Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Polymers. Part III.† Determination of Tacticity in Monomer Sequence Distribution Triads in Styrene–Methyl Methacrylate Copolymer

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In the ^{13}C n.m.r. spectrum of styrene (S)–methyl methacrylate (M) the aromatic C-1 in the styrene units and the methyl carbon atom in the methyl methacrylate units are sensitive to tacticity in the various monomer sequence triads. Measurements of chemical shifts for MMM, SSS, SMS, and MSM tactic triads allow estimation of chemical shifts for SSM and MMS triads. Intensities for MMM, SSS, and MSM tactic triads show the distribution due to tacticity for such monomer sequence triads. The ten M-centred and ten S-centred tactic monomer sequence populations calculated over a whole range of styrene–methyl methacrylate copolymers allow computer simulation of peaks the results of which agree well with experimental observations. The copolymer is random with regard to monomer sequence and tacticity except that blocks of methyl methacrylate or styrene are predominantly syndiotactic.

NOISE-DECOUPLED ^{13}C n.m.r. spectra aid the analysis of copolymers:[1-4] such spectra are relatively simple compared to corresponding ^{1}H n.m.r. spectra. Thus, whereas the ^{1}H n.m.r. spectrum of a copolymer of styrene (S) and methyl methacrylate (M) (40% S and 60% M) ‡ is poorly resolved (Figure 1) the noise-decoupled and coupled ^{13}C n.m.r. spectra of the same sample (Figure 2) are readily interpreted. The simplicity stems from the large chemical shifts and the relatively narrow linewidths that are not critically broadened by dipolar interactions.[2]

Coupled spectra linked with noise-decoupled spectra aid the peak assignments given in Figure 2. The peaks due to carbon atoms with no, one, and three hydrogen atoms attached to them appear in the coupled spectrum as singlets, doublets, and quartets, respectively. Some absorptions in the noise-decoupled spectra exhibit multiplicity due to the carbon resonances being sensitive to the stereochemistry and/or structural features of the chain.

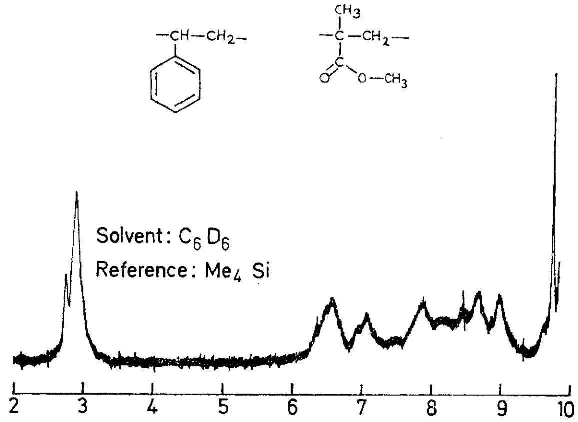

FIGURE 1 100 MHz ^{1}H N.m.r. spectrum of a copolymer of styrene (40%) and methyl methacrylate (60%) at ambient temperature in hexadeuteriobenzene

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† Part II, A. R. Katritzky and D. E. Weiss, preceding paper.

‡ All percentages are expressed as mole %.

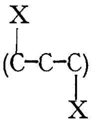
[1] J. Schaefer, *Macromolecules*, 1971, **4**, 107.

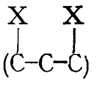
[2] J. Schaefer, *Macromolecules*, 1969, **2**, 210.

[3] C. J. Carman and C. E. Wilkes, *Rubber Chem. Technol.*, 1971, 781.

[4] W. O. Crain, jun., A. Zambelli, and J. D. Roberts, *Macromolecules*, 1971, **4**, 330.

Two types of structural features must be considered. Sequence variation will arise in all copolymers. Tacticity will arise in all polymers containing asymmetric units. Structure is described in terms of triads, which define the nearest neighbours to any particular unit. In styrene–methyl methacrylate we are concerned with both sequence-triads and tacticity-triads. We use S and M to denote monomer units, and r and m to denote relative configuration. Thus the environment of a unit in terms of the nearest neighbours is completely described by a five-digit set. Thus, MrSmS denotes a triad with an S-centre linking an M and another S unit, in which the MS relation is racemic (I) and the SS relation is *meso* (II).


(I)


(II)

In general there will be twenty different triads: ten S-centred (illustrated in Table 1) and ten M-centred.

Styrene–methyl methacrylate copolymers have now been investigated by ^{13}C n.m.r. spectroscopy for the first time although both polystyrene [1,5] and poly(methyl methacrylate) [5-7] have been previously studied by this method. Previous studies of styrene–methyl methacrylate limited to 60 MHz ^1H n.m.r. provided knowledge of monomer distribution available only from the methoxy-absorption, which was split into three peaks only.[8,9] A more recent ^1H n.m.r. study at 100 MHz showed one

