Carbon-13 Nuclear Magnetic Resonance Determination of the Sequence Structure of Styrene–Butadiene Copolymers

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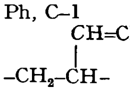
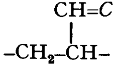
Summary Twenty-six peaks occurring in the ^{13}C n.m.r. spectra of styrene–butadiene copolymers are assigned to the 16 diads that arise from the 4 individual repeating structural units; styrene, vinyl, *cis*-, and *trans*-buta-1,4-diene; diad populations are determined from deduced relationships with peak intensities and average block lengths are calculated for each unit individually and in pairs.

STYRENE–BUTADIENE copolymers are of great commercial importance. Previous knowledge of the detailed sequence structure is limited to a 60 MHz proton n.m.r. determination of block and nonblock styrene, and buta-1,2- and -1,4-diene content.[1] I.r. studies are routinely used to determine the percentage of *trans*- and *cis*-buta-1,4-diene content as well as the proportion of buta-1,2-diene units (often referred to as vinyl).[2]

Comparison of the ^{13}C n.m.r. spectra of styrene–butadiene polymer samples with published spectra for poly(styrene)[3] and poly(butadiene),[4] now allows the assignment of peaks to individual copolymer diads† as summarised in Table 1. As will be shown in the full paper, these assign-

TABLE 1
Assignment of peaks to carbon environment, unit, and diad

Peak	Chem. shift[a]	Assignment[b]	Unit[c]	Diad(s)[c,d]
I	146·5 ± 0·1	Ph, C–1	S	all *S* diads
II	143·9 ± 0·1	 $\mathrm{-CH_2-CH(\mathit{CH}{=}CH_2)-}$	v	all *v*-diads
III[e]	132·8 ± 0·2	$\mathrm{-CH_2-CH{=}\mathit{CH}-CH_2-}$	c + t	*c*S, *t*S, *c*v, *t*v
IV	131·4 ± 0·1	$\mathrm{-CH_2-\mathit{CH}{=}\mathit{CH}-CH_2-}$	t	*t*t, c*t*, t*t*, *t*c
V	130·9 ± 0·1	$\mathrm{-CH_2-\mathit{CH}{=}\mathit{CH}-CH_2-}$	c	*c*c, *c*t, c*c*, t*c*
VI	129·6 ± 0·1	Ph, C-2,6	S	all *S*-diads
VII	129·1 ± 0·1	Ph, C-3,5	S	
VIII[f]	127·3 ± 0·0	Ph, C-4	S	
		$\mathrm{CH_2-\mathit{CH}{=}CH-CH_2-}$	c + t	St, S*c*, v*t*, v*c*
IX	115·9 ± 0·1	 $\mathrm{-CH_2-CH(CH{=}\mathit{CH_2})-}$	v	all *v*-diads
X	47·2 ± 0·0	CH	S	t*S*, c*S*
XI	45·0 ± 0·0	CH	v	t*v*, c*v*
XII	44·4 ± 0·2	CH_2	v, S	*v*S, *S*v
XIII	42·6 ± 0·0	CH_2	S, v	*S*S, *v*v
XIVa	41·7 ± 0·0	CH_2 +	t	*t*S
XIVb		CH	S	S*S*, v*S*
XV	40·6 ± 0·2	CH	v	v*v*, S*v*
XVI	39·8 ± 0·0	CH_2	t	*t*v
XVII	39·1 ± 0·2	CH_2	c	*c*S
XVIII	37·3 ± 0·0	CH_2	S	*S*t, *S*c
XIX	36·9 ± 0·3	CH_2	c	*c*v
XX	35·6 ± 0·1	CH_2	v	*v*t, *v*c
XXI	34·2 ± 0·0	CH_2	t	t*t*, c*t*, *t*t, *t*c
XXII	32·0 ± 0·1	CH_2	t	S*t*
XXIII	31·7 ± 0·1	CH_2	t	v*t*
XXIV	29·0 ± 0·1	CH_2	c	*c*c, *c*t, c*c*, t*c*
XXV	26·9 ± 0·2	CH_2	c	S*c*
XXVI	26·6 ± 0·2	CH_2	c	v*c*

[a] Chemical shifts expressed in p.p.m. downfield from Me_4Si. [b] Ph, phenyl; CH, methine; CH_2, methylene. [c] S = styrene; butadiene (c = *cis*, t = *trans*, v = vinyl). [d] Italics denote unit containing the observed carbon. [e] Peak III was observed to be split in samples 5 and 9. [f] Peak VIII broadened as % styrene increased.

