

# Graded block and randomized copolymers of butadiene–styrene

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Graded block and randomized copolymers of butadiene–styrene were prepared anionically by polymerizing a mixture of butadiene and styrene with *n*-BuLi, in the absence and in the presence of *t*-BuOK respectively. Determination of the monomer composition and microstructure of the polybutadiene sequence was achieved by 300 MHz <sup>1</sup>H n.m.r. and infra-red spectroscopy. <sup>1</sup>H n.m.r. equations developed previously for butadiene–styrene copolymers were modified and extended. In this way, *cis*, *trans* butadiene contents were determined from the aliphatic region of the n.m.r. spectra. The monomer sequence distribution of the copolymers has been investigated by examination of the morphology and their dynamic mechanical properties. The experimental conditions have been established for the preparation of random copolymers with inter- and intramolecular composition distribution.

(Keywords: butadiene–styrene copolymers; characterization; properties; nuclear magnetic resonance; infra-red; monomer composition; microstructure)

## INTRODUCTION

In anionic homopolymerizations butadiene polymerizes at a slower rate than styrene, yet in copolymerization butadiene is incorporated more rapidly than styrene<sup>1–3</sup>. Consequently, copolymerization of a butadiene–styrene mixture in hydrocarbon solvent with alkyl lithium yields a graded block polymer. The monomer sequence distribution in the chain can be visualized as (butadiene)(butadiene→styrene)(styrene), in which initially, the middle block is richer in butadiene with a gradual change in composition until eventually it becomes richer in styrene<sup>4</sup>.

Incremental addition of polar compounds (ethers, *t*-amines), causes an increase in the rate of incorporation of styrene in the polybutadiene block, resulting in a more random copolymer<sup>5</sup>. The length of the polybutadiene and polystyrene blocks in the copolymer chain is expected to decrease as the degree of randomness increases. In these copolymers (designated 'randomized' in this work) the monomer sequence distribution is best represented as (butadiene→styrene)(styrene). Further increase in the relative amount of polar compound can lead to a completely random copolymer with no detectable blocks of polystyrene.

Here we report on the anionic preparation and characterization of graded block and randomized copolymers of butadiene–styrene of predetermined molecular weight and of variable polystyrene block length. These polymers have been used to prepare new grades of toughened polystyrene<sup>6</sup>. Similar materials have been described before<sup>7,8</sup> and some physical properties recorded. We have attempted a more complete characterization of structure and morphology and a more extensive study of dynamic mechanical properties.

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## EXPERIMENTAL

### *Synthesis by anionic copolymerization*

The graded block polymers of butadiene–styrene were synthesized from mixtures of butadiene and styrene with *n*-BuLi in benzene<sup>9</sup>. The randomized copolymers were synthesized by introducing potassium-*tert*-butoxide (*tert*-BuOK) in the above system<sup>10</sup>. To fulfill the conditions of precise control over copolymer composition and molecular weight, all monomer and solvent purifications and polymerizations were carried out in an all-glass, high vacuum system or in sealed, evacuated glass vessels. Benzene, styrene (BDH Lab. Reagent) and butadiene (Shell Chemical Co., 99.5% purity) were purified by procedures described by M. Morton *et al.*<sup>11</sup> *n*-BuLi initiator (Aldrich Chemical Co., 1.6 M) was diluted with *n*-hexane to give a stock solution of 0.0388 M. This solution was used to fill individual ampoules of 10 to 12 ml. Potassium *tert*-butoxide (BDH Lab. Reagent) was dissolved in purified benzene to give a stock solution of 0.118 M. This solution was also transferred to pre-calibrated ampoules. In this way, individual ampoules of 0.01, 0.03, 0.05 and 0.1 moles of potassium-*tert*-butoxide per 1 mole of *n*-BuLi were obtained. Temperature of polymerization was 40°–43°C and complete conversion was achieved after 4–6 h.

### *Structural characterization*

<sup>1</sup>H n.m.r. spectra were recorded at room temperature on a Varian 300 MHz spectrometer, from solutions of the copolymers in deuterated chloroform. CHCl<sub>3</sub> was used as an internal standard giving a peak at 7.25 δ. Infra-red spectra from solutions of the copolymers in CS<sub>2</sub> were recorded on a Perkin-Elmer 580B spectrophotometer coupled to a computer. Gel permeation chromatograms were obtained from PSCC of RAPRA. A differential refractometer and an ultra-violet spectrometer set at

254  $\mu\text{m}$  were used as detectors connected in series. Four crosslinked polystyrene columns of gel 'pore sizes'  $10^6$ ,  $10^5$ ,  $10^4$  and  $10^3$  Å were used. The refractometer trace has been used for the calculation of molecular weights through a calibration curve derived from narrow MWD polystyrene standards. Dynamic-mechanical properties of the crosslinked samples of the copolymers were measured with the Rheovibron DDV-II viscoelastometer, with a fixed frequency of 11 Hz. Crosslinking was achieved with 0.3% and 0.6% dicumyl peroxide. Electron micrographs were taken with a JEOL JEM 100 B, 100 KV transmission electron microscope. Uncrosslinked samples of the copolymers, compression-moulded at 140°C, were used. Heat was removed by convection only, at a cooling rate of about 2.5°C/min. Sectioning took place at liquid nitrogen temperatures after staining with  $\text{OsO}_4$  following Kato's method<sup>12</sup>.

