of these two peaks were measured with the aid of a Du Pont 310 curve resolver using generated peaks of approximately Lorentzian shape. The former peak can be assigned to syndiotactic MMM triads at the center of BMMMB, BMMMM, and MMMMB pentads, and the latter to syndiotactic MMM triads at the center of MMMMM pentads (see Table 4).

For the random copolymers containing the least methyl methacrylate (MB 4, 5, and 6), Region A of the α-methyl peaks consists almost entirely of two main peaks at 1.13 and 1.10 δ, respectively. The ratio

TABLE 3. Measured and Calculated M-Centered Triad Fractions

	Total MMM (%)		Racemic BMM and MMB (%)		BMB + meso-MMB and BMM (%)	
Copolymer	Meas	Calc	Meas	Calc	Meas	Calc
MB 1	62	61	22	25	16	14
MB 2	31	38	37	35	32	27
MB 3	24	25	39	37	37	38
MB 4	12	17	42	37	46	46
MB 5	12	8	34	31	54	61
MB 6	7	2	18	19	75	79
Alt-MB	7	-	12	-	81	-

TABLE 4. Measured and Calculated BMMMB + MMMMB + BMMMM and MMMMM Pentad Fractions Containing a Central Syndiotactic MMM Triad

	MMMMB + BMMMB (containing syndio-MMM) (%)		MMMMM (containing syndio-MMM) (%)	
Polymer	Meas	Calc	Meas	Calc
MB 1	13	14	23	21
MB 2	10	14	8	9
MB 3	10	11	4	3
MB 4	5	8	2	2

of these two peaks (obtained with the aid of the curve resolver) is 36:64 for all three samples. Since Region A in these copolymers arises almost entirely from the BMB triads, it is reasonable to suppose that the two components reflect some configurational degeneracy of these triads. However, the invariance of the peak ratio rules out pentad effects. It is therefore suggested that the splitting reflects the cis-1,4- and trans-1,4-configurations of one of the BU units in the BMB triads. The most likely diene unit to be involved is that which has the

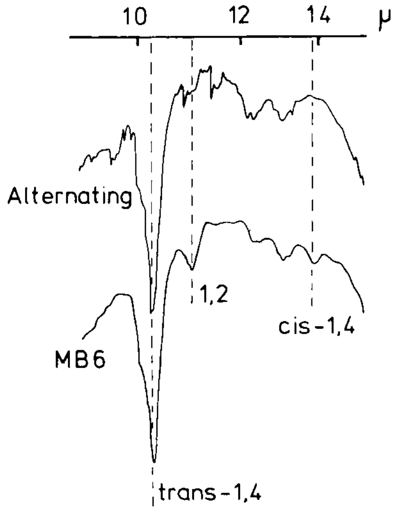

FIG. 3. IR spectra of copolymer MB 6 and alternating copolymer.

carbon-carbon double bond nearest to the α-methyl group of the central MMA unit, namely the diene unit attached to the MMA α-carbon atom. To confirm these assignments, the proportions of cis-1,4-, trans-1,4-, and 1,2-BU units in copolymer MB 6 were estimated from its IR spectrum (Fig. 3) following the procedure of Haslam and Willis [19] and using the bands at 10.3, 11.0, and 13.8 μ as being characteristic of trans-1,4-, 1,2-, and cis-1,4-units, respectively. Estimation of the absorbance of the 10.3-μ band is made difficult by the overlap of this band with that at 10.1 μ arising from the MMA units. However, the IR data suggests an overall cis-trans ratio of approximately 30:70. Thus it seems likely that the two PMR peaks in Region A reflect the cis-trans ratio in the BMB triads and in the copolymer as a whole. Further confirmation is provided by the observation that for the alternating copolymer, the peak ratio is 13:87 and that the IR spectrum of this copolymer (Fig. 3) contains a pronounced band at 10.3 μ (characteristic of trans-1,4-diene units) but no visible band at 13.8 μ (characteristic of cis-1,4-units).