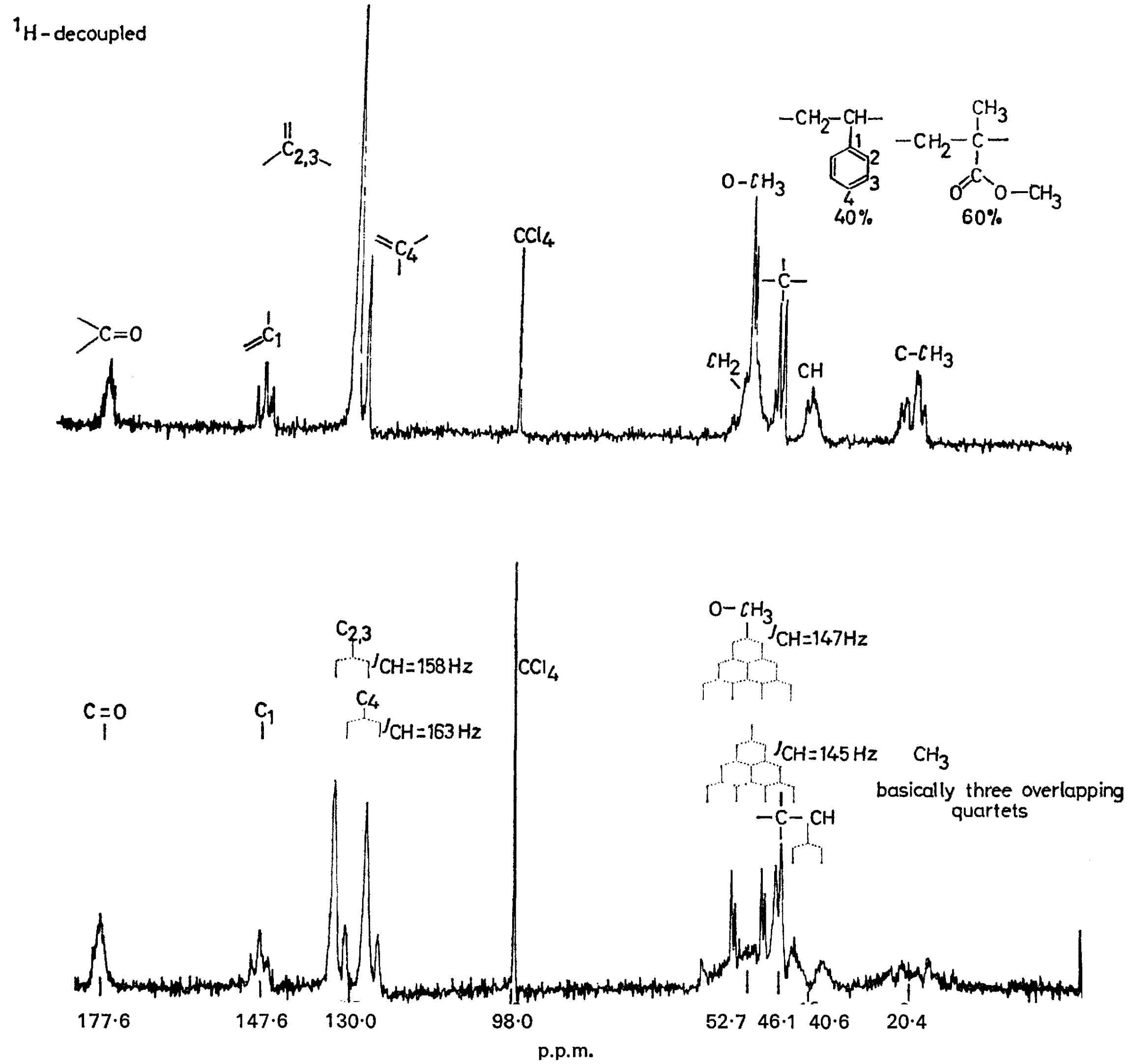


FIGURE 2 ^{13}C N.m.r. spectra of a copolymer of styrene (40%) and methyl methacrylate (60%), obtained at 25·2 MHz in CCl_4 at ambient temperature (p.p.m. downfield from Me_4Si)

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[5] L. F. Johnson, F. Heatley, and F. A. Bovey, *Macromolecules*, 1970, **3**, 175.

[6] Y. Inoue, A. Nishioka, and R. Chûjô, *Polymer J.*, 1971, **4**, 535.

[7] I. R. Peat and W. F. Reynolds, *Tetrahedron Letters*, 1972, 1359.

[8] Y. Yamashita and K. Ito, *Appl. Polymer Symposia*, 1969, No. 8, 245.

[9] H. J. Harwood, A. K. Shah, R. E. Bockrath, and W. M. Ritchey, *Appl. Polymer Symposia*, 1969, No, 8. 227.

of the three methoxy-peaks to have two shoulders and another to have one shoulder.[10]

Table 1

Five-digit sets used to describe the ten possible S-centred tactic monomer sequence distribution triads [a]

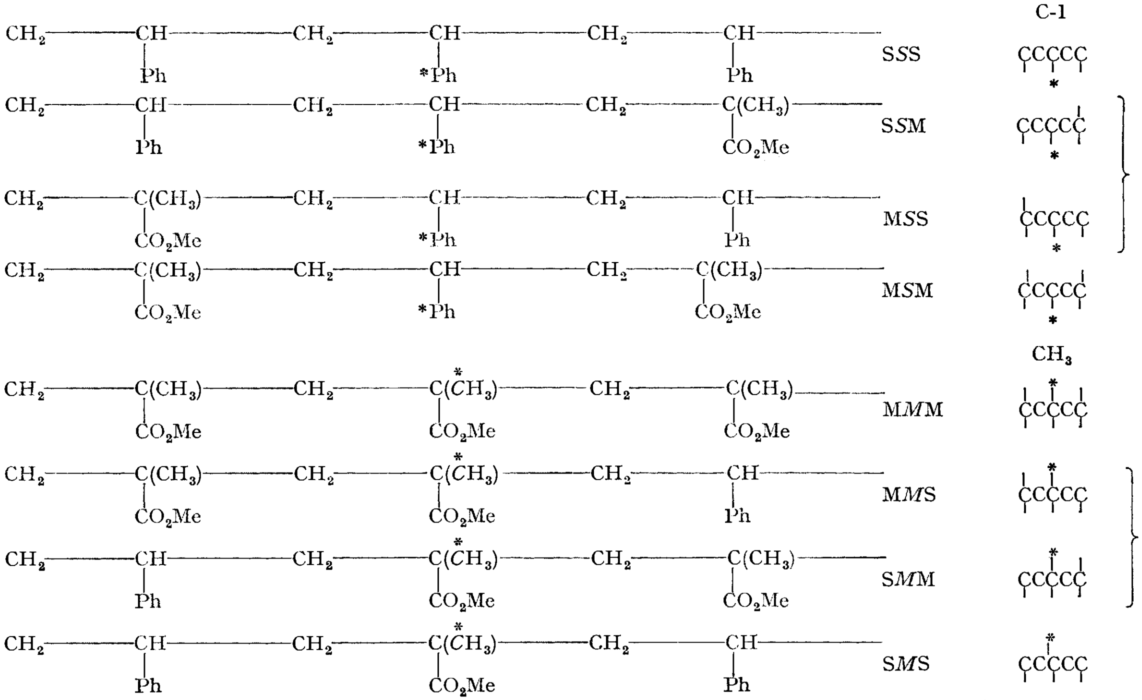
S-Centred triads				
SmSmS		SmSrS		SrSrS
MmSmS	MmSrS		MrSmS	MrSrS
MmSmM		MmSrM		MrSrM