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† Chemical shifts are determined by the nature of (i) the type of bonding of the carbon atom, (ii) the monomer unit involved and (iii) the monomer unit nearest to the carbon atom in question. Diad structure is thus significant: *e.g.*, the CH_2 of S*t* designates the CH_2 of a *trans*-butadiene unit next to a styrene unit in the environment $\mathrm{CH_2{\cdot}CHPh{\cdot}\mathit{CH_2}{\cdot}CH{:}CH{\cdot}CH_2}$.

Table 2

Characterisation of styrene–butadiene copolymers in terms of the 16 diads and average block lengths

	Sample	1	2	3	4
Diad populations	vS	2·0	0·0	0·7	2·1
	Sv	0·3	0·8	0·0	1·7
	cv	1·0	0·6	2·2	3·9
	tv	9·3	5·5	11·0	3·9
	vv	2·4	0·0	3·5	3·6
	vt	8·0	5·5	12·6	6·7
	vc	0·1	1·6	3·4	2·2
	cS	0·6	0·0	0·0	2·8
	tS	6·0	3·9	7·4	11·5
	SS	3·4	7·4	9·3	19·4
	St	7·8	2·2	7·1	13·0
	Sc	0·0	0·8	4·4	3·4
	tt	49·0	25·2	15·6	9·9
	ct	4.3	18·2	10·3	7·4
	tc	5·3	16·4	7·9	4·8
	cc	0·5	11·9	5·3	3·7
	%S	11·6	11·2	19·0	37·0
Average block lengths for monomer units	n_{v}	1·2 ± 0·05	1·0 ± 0·0	1·2 ± 0·0	1·4 ± 0·0
	n_{S}	1·4 ± 0·0	2·8 ± 0·2	2·0 ± 0·2	2·1 ± 0·0
	n_{c}	1·1 ± 0·0	1·6 ± 0·0	1·4 ± 0·0	1·3 ± 0·1
	n_{t}	3·4 ± 0·0	2·0 ± 0·0	1·6 ± 0·0	1·4 ± 0·1
Average block lengths for mixed monomer units	$n_{\mathrm{S,v}}$	1·7 ± 0·1	1·8 ± 0·0	1·5 ± 0·1	2·2 ± 0·0
	$n_{\mathrm{c,t}}$	5·4 ± 0·7	8·1 ± 0·0	2·7 ± 0·2	2·1 ± 0·1
	$n_{\mathrm{S,c}}$	1·3 ± 0·0	1·9 ± 0·0	1·9 ± 0·0	2·2 ± 0·1
	$n_{\mathrm{v,c}}$	1·3 ± 0·0	1·6 ± 0·0	1·6 ± 0·0	1·6 ± 0·0
	$n_{\mathrm{v,t}}$	6·1 ± 0·1	1·7 ± 0·0	3·0 ± 0·0	2·0 ± 0·0
	$n_{\mathrm{S,t}}$	5·4 ± 0·1	2·6 ± 0·0	2·7 ± 0·0	3·8 ± 0·0

ments may be checked by numerous identities which relate the intensities of the various peaks. Such identities between the measured intensities of the sp^3-hybridised carbon absorptions hold well, showing that nuclear Overhauser enhancement differences are negligible. Percentage composition in terms of styrene, vinyl, *cis*-, and *trans*-buta-1,4-diene units as determined from the sp^3-hybridised carbon absorptions are satisfactorily correlated by empirical factors with the relative intensities of the sp^2- and sp-hybridised carbon absorptions.