## RESULTS AND DISCUSSION

Table 1 contains the compositions and molecular weights of the samples prepared, as determined from the stoichiometry of the reaction mixtures. Samples SB-1 and SB-2 were prepared in the absence of t-BuOK and thus are graded block copolymers. This is inferred in the colour changes observed during polymerization. The orange colour, typical of the polystyryl anion, appears approximately 2½ h after initiation of the reaction when most of the butadiene has reacted.

Five copolymers labelled SB-4, SB-5, SB-3, SB-7, SB-6 were prepared using the initiator system n-BuLi t-BuOK. A correlation was observed between the amount of t-BuOK used and the appearance of the orange colour of the polystyryl anions, judged in terms of the proportion of monomer converted, and also of the rate of polymerization. The orange colour appears earlier during conversion as the proportion of t-BuOK is increased and a faster rate of polymerization is observed. In sample SB-3 which contains the largest proportion of t-BuOK, the orange colour developed immediately and the reaction was substantially complete in 30 min.

### Characterization

*Gel permeation chromatography.* Figure 1 shows the refractometer (RI) and ultra-violet (u.v.) traces obtained in THF solution from two of the butadiene–styrene copolymers. Inspection of the g.p.c. charts indicates that the composition is the same across the molecular size range, hence the prepared copolymers have uniform intermolecular composition. Furthermore, the agreement between the calculated molecular weights and the experimental ones, as shown in Table 1, is satisfactory.

*N.m.r. spectroscopy.* Figure 2 shows the 300 MHz  $^1\text{H}$  n.m.r. spectrum of an anionically prepared polystyrene with the characteristic proton chemical shifts of the styrene unit. The intensities of the resonance due to the ortho protons ( $\text{H}_o$ ) and the meta plus para protons ( $\text{H}_m + \text{H}_p$ ) are in a ratio of 2:3. The chemical shift of the ortho protons towards a higher field is explained as a 'ring current' effect due to the phenyl rings of the neighbouring styrene units<sup>13</sup>. In statistically random copolymers of styrene this chemical shift is not observed and all the phenyl protons are equivalent. These observations serve as a basis for the determination of the amount of block styrene in butadiene–styrene copolymers<sup>14</sup>.

For comparison, Figure 3 shows the 300 MHz  $^1\text{H}$  n.m.r. spectra of two polybutadiene samples containing the three structural units 1,2 vinyl; *cis*-1,4; *trans*-1,4 with their characteristic chemical shifts. LCPB is an anionically prepared butadiene containing all the three structural units; HCPB has predominantly high *cis*-1,4 content; the 1,4 methylenes and the 1,4 olefinic proton responses show a split into two peaks, corresponding to *cis*-1,4 and *trans*-1,4. Hence, using 300 MHz  $^1\text{H}$  n.m.r. spectroscopy, it is possible to determine the microstructure of polybutadienes<sup>15</sup>.

The percentages of block and random styrene and the microstructure of the butadiene portion of the copolymers were calculated from the areas  $A$  under the peaks, which correlate with the number of protons contributing to them. The following set of equations was used.

$$5M_1 + 3M_2 = A_A \quad (1)$$

$$2M_2 = A_B \quad (2)$$

$$2M_3 = A_T \quad (3)$$

$$2M_4 + M_3 = A_N \quad (4)$$

$$4M_4 + M_2 + 4M_1 = A_M \quad (5)$$

where  $M_1$  = relative number of moles of non-block styrene

$M_2$  = relative number of moles of block styrene

$M_3$  = relative number of moles of 1,2-butadiene

$M_4$  = relative number of moles of 1,4-butadiene

and  $A_A$ ,  $A_B$ ,  $A_T$ ,  $A_N$  and  $A_M$  are the relative areas under peaks A, B, T, N and M respectively in Figure 4. The spectrum of the SB-1 graded block polymer is also shown. The areas  $A_B$  and  $A_M$  are the portions of the spectra between 6.30–6.88 and 1.70–2.40 ppm respectively. The area  $A_M$  includes the resonances at 2.06 and 2.02 ppm due to *cis*-1,4 and *trans*-1,4 methylenes of the butadiene unit,

Table 1 Composition and molecular weights of butadiene–styrene copolymers

Polymer	Composition % feed ST:BD	n-BuLi concn. $\times 10^4$ (moles)	moles t-BuOK 1 mole n-BuLi	$\bar{M}_k \times 10^{-4} b$ (g.mole <sup>-1</sup> )	$\bar{M}_n \times 10^{-4}$ (g.mole <sup>-1</sup> )	$\bar{M}_w = 10^{-4}$ (g.mole <sup>-1</sup> )	$\bar{M}_w/\bar{M}_n$
SB-1	32.2:67.7 <sup>a</sup>	3.069	—	19.0	20.0	22.0	1.10
SB-2	41.5:58.5	4.345	—	19.3	21.2	23.5	1.11
SB-4	45.2:54.8	4.423	0.03	18.2	20.8	22.5	1.08
SB-5	44.8:55.2	4.448	0.05	18.3	17.5	20.6	1.18
SB-3	45.5:54.5	4.539	0.1	17.9	19.5	23.2	1.19
SB-7	30:70	4.656	0.028	19.3	21.9	24.6	1.13
SB-6	30:70	4.656	0.048	19.3	23.8	26.2	1.10