[a] S and M denote styrene and methyl methacrylate and m and r denote *meso* and racemic, respectively.

Table 2 illustrates the possible environments for the two classes of carbon atom in a copolymer of styrene and methyl methacrylate which we have found to be of the most use without regard to tacticity. According to Table 2, C-1 of the phenyl groups derived from styrene units and the methyl carbon atom of the methyl methacrylate units should each give three peaks. Inspection shows that the methine carbon atom of the styrene units and the carbonyl, methoxy, and quaternary carbon atoms of the methyl methacrylate units also occur in three types of environment but their overlap with other carbon absorptions and/or lack of sensitivity limits their use as a source of information for tactic monomer sequence triads.

Table 2

Different MSD environments possible for the styrene aromatic C-1 and methyl methacrylate methyl carbon absorptions in a copolymer of styrene (S) and methyl methacrylate (M) [a]



[a] $\overset{*}{\mathrm{C}}$ denotes the carbon atom being investigated, C the methylene carbons, $\underset{|}{\mathrm{C}}$ the methine carbons, and $\overset{|}{\underset{|}{\mathrm{C}}}$ the quaternary carbon atoms.

Figure 3 gives the spectra for a series of styrene–methyl methacrylate copolymers with varying styrene content, and for polystyrene and poly(methyl methacrylate) polymerised under the same conditions as the copolymers. Hexadeuteriobenzene was used as reference and lock signal. The spectrum for the 40% styrene copolymer is essentially the same in both hexadeuteriobenzene and carbon tetrachloride, showing that solvent effects are small.

The most environment-sensitive and the least overlapped absorptions are those of the methyl methacrylate CH_3 (providing information concerning M-centred triads) and the styrene C-1 (providing information concerning S-centred triads). In polystyrene, the aromatic C-1 signal is split into three peaks which are due to this carbon in isotactic (SmSmS), heterotactic (SmSrS), and syndiotactic (SrSrS) triads in order of increasing field.[11] In the 10% styrene sample, the styrene C-1 signal is also split into three peaks but this must be due to tacticity of the MSM triad and we assume that this is in the same order as for polystyrene above. Likewise, in poly(methyl methacrylate), the CH_3 resonance appears [6] as three peaks which are due to CH_3 units in tactic arrangement corresponding to those for polystyrene. In the 80% styrene sample, the CH_3 signal shows splitting mostly due to tacticity of the SMS triad. Peak

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[10] A. D. Jenkins and M. G. Rayner, *European Polymer J.*, 1972, **8**, 221.

[11] Y. Inoue, A. Nishioka, and R. Chûjô, *Makromol. Chem.*, 1972, **156**, 207.

intensities and chemical shifts for these two absorptions are recorded in Table 3.