Table 2 records the diad populations for a variety of commercial styrene–butadiene copolymers. These were obtained from the peak intensities using equations (1—16). The deduction of these equations will be discussed in detail in the full paper;[5] the sole additional assumption required is that the **tt**, tc and ct, cc diads are distributed randomly as in poly(butadiene).[6,7] Equations (15) and (16) contain additional factors which allow for measured differences in the ct and tc populations.

$$\mathrm{Sc} = 0\cdot5[\mathrm{XXV} + \mathrm{XVIII} - \mathrm{XXII}] \pm 0\cdot5[\mathrm{XVIII} - \mathrm{XXV} - \mathrm{XXII} \tag{1}$$

$$\mathrm{St} = 0\cdot5[\mathrm{XXII} + \mathrm{XVIII} - \mathrm{XXV}] \pm 0\cdot5[\mathrm{XVIII} - \mathrm{XXV} - \mathrm{XXII}] \tag{2}$$

$$\mathrm{vc} = 0\cdot5[\mathrm{XXVI} + \mathrm{XX} - \mathrm{XXIII}] \pm 0\cdot5[\mathrm{XX} - \mathrm{XXVI} - \mathrm{XXIII}] \tag{3}$$

$$\mathrm{vt} = 0\cdot5[\mathrm{XXIII} + \mathrm{XX} - \mathrm{XXVI}] \pm 0\cdot5[\mathrm{XX} - \mathrm{XXVI} - \mathrm{XXIII}] \tag{4}$$

$$\mathrm{cS} = 0\cdot5[\mathrm{XVII} + \mathrm{X} - \mathrm{XIVa}] \pm 0\cdot5[\mathrm{X} - \mathrm{XVII} - \mathrm{XIVa}] \tag{5}$$

$$\mathrm{tS} = 0\cdot5[\mathrm{XIVa} + \mathrm{X} - \mathrm{XVII}] \pm 0\cdot5[\mathrm{X} - \mathrm{XVII} - \mathrm{XIVa}] \tag{6}$$

$$\mathrm{cv} = 0\cdot5[\mathrm{XIX} + \mathrm{XI} - \mathrm{XVI}] \pm 0\cdot5[\mathrm{XI} - \mathrm{XIX} - \mathrm{XVI}] \tag{7}$$

$$\mathrm{tv} = 0\cdot5[\mathrm{XI} + \mathrm{XVI} - \mathrm{XIX}] \pm 0\cdot5[\mathrm{XI} - \mathrm{XIX} - \mathrm{XVI}] \tag{8}$$

$$\mathrm{vS} = 0\cdot5[\mathrm{XI} + \mathrm{XII} + \mathrm{XVIII} - \mathrm{X} - \mathrm{XX}] \pm 0\cdot5[\mathrm{X} + \mathrm{XI} - (\mathrm{XVIII} + \mathrm{XX})] \tag{9}$$

$$\mathrm{Sv} = 0\cdot5[\mathrm{X} + \mathrm{XII} + \mathrm{XX} - \mathrm{XVIII} - \mathrm{XI}] \pm 0\cdot5[\mathrm{X} + \mathrm{XI} - (\mathrm{XVIII} + \mathrm{XX})] \tag{10}$$

$$\mathrm{SS} = 0\cdot25[\mathrm{X} - 2\mathrm{XI} + 2\mathrm{XIII} + \mathrm{XIVa} + 2\mathrm{XIVb} - 2\mathrm{XV} + \mathrm{XVII} - 2\mathrm{XVIII} + 2\mathrm{XX}] \tag{11}$$

$$\mathrm{vv} = \mathrm{XV} - 0\cdot5[\mathrm{X} + \mathrm{XII} + \mathrm{XX} - \mathrm{XVIII} - \mathrm{XI}] \pm 0\cdot5[\mathrm{X} + \mathrm{XI} - (\mathrm{XVIII} + \mathrm{XX})] \tag{12}$$

$$\mathrm{tt} = 0\cdot5\mathrm{XXI}^2/(\mathrm{XXI} + \mathrm{XXIV}) \tag{13}$$

$$\mathrm{cc} = 0\cdot5\mathrm{XXIV}^2/(\mathrm{XXI} + \mathrm{XXIV}) \tag{14}$$

$$\mathrm{tc} = 0\cdot5\frac{\mathrm{XXIV}\cdot\mathrm{XXI}}{(\mathrm{XXI} + \mathrm{XXIV})} - 0\cdot25[\mathrm{XIVa} + \mathrm{XVI} + \mathrm{XXV} + \mathrm{XXVI} - (\mathrm{XVII} + \mathrm{XIX} + \mathrm{XXII} + \mathrm{XXIII})] \tag{15}$$