<sup>a</sup> Feed ratio in weight %

<sup>b</sup>  $\bar{M}_k$  is the calculated molecular weight from the known amounts of monomer feed and initiator

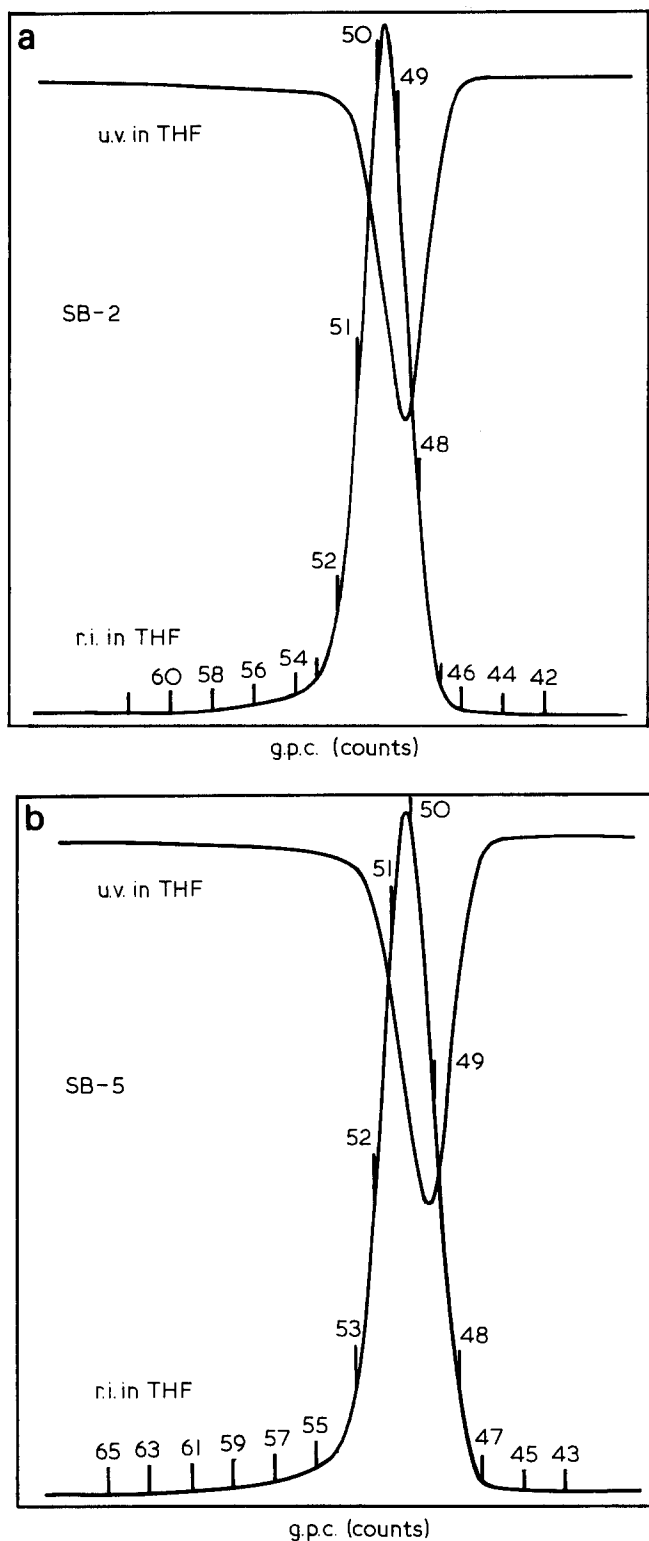
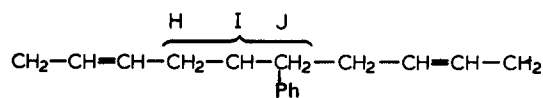


Figure 1 Typical gel permeation chromatograms of the synthesized butadiene-styrene copolymers

and smaller resonance peaks due to the random placement of styrene units between the butadiene units, i.e.



Assuming the chemical shifts of  $-\text{CH}$  and  $>\text{CH}_2$  depend

only on adjacent units, the protons, I, J, H should show distinct peaks in the spectrum. We have assigned<sup>16</sup> the shifts of I, J and H protons at 2.54 ppm, 2.24 ppm and 1.94

ppm respectively (see Figure 4). Hence equation (5) was based on the above resonance peaks plus the resonance peak at 1.84 ppm due to methines of block styrene sequences.

Two sets of results were independently calculated and these are given in Table 2 with the infra-red results for comparison. One set of results was obtained from the olefinic region using equation (1) to equation (4) and designated n.m.r. (A). The other set is obtained from equations (1), (2), (3) and (5) from the aliphatic region and designated n.m.r. (B). *Cis*-1,4 and *trans*-1,4 were obtained independently from the expanded olefinic and aliphatic regions by electronic integration of the areas under the peaks, as shown in Figure 5. Equations (6) and (7) were used in the olefinic region and equations (8) and (9) in the aliphatic.