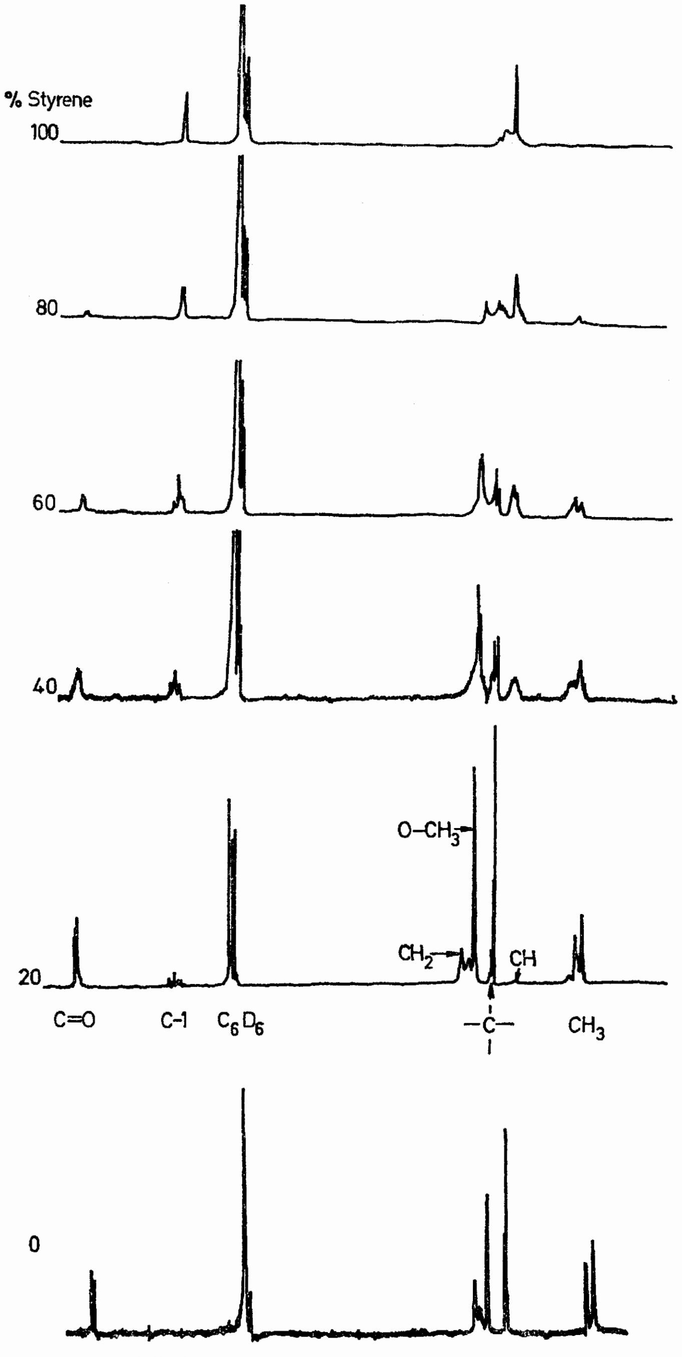

FIGURE 3 ^{13}C N.m.r. spectra of copolymers of styrene and methyl methacrylate, obtained at 25·2 MHz in hexadeuteriobenzene at ambient temperature

Structural features in the chain complicate the spectra of the 60 and 40% styrene copolymers. However, measurements of chemical shifts and intensities for those features already pointed out enable us to apply the statistics developed by Bovey[12] to describe completely for the first time all twenty possible triad environments for a copolymer such as styrene–methyl methacrylate. Further, with the aid of computer simulation, we show that the intensities predicted by these statistics for all our samples of styrene–methyl methacrylate copolymer are a legitimate and accurate description.

In their simplest form, these statistics can be used to describe monomer sequence distribution only. As illustrated below for M-centred triads [MMM, MMS-(SMM), and SMS] one need only calculate the probability that methyl methacrylate will add to itself (P_{MM}). The probability of addition to styrene then is simply ($1 - P_{MM}$). Thus, in a styrene–methyl methacrylate copolymer, the fraction of MMM (F_{MM}) in any given sample is $P_{MM}P_{MM}$. It then follows that the fraction of SMS (F_{SMS}) in this same sample is $(1 - P_{MM})^2$, which is the probability that M will have two S neighbours. For MMS and SMM together (F_{SMM}) we sum $P_{MM}(1 - P_{MM}) + (1 - P_{MM})P_{MM}$. Adding the right hand sides of equations (1)—(3) we find that F_{MMM}, F_{SMM}, and F_{SMS} always sum to unity. A similar treatment follows for styrene-centred triads.

$$F_{MMM} = P_{MM}^2 \quad (1)$$

$$F_{MMS} + F_{SMM} = 2P_{MM}(1 - P_{MM}) \quad (2)$$

$$F_{SMS} = (1 - P_{MM})^2 \quad (3)$$

$$P_{MM} = \rho_M f_M/(1 - f_M + \rho_M f_M) \quad (4)$$

The value for P_{MM} in any given sample is calculated from equation (4) by substituting the appropriate reactivity ratios (ρ) and feed ratios (f). Reactivity ratios are the measure of a monomer's preference to react with itself as opposed to the other monomer present: here $\rho_M = 0{\cdot}46$ for methyl methacrylate[12] and $\rho_S = 0{\cdot}52$ for styrene.[12] Feed ratios (*cf.* Table 4) are the mole ratios of the monomers present at the initiation of polymerisation (f_M and f_S).

For the four copolymer samples, we have tabulated the populations for all six monomer sequence triads [MMM (F_{MMM}), MMS (F_{MMS}), SMS (F_{SMS}), SSS (F_{SSS}), SSM (F_{SSM}), and MSM (F_{MSM})] in Table 4 and illustrate the normalised curves for these triads in Figure 4 to show their populations over a whole range of styrene–methyl methacrylate copolymers. The curves reflect the monomer distribution of a random copolymer (expected for

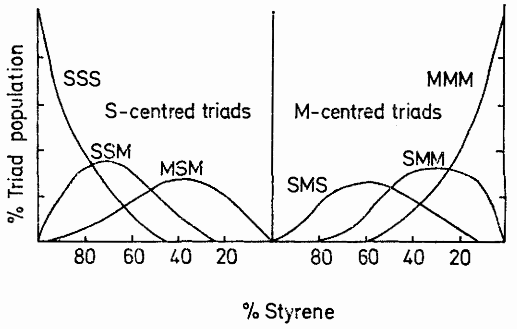

FIGURE 4 Normalised statistical monomer sequence distribution triad populations *vs.* % styrene in styrene–methyl methacrylate copolymer; data plotted appear in Table 4

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[12] F. A. Bovey, *J. Polymer Sci.*, 1962, **62**, 197.

TABLE 3

Peak intensities and chemical shifts measured from the spectra in Figures 3 and 4 for the styrene aromatic C-1 absorption and the methyl methacrylate CH_3 absorption [a]

Mole % styrene:		100		80		60		40		10		0	
Carbon	Unit	Shift	Int.	Shift	Int.	Shift	Int.	Shift	Int.	Shift	Int.	Shift	Int.
C-1	S	152·6	17	152·6	8	153·6	16	153·6	17	153·6	24		
		152·2	29	152·3	54	152·2	48	152·3	54	152·4	52		
		151·7	54	151·7	38	151·3	36	150·6	29	150·6	24		
CH_3	M			28·0	23	28·6	26	28·0	13	26·6	14	26·6	6
				26·9	61	27·0	42	27·0	11	24·8	47	25·6	36
				25·0	16	25·1	32	26·6	8	23·7	39	23·7	58
								25·3	24				
								24·8	26				
								23·9	18				

[a] Chemical shifts expressed in p.p.m. relative to Me_4Si, intensities expressed as % absorption of carbon atom in question.