$$\mathrm{ct} = 0\cdot5\frac{\mathrm{XXIV}\cdot\mathrm{XXI}}{(\mathrm{XXI} + \mathrm{XXIV})} + 0\cdot25[\mathrm{XIVa} + \mathrm{XVI} + \mathrm{XXV} + \mathrm{XXVI} - (\mathrm{XVII} + \mathrm{XIX} + \mathrm{XXII} + \mathrm{XXIII})] \tag{16}$$

$$n_{\mathrm{A}} = 0\cdot5\left[\left(1 + \frac{\mathrm{AA}}{\mathrm{AB} + \mathrm{AC} + \ldots + \mathrm{AX}}\right)\right.$$

$$+\left(1+\frac{\mathrm{AA}}{\mathrm{BA}+\mathrm{CA}+\ldots+\mathrm{XA}}\right)\Bigg]$$

$$\pm\, 0{\cdot}5\Bigg[\left(1+\frac{\mathrm{AA}}{\mathrm{AB}+\mathrm{AC}+\ldots+\mathrm{AX}}\right)$$

$$-\left(1+\frac{\mathrm{AA}}{\mathrm{BA}+\mathrm{CA}+\ldots+\mathrm{XA}}\right)\Bigg] \tag{17}$$

$$n_{\mathrm{AB}} = 0{\cdot}5\Bigg[\left(1+\frac{\mathrm{AA}+\mathrm{AB}+\mathrm{BA}+\mathrm{BB}}{\mathrm{AC}+\ldots+\mathrm{AX}+\mathrm{BC}+\ldots+\mathrm{BX}}\right)$$

$$+\left(1+\frac{\mathrm{AA}+\mathrm{AB}+\mathrm{BA}+\mathrm{BB}}{\mathrm{CA}+\ldots+\mathrm{XA}+\mathrm{CB}+\ldots+\mathrm{XB}}\right)\Bigg]$$

$$\pm\, 0{\cdot}5\Bigg[\left(1+\frac{\mathrm{AA}+\mathrm{AB}+\mathrm{BA}+\mathrm{BB}}{\mathrm{AC}+\ldots+\mathrm{AX}+\mathrm{BC}+\ldots+\mathrm{BX}}\right)$$

$$-\left(1+\frac{\mathrm{AA}+\mathrm{AB}+\mathrm{BA}+\mathrm{BB}}{\mathrm{CA}+\ldots+\mathrm{XA}+\mathrm{CB}+\ldots+\mathrm{XB}}\right)\Bigg] \tag{18}$$

The average block length n_{A} for an individual unit A in a polymer containing units A, B, C - - - X is related to the diad populations by equation (17). Values of n_{S}, n_{V}, n_{C}, n_{t} for the commercial samples investigated are listed in Table 2. The average length of mixed blocks containing two units A, B of a polymer containing units A, B, C, - - - X is given by equation (18). Values of the mixed block lengths for the commercial samples are listed in Table 2.

The ^{13}C n.m.r. investigation thus results in a description of the sequence structure of styrene–butadiene copolymers far more detailed than anything previously available. The methods described in this communication have general applicability and should increase our understanding of copolymer structure considerably.‡

We thank Professor E. W. Duck and Dr. S. Wallis of the International Synthetic Rubber Company for help in many ways and the International Institute of Synthetic Rubber Producers for a grant.

(*Received*, 28*th December* 1973; *Com.* 1727.)

‡ *Note added in proof:* In the application of equations (9—16) to the determination of copolymer microstructure, it is preferable in practice to express these in terms of diad populations defined by equations (1—8) rather than simply in terms of peak intensities. Details will be included in the full paper.[5] (We thank Dr. S. Wallis, International Synthetic Rubber Company Southampton, for this information).

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