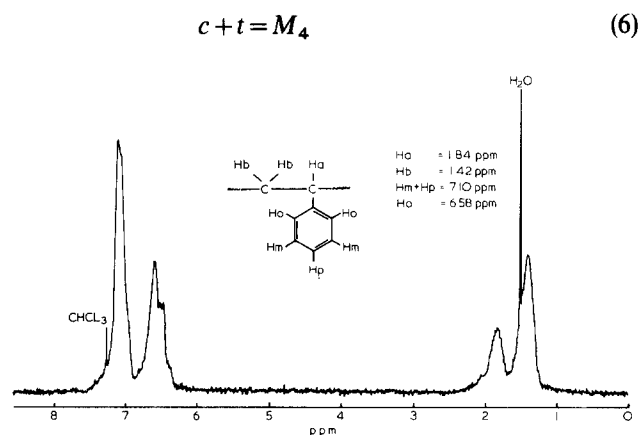


Figure 2 300 MHz 91 <sup>1</sup>H n.m.r. of an anionically prepared polystyrene

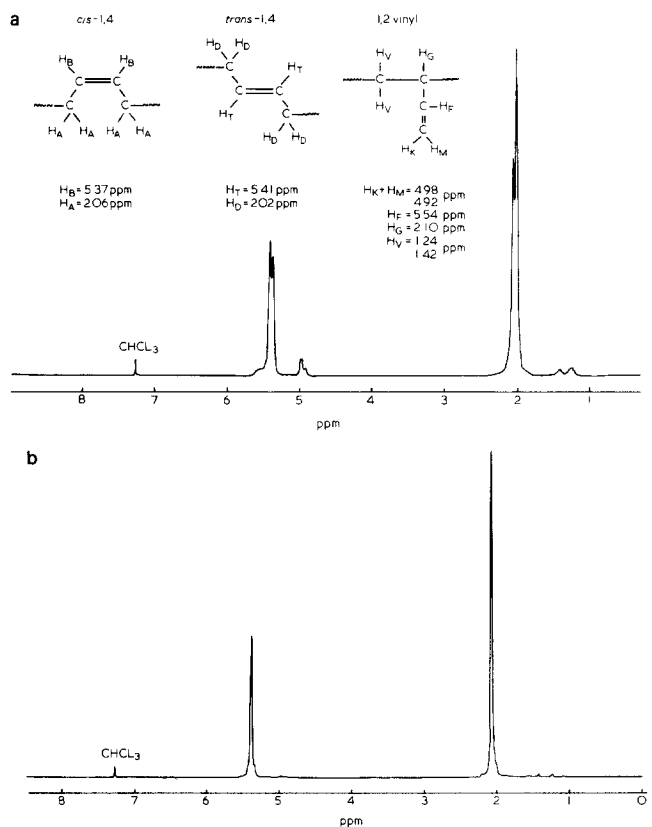


Figure 3 300 MHz 91 <sup>1</sup>H n.m.r. of polybutadienes: (a) low *cis*-1,4 polybutadiene (LCPB); (b) high *cis*-1,4 polybutadiene (HCPB)

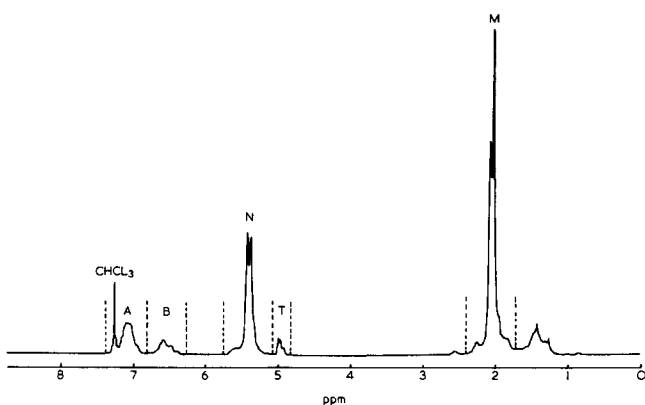


Figure 4 300 MHz  $^1\text{H}$  n.m.r. spectrum of SB-1 graded block polymer. Broken lines define the relative areas under peaks A, B, T, N and M which have been used in the analytical calculations

$$\frac{c}{t} = \frac{C}{T - M_3} \quad (7)$$

$$c + t = M_4 \quad (8)$$

$$\frac{c}{t} = \frac{C - 2M_1}{T - (2M_1 + M_2)} \quad (9)$$

The above equations differ from those used by Mochel<sup>14</sup> in two ways. They permit calculation of the *cis*-1,4 and *trans*-1,4 contents of the butadiene portion of the copolymers. Secondly, empirical factors have not been used to match the n.m.r. results with those of infra-red spectroscopy. From his usage of 60 MHz  $^1\text{H}$  n.m.r. Mochel suggests that sequences as small as 2 or 3 styrene units can possibly be detected by n.m.r. as 'block styrene'. At 300 MHz the aromatic peaks are further separated, and the ortho proton resonance is more readily seen. Hence, short sequences of styrene can be detected and calculated as block-styrene content in Table 2.

The  $^1\text{H}$  n.m.r. spectra in  $\text{CDCl}_3$  of SB-2, SB-4, SB-5, SB-3 are shown in Figure 6. The proportion of *t*-BuOK in the reaction mixture increases along the series SB-4 to SB-3.

The i.r. analyses of the copolymers listed in Table 2, i.e. *trans*-1,4; 1,2 vinyl; *cis*-1,4 and total styrene contents, were calculated from the measured absorbances at 965  $\text{cm}^{-1}$ , 910  $\text{cm}^{-1}$ , 724  $\text{cm}^{-1}$  and 699  $\text{cm}^{-1}$  respectively,

and by using Hampton's values<sup>17,18</sup> for the major and minor absorptivities of the above units at the four wave numbers. The *b* values in Table 2 are the ratios of the absorbances at 560  $\text{cm}^{-1}$  and 540  $\text{cm}^{-1}$ , and provide an approximation of the 'blockiness' in butadiene–styrene copolymers. A uniformly random copolymer has a value  $b=0.88$ , and for an ideal block polymer  $b=1.92$ <sup>7</sup>.