TABLE 4

Tabulation of the six monomer sequence distribution triads calculated from monomer reactivity ratios and feed ratios [a] for 80, 60, 40, and 10 mole % styrene in styrene–methyl methacrylate copolymers

	Mole % styrene			
M-Centred triads	80	60	40	10
f_M	0·2	0·4	0·6	0·9
P_{MM}	0·11	0·24	0·41	0·78
F_{MMM}	0·01	0·06	0·17	0·60
F_{SMM}	0·19	0·36	0·48	0·35
F_{SMS}	0·80	0·58	0·35	0·05
S-Centred triads				
f_S	0·8	0·6	0·4	0·1
P_{SS}	0·66	0·44	0·26	0·05
F_{SSS}	0·44	0·19	0·07	0·00
F_{MSS}	0·44	0·50	0·38	0·10
F_{MSM}	0·12	0·31	0·55	0·90

[a] Supplied by the International Synthetic Rubber Co., Southampton.

monomers with similar reactivity ratios). This conclusion has been drawn previously and it has been further shown that percent conversion, the completeness with which the monomers react to form the polymer, for this copolymer has little effect on monomer sequence.[13] Tactic distribution, however, is definitely not random, in contrast to the case of the homopolymers, and differs considerably with reference to MS and SM diads. This factor is taken into account in Bovey's expanded statistical treatment [12] used to describe tacticity and monomer sequence. In Table 5 are illustrated the equations of the expanded statistics used to describe the ten tactic monomer sequence M-centred triads. The same treatment follows for the ten S-centred triads. These equations follow directly from those used to describe monomer sequence only but include a new term, σ, which is the probability that any two monomer units will add in a ' coisotactic ' (m) fashion in the nomenclature of Bovey.[12] Thus, $(1 - \sigma)$ is the probability of ' cosyndiotactic ' (r) addition. Equations (5)—(7) describe the tacticity for any homopolymer in terms of triads. Thus the probability of any monomer X being found in an XmXmX (F_{mm}) environment is σ^2. These terms σ_{MM}, σ_{MS}, and σ_{SS} are used to describe the probability of MmM MmS, SmM, and SmS, respectively. In the same manner that P_{MM}^2 describes the fraction of MMM, σ_{MM}^2 describes the fraction of MmMmM. Thus in each equation in Table 5; P, $(1 - P)$, and $P(1 - P)$ describe that part of the equation pertaining to the monomer sequence triad and σ^2, $(1 - \sigma)^2$, and $\sigma(1 - \sigma)$ describe the tacticity of that monomer sequence triad. For F_{MrMrM}, P_{MM}^2 describes the monomer sequence triad (MMM or F_{MMM}) and $(1 - \sigma_{MM})^2$ describes the tacticity (rr or F_{rr}) of that monomer sequence triad. The factor is calculated by the following method. For each sequence MMM, SSS, SMS, and MSM, the three tactic triads (mm, mr, and rr) observed in our spectra are defined by σ^2, $(1 - \sigma)$, and $(1 - \sigma)^2$; therefore, we determine the appropriate σ (*i.e.* σ_{MM}, σ_{MS}, σ_{SM}, σ_{SS}) from the square root of the measured % mm tactic triad from the appropriate absorption of MMM, MSM, SMS, or SSS, respectively. The product $\sigma(1 - \sigma)$ should now equal $1/2F_{mr}$ and $(1 - \sigma)^2$ should equal the value for F_{rr}. Table 6 gives calculated values of σ_{MM}, σ_{MS}, σ_{SM}, and σ_{SS}: $\sigma_{MM} = 0·23$ gives F_{mm}, F_{mr}, and F_{rr} [from equations (5)—(7)] of 5·3, 35·4, and 59·3, respectively. This agrees well with experimental values (*cf.* Table 6). For σ_{SM} and σ_{MS} (both are required to determine tactic distribution for MSM) only a value of 0·5 for each will give the observed distribution in the 80% styrene MSM triad of almost exactly 1 : 2 : 1 for mm, mr, and rr, respectively. This is also confirmed by the SMS absorpin 80% styrene which also involves σ_{MS} and σ_{SM}. If one takes care to subtract the 20% absorption due to MMS (by observation of differences in intensity distribution in the 60% styrene absorption where MMS is almost 40% of the absorption) then an intensity distribution of 1 : 3 remains. This is, we believe, a collapsed 1 : 2 : 1 triplet due to the weak chemical shift of an mS unit, thus confirming our values for σ_{SM} and σ_{MS}. For σ_{SS}, evaluation is difficult owing to the weak mS shift, and the closely overlapping peaks for mm, mr, and rr do not precisely fit any σ values. A weighted average (mm + rr against mr) gives values for mm, mr, and rr of 8, 40, and 52, respectively, which we feel adequately reflect the tacticity of polystyrene. The σ value is essentially the same for SS and MM (0·25) and only half that for SM and MS (0·5);

[13] K. Ito and Y. Yamashita, *J. Polymer Sci., Part B, Polymer Letters*, 1968, **6**, 227.

thus the two monomers prefer to add to one another in a totally random fashion with regard to monomer sequence and tacticity but where blocking occurs they prefer to add in a highly syndiotactic manner.