MMA Methoxy Peaks in C_5D_5N Solvent

The PMR spectra of the random copolymers recorded in C_5D_5N show little fine structure in the α-methyl region. However, in this solvent the MMA methoxy resonance is split into three partially

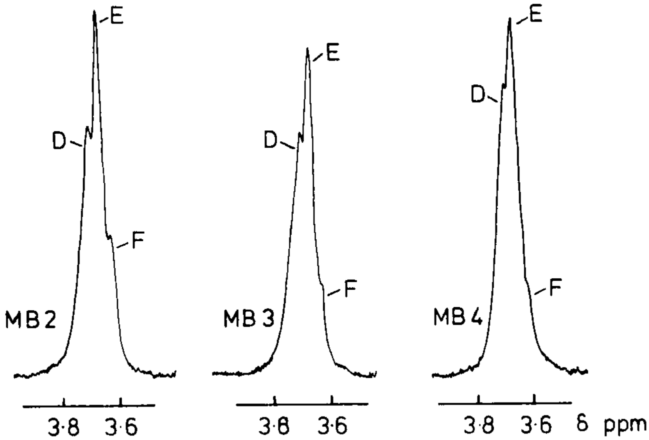

FIG. 4. MMA methoxy peaks in C_5D_5N.

TABLE 5. Analyses of MMA Methoxy Peaks in C_5D_5N and M-Centered Triad Fractions Based on Them

Copolymer	Methoxy peaks D (%)	E (%)	F (%)	Total MMM (%)	Racemic MMB + BMM	BMB + meso-BMM + MMB
MB 1	21	35	34	59	14	18
MB 2	31	45	24	41	30	28
MB 3	35	49	16	28	39	33
MB 4	38	54	8	14	49	37
MB 5	47	49	4	7	47	47
MB 6	73	27	0	0	27	73

resolved peaks (D, E, and F) centered at 3.70, 3.66, and 3.62 δ, respectively. The peaks for MB 2, 3, and 4 are shown in Fig. 4. The relative areas of these component peaks are related to the MMA-centered triad fractions in the same way as the MMA α-methyl peaks in $CDCl_3$ solvent. Deconvolution of the methoxy peaks was accomplished using the curve resolver and the results are presented in Table 5, together with the M-centered triad fractions obtained from them assuming that Peak D = isotactic MMM + BMB + meso MMB and BMM, that

Peak E = heterotactic MMM + racemic MMB and BMM, and that Peak F = syndiotactic MMM. The calculated triad fractions are in reasonable agreement with those obtained from the reactivity ratios and those from the α-methyl peaks (Table 3).

The alternating copolymer exhibits a pronounced methoxy peak at 3.70 δ, as would be expected for a copolymer in which all, or nearly all, of the MMA units are at the center of BMB triads.

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REFERENCES

[1] H. A. Willis and M. E. A. Cudby, Appl. Spectrosc. Rev., 1, 237 (1968).
[2] F. A. Bovey, High Resolution NMR of Macromolecules, Academic, New York, 1972, Chaps. X and XI.
[3] V. D. Mochel, J. Macromol. Sci.—Revs. Macromol. Chem., C8, 289 (1972).
[4] P. Kuzay and W. Kimmer, Plaste Kaut., 18, 743 (1971).
[5] R. Schmolke, W. Kimmer, P. Kuzay, and W. Hufenreuter, Ibid., 18, 95 (1971).
[6] K. F. Elgert, E. Seiler, G. Puschendorf, and H.-J. Cantow, Makromol. Chem., 165, 245, 261 (1973).
[7] J. C. Bevington and J. R. Ebdon, Ibid., 153, 173 (1972).
[8] E. Oikawa and K. Yamamoto, Polym. J. (Japan), 1, 669 (1971).
[9] T. Suzuki, Y. Takegami, J. Furukawa, and R. Hirai, J. Polym. Sci., B, 9, 931 (1971).
[10] A. Masaki, J. Macromol. Sci.—Chem., A6, 1267 (1972).
[11] N. G. Gaylord, M. Stolka, and B. K. Patnaik, Ibid., A6, 1435 (1972).
[12] Y. Koma, K. Iimura, and M. Takeda, J. Polym. Sci., Polym. Chem. Ed., 10, 2983 (1972).
[13] Ref. 2., p. 224.
[14] M. Fineman and S. D. Ross, J. Polym. Sci., 5, 259 (1950).
[15] N. W. Johnston and H. J. Harwood, Macromolecules, 3, 20 (1970).
[16] F. R. Mayo and F. M. Lewis, J. Amer. Chem. Soc., 66, 1594 (1944).
[17] F. A. Bovey and G. V. D. Tiers, J. Polym. Sci., 44, 173 (1960).

[18] H. J. Harwood, N. W. Johnston, and H. Piotrowski, J. Polym. Sci., C, 25, 23 (1968).
[19] J. Haslam and H. A. Willis, Identification and Analysis of Plastics, Iliffe, London, 1965, p. 190.

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