As indicated in Table 2 the  $^1\text{H}$  n.m.r. analyses of the aromatic protons in SB-1 and SB-2 show that the copolymerization of the butadiene and styrene mixture in benzene with *n*-BuLi led to grade block polymers. The microstructure of the butadiene portion is the same as that of LCPB as may be expected from the absence of any polar substances during polymerization. By increasing

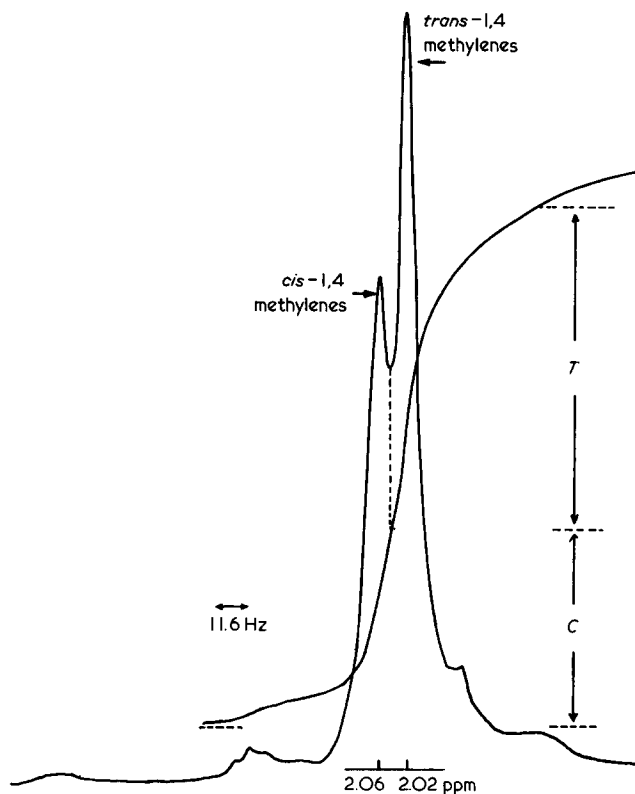


Figure 5 Expanded aliphatic region of SB-1 graded block polymer. *Cis*-1,4 and *trans*-1,4 contents were obtained by electronic integration of the areas under the peaks

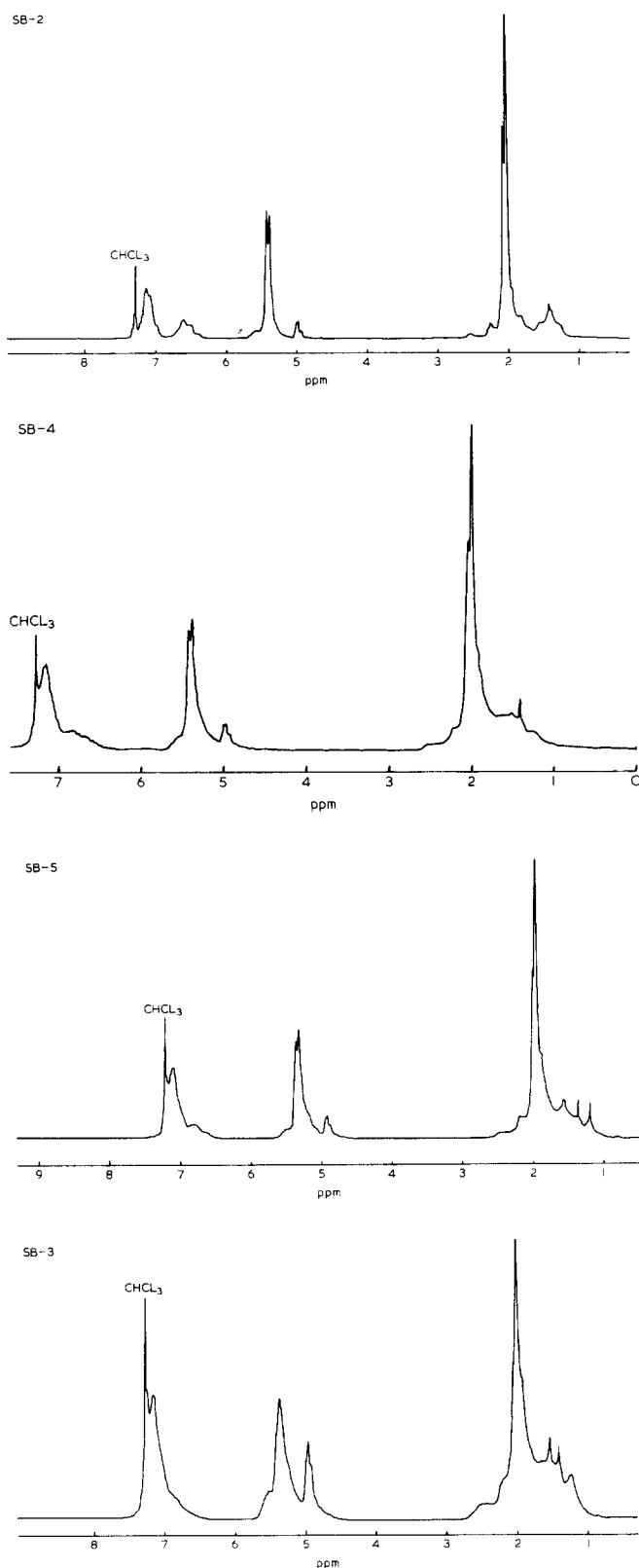
Table 2 Analyses of butyllithium catalysed butadiene–styrene copolymers (compositions in wt %)