$$\sigma^2 = F_{\mathrm{mm}} \quad (5)$$

$$2\sigma(1 - \sigma = F_{\mathrm{mr}} + F_{\mathrm{rm}} \quad (6)$$

$$(1 - \sigma)^2 = F_{\mathrm{rr}} \quad (7)$$

TABLE 5

Statistics describing tactic monomer sequence distribution for M-centred triads [a]

$$F_{\mathrm{MMM}} = F_{\mathrm{MmMmM}} + F_{\mathrm{MmMrM}} + F_{\mathrm{MrMmM}} + F_{\mathrm{MrMrM}} \quad (8)$$

$$F_{\mathrm{MmMmM}} = \sigma^2{}_{\mathrm{MM}}P^2{}_{\mathrm{MM}} \quad (9)$$

$$F_{\mathrm{MrMmM}} + F_{\mathrm{MmMrM}} = 2\sigma_{\mathrm{MM}}(1 - \sigma_{\mathrm{MM}})P^2{}_{\mathrm{MM}} \quad (10)$$

$$F_{\mathrm{MrMrM}} = (1 - \sigma_{\mathrm{MM}})^2P^2{}_{\mathrm{MM}} \quad (11)$$

$$\left.\begin{aligned} F_{\mathrm{SMM}} &= F_{\mathrm{SmMmM}} + F_{\mathrm{SmMrM}} + F_{\mathrm{SrMmM}} + F_{\mathrm{SrMrM}} \\ F_{\mathrm{MMS}} &= F_{\mathrm{MmMmS}} + F_{\mathrm{MmMrS}} + F_{\mathrm{MrMmS}} + F_{\mathrm{MrMrS}} \end{aligned}\right\} \quad (12)$$

$$F_{\mathrm{SmMmM}} + F_{\mathrm{MmMmS}} = \sigma_{\mathrm{MM}}(\sigma_{\mathrm{SM}} + \sigma_{\mathrm{MS}})P_{\mathrm{MM}}(1 - P_{\mathrm{MM}}) \quad (13)$$

$$F_{\mathrm{SrMmM}} + F_{\mathrm{MmMrS}} = \sigma_{\mathrm{MM}}[(1 - \sigma_{\mathrm{SM}}) + (1 - \sigma_{\mathrm{MS}})]P_{\mathrm{MM}}(1 - P_{\mathrm{MM}}) \quad (14)$$

$$F_{\mathrm{SmMrM}} + F_{\mathrm{MrMmS}} = (1 - \sigma_{\mathrm{MM}})(\sigma_{\mathrm{SM}} + \sigma_{\mathrm{MS}})P_{\mathrm{MM}}(1 - P_{\mathrm{MM}}) \quad (15)$$

$$F_{\mathrm{SrMrM}} + F_{\mathrm{MrMrS}} = (1 - \sigma_{\mathrm{MM}})[(1 - \sigma_{\mathrm{SM}}) + (1 - \sigma_{\mathrm{MS}})]P_{\mathrm{MM}}(1 - P_{\mathrm{MM}}) \quad (16)$$

$$F_{\mathrm{SMS}} = F_{\mathrm{SmMmS}} + F_{\mathrm{SmMrS}} + F_{\mathrm{SrMmS}} + F_{\mathrm{SrMrS}} \quad (17)$$

$$F_{\mathrm{SmMmS}} = \sigma_{\mathrm{SM}}\sigma_{\mathrm{MS}}(1 - P_{\mathrm{MM}})^2 \quad (18)$$

$$F_{\mathrm{SmMrS}} + F_{\mathrm{SrMmS}} = [\sigma_{\mathrm{MS}}(1 - \sigma_{\mathrm{SM}}) + \sigma_{\mathrm{SM}}(1 - \sigma_{\mathrm{MS}})](1 - P_{\mathrm{MM}})^2 \quad (19)$$

$$F_{\mathrm{SrMrS}} = (1 - \sigma_{\mathrm{SM}})(1 - \sigma_{\mathrm{MS}})(1 - P_{\mathrm{MM}})^2 \quad (20)$$

[a] These equations are taken essentially as they appear in Bovey's paper [12] except for correction of an error in which equations (13)—(16) had been multiplied by a factor of 2. We would also like to draw attention to different usage for terms m and r. We use m and r to denote a stereochemical relationship between two units whereas Bovey used these terms to describe the position of a feature as above (m) or below (r) the polymer chain.

The populations for all twenty tactic monomer sequence triads in the four samples are calculated from feed ratios, reactivity ratios, and the newly determined σ values by the equations in Table 5 and are tabulated in Table 7. In Figure 5, these data have been normalised and plotted to show the curves for a whole range of styrene–methyl methacrylate copolymers. It is interesting to note the nearly total symmetry between S- and M-centred triads as reflected by the nearly identical reactivity ratios and σ values.

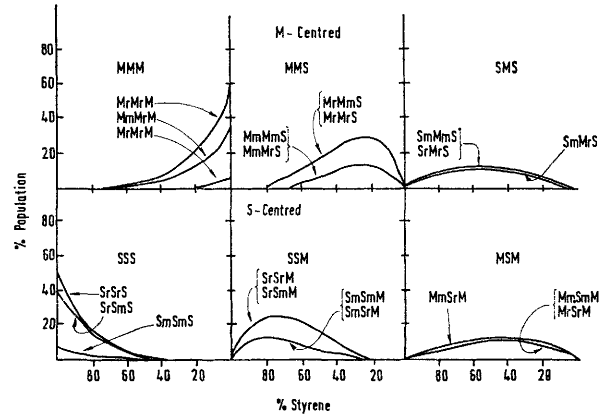
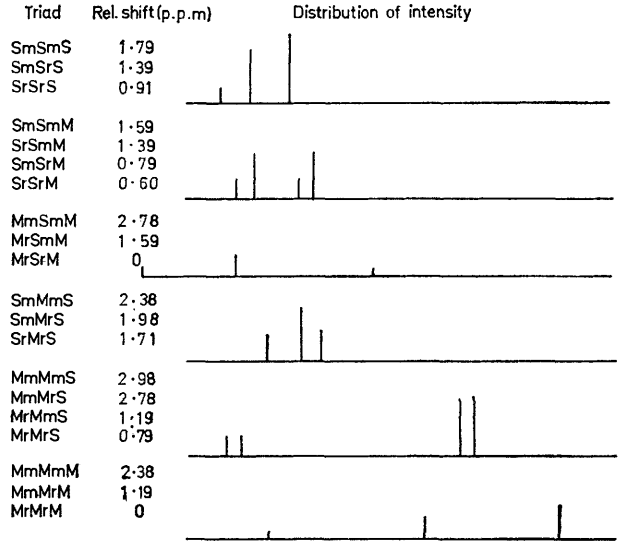


FIGURE 5 Plot of normalised data for twenty tactic monomer sequence triads



Triad	Rel. shift (p.p.m)
SmSmS	1·79
SmSrS	1·39
SrSrS	0·91
SmSmM	1·59
SrSmM	1·39
SmSrM	0·79
SrSrM	0·60
MmSmM	2·78
MrSmM	1·59
MrSrM	0
SmMmS	2·38
SmMrS	1·98
SrMrS	1·71
MmMmS	2·98
MmMrS	2·78
MrMmS	1·19
MrMrS	0·79
MmMmM	2·38
MmMrM	1·19
MrMrM	0

FIGURE 6 Tabulation of relative chemical shifts for all twenty tactic monomer sequence triads and ' stick ' caption showing relative distributions of intensity

Chemical shifts for all twenty tactic monomer sequence triads are recorded in Table 7 and shift differences are shown in Figure 6 along with ' stick ' spectra to show the

TABLE 6

Tabulation of data pertinent to calculation of values for σ_{MM}, σ_{MS}, σ_{SM}, and σ_{SS} [a]

Sample	Carbon	Triad	Peaks Freq.	Peaks Design.	Exp. int.	Lit.[b] int.	Calc. int.	σ Value
100%S	C-1	SSS	152·6	mm	17	14	8	
			152·2	mr	29	30	40	$\sigma_{\mathrm{SS}} = 0{\cdot}29$
			151·7	rr	54	56	52	
0%S	CH_3	MMM	26·6	mm	6	5	5	
			25·6	mr	36	34	35	$\sigma_{\mathrm{MM}} = 0{\cdot}23$
			23·7	rr	58	61	60	
10%S	C-1	MSM	153·6	mm	24		25	
			152·4	mr	52		50	$\sigma_{\mathrm{MS}} = 0{\cdot}5$
			150·6	rr	24		25	$\sigma_{\mathrm{SM}} = 0{\cdot}5$

[a] Experimental and calculated values for tactic triad distribution are shown. Frequencies are reported in p.p.m. relative to Me_4Si; intensities as % carbon absorption. [b] Literature values for polystyrene are from ref. 11 and those for poly(methyl methacrylate) are from ref. 6.

TABLE 7

Evaluation of the ten tactic monomer sequence distribution triads for M-centred and S-centred groups [a]

	80%S	60%S	40%S	10%S	Chem. shifts (p.p.m.)
$F_{\mathrm{MmMmM}} = 0{\cdot}05F_{\mathrm{MMM}}$	0·00	0·00	0·01	0·03	27·6
$F_{\mathrm{MmMrM}} = 0{\cdot}35F_{\mathrm{MMM}}$	0·00	0·02	0·06	0·21	26·4
$F_{\mathrm{MrMrM}} = 0{\cdot}60F_{\mathrm{MMM}}$	0·00	0·04	0·10	0·36	25·2
$F_{\mathrm{MmMmS}} = 0{\cdot}12F_{\mathrm{MMS}}$	0·03	0·04	0·06	0·04	28·2 [b]
$F_{\mathrm{MmMrS}} = 0{\cdot}11F_{\mathrm{MMS}}$	0·02	0·04	0·05	0·04	28·0 [b]
$F_{\mathrm{MrMmS}} = 0{\cdot}39F_{\mathrm{MMS}}$	0·08	0·14	0·19	0·14	26·2 [b]
$F_{\mathrm{MrMrS}} = 0{\cdot}38F_{\mathrm{MMS}}$	0·07	0·14	0·18	0·13	26·0 [b]
$F_{\mathrm{SmMmS}} = 0{\cdot}25F_{\mathrm{SMS}}$	0·20	0·14	0·08	0·01	27·6
$F_{\mathrm{SrMmM}} = 0{\cdot}50F_{\mathrm{SMS}}$	0·40	0·29	0·18	0·03	27·2
$F_{\mathrm{SrMrS}} = 0{\cdot}25F_{\mathrm{SMS}}$	0·20	0·15	0·09	0·01	26·9
$F_{\mathrm{SmSmS}} = 0{\cdot}08F_{\mathrm{SSS}}$	0·04	0·02	0·00	0·00	152·6
$F_{\mathrm{SmSrS}} = 0{\cdot}041F_{\mathrm{SSS}}$	0·18	0·08	0·03	0·00	152·2
$F_{\mathrm{SrSrS}} = 0{\cdot}50F_{\mathrm{SSS}}$	0·22	0·09	0·04	0·00	151·7
$F_{\mathrm{SmSmM}} = 0{\cdot}14F_{\mathrm{SSM}}$	0·06	0·07	0·06	0·01	152·4 [b]
$F_{\mathrm{SmSrM}} = 0{\cdot}15F_{\mathrm{SSM}}$	0·07	0·07	0·06	0·01	151·6 [b]
$F_{\mathrm{SrSmM}} = 0{\cdot}35F_{\mathrm{SSM}}$	0·15	0·18	0·13	0·04	152·2 [b]
$F_{\mathrm{SrSrM}} = 0{\cdot}36F_{\mathrm{SSM}}$	0·16	0·18	0·13	0·04	151·4 [b]
$F_{\mathrm{MmSmM}} = 0{\cdot}25F_{\mathrm{MSM}}$	0·03	0·08	0·14	0·23	153·6
$F_{\mathrm{MmSrM}} = 0{\cdot}50F_{\mathrm{MSM}}$	0·06	0·15	0·27	0·45	152·4
$F_{\mathrm{MrSrM}} = 0{\cdot}25F_{\mathrm{MSM}}$	0·03	0·08	0·14	0·22	150·8