Polymer	Block styrene		Total styrene			1,2 vinyl			<i>cis</i> -1,4			<i>trans</i> -1,4			<i>b</i>
	n.m.r. (A)	n.m.r. (B)	n.m.r. (A)	n.m.r. (B)	i.r.	n.m.r. (A)	n.m.r. (B)	i.r.	n.m.r. (Olef)	n.m.r. (Aliph)	i.r.	n.m.r. (Olef)	n.m.r. (Aliph)	i.r.	
LCPB	—	—	—	—	—	11.0	11.0	10.2	41.5	37.7	35.8	48.0	53.0	51.4	—
HCPB	—	—	—	—	—	—	—	0.73	—	—	101.0	—	—	1.3	—
SB-1	25.2	24.9	32.4	32.0	29.9	6.0	6.0	6.0	33.8	23.0	24.3	27.7	38.9	32.6	1.62
SB-2	33.0	32.8	41.0	40.8	37.3	5.8	5.7	5.3	33.5	20.0	21.4	19.5	32.5	28.7	1.68
SB-4	27.7	28.3	45.7	46.8	42.7	8.1	8.3	6.9	28.8	18.7	19.4	17.3	26.0	25.2	1.24
SB-5	24.8	25.9	44.3	46.0	41.5	9.6	9.9	7.8	32.0	12.1	19.8	14.0	31.7	25.1	1.13
SB-3	12.4	12.6	45.8	46.5	46.6	18.7	19.0	17.2	34.5 <sup>1</sup>	—	15.4	—	—	22.2	0.94
SB-7	11.5	11.6	28.6	28.8	29.2	8.5	8.6	10.2	38.8	21.3	24.7	24.0	41.3	32.4	1.20
SB-6	9.7	9.9	29.6	30.0	28.8	9.3	9.5	8.1	39.6	19.0	22.4	21.5	41.7	32.4	1.02
SB-8 <sup>2</sup>	25.3	26.2	38.3	39.6	40.0	4.9	5.1	6.3	30.4	21.0	19.0	26.3	34.0	34.9	—
Solprene <sup>3</sup> 1205	15.6	15.6	23.6	23.5	24.9	9.0	9.0	6.7	36.5	24.9	28.5	30.7	42.5	40.0	—
Solprene 1204	2.4	2.5	22.8	23.2	24.8	22.4	22.8	22.5	53.9 <sup>1</sup>	—	20.3	—	—	32.3	—
Solprene 1206	3.26	3.3	23.2	23.5	24.1	23.3	23.6	22.7	52.7 <sup>1</sup>	—	20.5	—	—	32.6	—

<sup>1</sup> Total *cis*-1,4 + *trans*-1,4

<sup>2</sup> SB-8: graded tri-block SBS polymer supplied through S. L. Aggarwal, General Tire and Rubber Co

<sup>3</sup> Solprenes: anionically prepared butadiene–styrene copolymers by Phillips Petroleum Co



**Figure 6** 300 MHz  $^1\text{H}$  n.m.r. spectra of braded block and randomized butadiene-styrene copolymers. Amount of tert-BuOK increases along the SB-4 to SB-3

the added amount of tert-BuOK as in copolymers SB-4, SB-5, SB-3 (having the ST:BD  $\approx$  45:55 composition), more styrene is incorporated at random in the butadiene block. In a similar way, the  $b$  values are decreased towards the limit of 0.88 (uniform random copolymers). The same remarks are valid for the copolymers SB-7, SB-6 (having the ST:BD ratio of 30:70).

Examination of the spectra in *Figure 6* and *Table 2*, may lead to the following interpretations:

(1) The resonance peak of the *o*-proton at 6.58 ppm, characteristic of block styrene sequences longer than about 2 to 3 units, decreases along the copolymers and moves towards the *m+p* resonance peak. This progressive shift of the *o*-protons towards the low field shows that the block styrene sequences decrease in length as the randomness of the copolymers increases.

Block and total styrene contents calculated from equations (1) to (4) and equations (1) to (3) and (5) respectively are in very good agreement. The total amount of styrene found with n.m.r. is consistent with the added amount of monomers in the initial feed, and there is a maximum error of  $\pm 3.5\%$  for the total styrene calculated from infra-red.

(2) The resonance peaks of the 1,2 vinyl units at 4.95 ppm are very distinctive from the 1,4 olefinic; this provides an accurate estimate of the 1,2 vinyl content, even in the case of SB-3 (having the highest vinyl content). The values of 1,2 vinyl units derived from the n.m.r. and infra-red are consistent, taking also into account the different values of the polybutadiene absorptivities given by various researchers<sup>18</sup>.

(3) Overlapping of *cis*-1,4 protons on *trans*-1,4 in the olefinic region causes overestimation of *cis*-1,4 content for all butadiene-styrene copolymers.