[a] The equations in Table 5 have been simplified; the σ values were calculated (numbers) and the expressions involving P_{XX} have been simplified and are expressed as F_{XXX}. The values for F_{XXX} are taken directly from Table 4. Chemical shifts are indicated. [b] Estimated chemical shifts.

intensity relationship between the tactic triads within each monomer sequence. Chemical shifts and shift differences (in the cases of MMM, SSS, SMS, and MSM) were measured directly from our spectra of polystyrene, poly(methacrylate), and the 80 and 10% styrene samples. Chemical shifts and shift differences for MMS, which predominate for the 60 and 40% styrene samples, were estimated by comparing differences in intensity distribution for these absorptions with those in the 80 and 10% styrene samples. These measured shift differences (Figure 6), coupled with peak intensities (Table 7), allowed us to simulate the C-1 and CH_3 absorptions for the 80, 60, 40, and 10% styrene samples. Our simulations and experimentally obtained absorptions can be directly compared in Figure 7. While not superimposable, there is a close similarity between the two sets of absorptions allowing for noise and the fact that our program is designed to simulate proton spectra only.

What is more important than chemical shifts is that the predicted intensities are in the same order and of the same magnitude as those appearing in our spectra. The fact that our calculations did not directly involve experimentally measured intensities, except to determine σ, indicates the reliability of the proposed statistical relationship for accurately predicting the distribution of environments in polymer chains. With the aid of statistical calculations and ^{13}C n.m.r. spectra we have

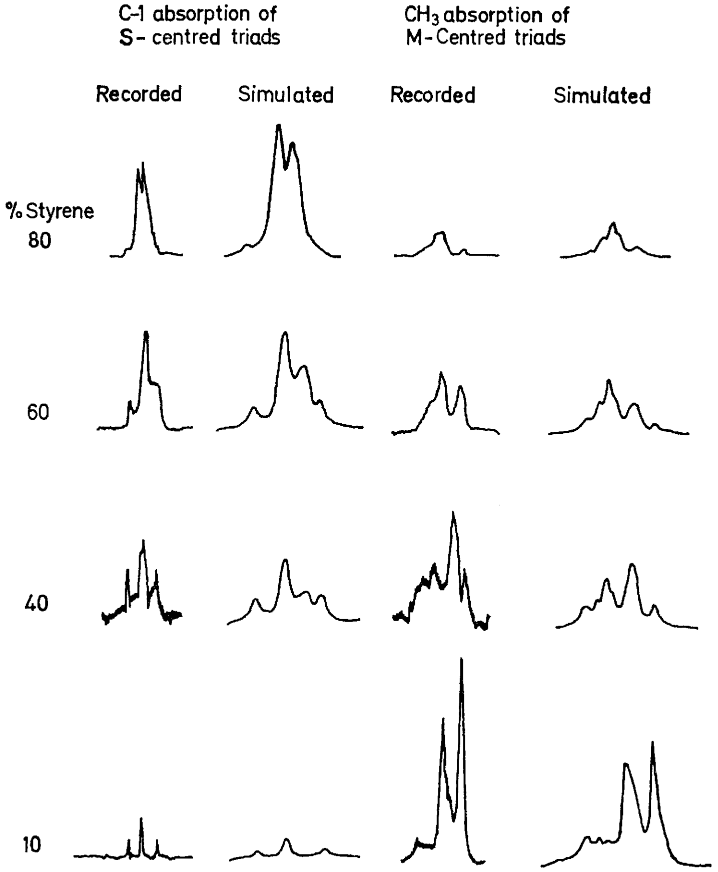


FIGURE 7 Computer-simulated and recorded absorptions for the C-1 aromatic carbon (S-centred triads) and the methyl carbon (M-centred triads) atoms for samples of styrene–methyl methacrylate copolymer of 80, 60, 40, and 10% styrene

completely characterised styrene–methyl methacrylate and show that for the most part it is a completely *random* copolymer in monomer sequence and tactic distribution except where blocks of M or S may be present, which are predominantly syndiotactic.

In general, tacticity of asymmetric monomer units can be determined for homopolymers and monomer sequence in all copolymers. Wider application of these statistics to other ^{13}C investigations of copolymers will allow more precise definition of polymer chains.

EXPERIMENTAL

The proton noise-decoupled Fourier transform ^{13}C n.m.r. spectra were obtained on a Varian XL100 instrument; 12 mm tubes containing *ca.* 700 mg of polymer in 2·5 ml of CCl_4 were used with a 5 mm tube containing D_2O fixed down the centre of each larger tube for an external lock. When C_6D_6 was the solvent it provided both the reference and the lock signal and no inserts were necessary. Chemical shifts were calculated in p.p.m. downfield from Me_4Si. The compositions of all samples are expressed as mole %. Samples were prepared by free-radical methods.[10]

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