*Cis*, *trans* contents of polybutadienes and block copolymers estimated from the aliphatic region are consistent with the infra-red results. As the degree of randomness of the copolymers increases, overlapping of *cis*, *trans* methylenes occurs, which decreases the accuracy of the results. This is the effect of the dependence of *cis*, *trans* resonance peaks on the immediate neighbouring units. In the randomized copolymers of butadiene-styrene the possibility is high that a *cis*-1,4 or *trans*-1,4 unit will have a styrene unit at each end and this tends to broaden the resonance peaks of *cis*, *trans* methylenes causing overlapping. The increase of 1,2 vinyl units distributed randomly between the *cis*, *trans* units may also contribute to peak broadening. As can be estimated from the data in *Table 2*, *cis*, *trans* contents calculated from the aliphatic region yield consistent results for copolymers having a ST:BD feed ratio of 45:55, when the block styrene content is higher than 50% of the total styrene. In the case of SB-7, SB-6 having a ST:BD feed ratio of 30:70 the block styrene content should be higher than about 30% of the total styrene. As a summary, the series of copolymers we have prepared are included in *Table 3*.

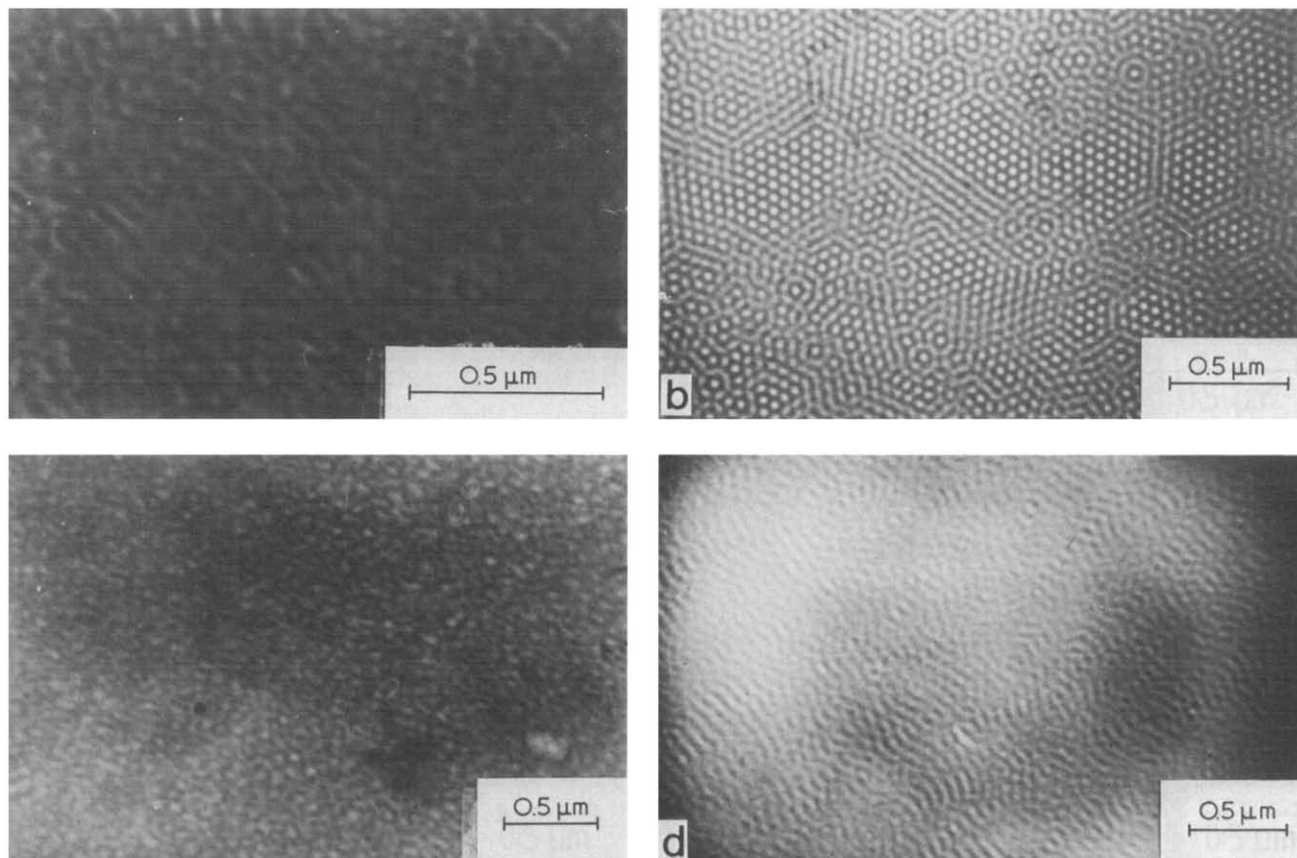
### Morphology

The electron micrographs of the prepared butadiene-styrene copolymers are shown in *Figure 7*. They indicate microphase separation of the polystyrene block of the copolymers forming discrete domains in the continuous polybutadiene phase. Ultrathin sections of copolymers SB-5 and SB-6 placed under the microscope did not show any separation into discrete domains. This further indicates the homogeneous composition distribution of these random copolymers. Identification of the shape of the domains is rather difficult, since the domains and their three-dimensional arrangements are viewed on two-dimensional sections. Moreover, the copolymer samples did not anneal, and owing to the small mobility of

**Table 3** Listing of butadiene–styrene copolymers investigated in this work

Polymer	$\bar{M}_n \times 10^{-4}$ (g.mole <sup>-1</sup> )	Type	Styrene content (wt %)	Block styrene (wt %)	Polybutadiene structure (wt %)		
					1,2 vinyl	<i>cis</i> -1,4	<i>trans</i> -1,4
SB-1	20.0	Graded block	32.4	25.2	6.0	23.0	38.9
SB-2	21.2	Graded block	41.0	33.0	5.8	20.0	32.5
SB-4	20.8	Randomized	45.7	27.7	8.1	18.7	26.0
SB-5	17.5	Randomized	44.3	24.8	9.6	19.8*	25.1*
SB-3	19.5	Randomized	45.8	12.4	18.7	15.4*	22.2*
SB-7	21.9	Randomized	28.6	11.5	8.5	24.7	41.3
SB-6	23.8	Randomized	29.6	9.7	9.3	22.4	41.7

n.b. All values have been obtained by 300 MHz <sup>1</sup>H n.m.r. except those marked (\*) which have been determined by i.r. spectroscopy.



**Figure 7** TEM photomicrographs of the synthesized butadiene–styrene copolymers: (a) SB-2; (b) SB-4; (c) SB-3; (d) SB-7

the polymer chains, it was not easy to obtain the dry sample in its thermodynamic equilibrium. However, we can complement the microscopic results with the other experimental methods referred to earlier.

The electron micrograph in *Figure 7a* corresponding to SB-2 graded block polymer shows short rods of polystyrene. This domain shape of the polystyrene block is in agreement with the morphology expected from the block styrene content in the copolymer found by n.m.r. (see *Table 3*). The two separate phases give rise to two glass transitions as is shown in *Figure 8*.

The polystyrene domains in SB-4 (*Figure 7b*) are arranged in a hexagonal array. To characterize this structure, one needs micrographs corresponding to sections of the sample in two perpendicular directions. However, in the present electron micrographs which correspond to sections in only one direction (perpendicular to the pressed surface) the structure can be examined by measuring the diameter of the circular domains ( $D_s$ ) and the distance between the axes of two

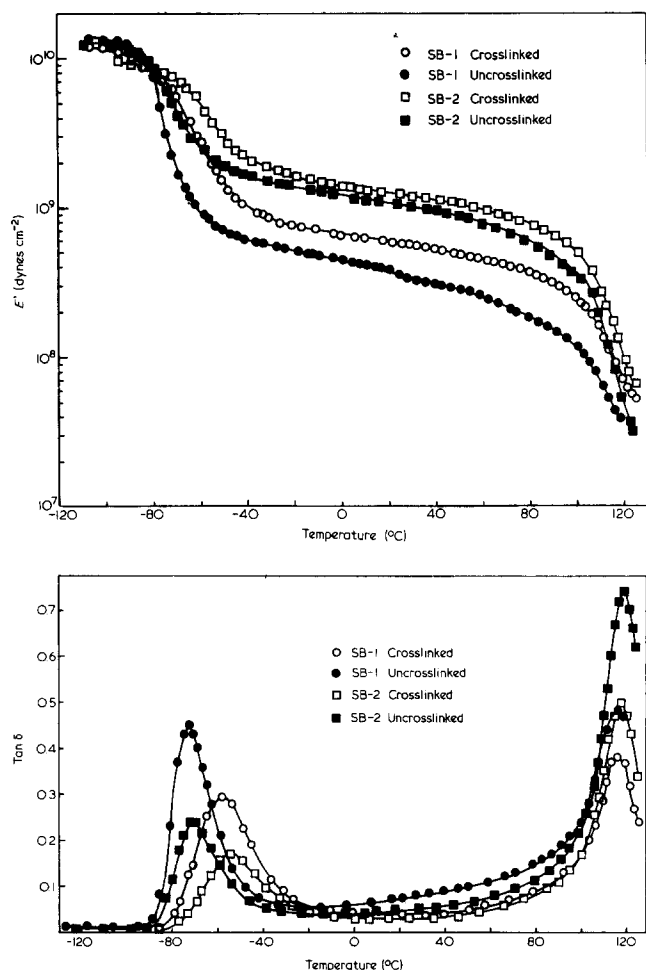
adjacent domains ( $d_{int}$ ). Furthermore, considering that the block styrene content of SB-4 copolymer is about 27%, the circular spots can be sections of either spheres or cylinders. Then the volume fraction of the polystyrene sequences in the copolymer (considering the hexagonal array) is given by the formula

$$\text{Spheres: } \phi = 0.74 \left( \frac{D_s}{d_{int}} \right)^3 = 8\%$$

$$\text{Cylinders: } \phi = 0.91 \left( \frac{D_s}{d_{int}} \right)^2 = 20\%$$

where  $D_s \approx 255 \text{ \AA}$ ,  $d_{int} \approx 535 \text{ \AA}$ .

It is therefore reasonable to propose that the circular spots seen in *Figure 7b* are sections perpendicular to the direction of the axis of polystyrene cylindrical of SB-4 domains. The shift of the polystyrene glass transition towards lower temperatures (see in *Figure 9*) is the result of a random placement of butadiene units within the



**Figure 8** Temperature dependence of dynamic Young's modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) of SB-1, SB-2 graded block polymers. SB-1, ST content: 32.4%. ST block: 25.2%. SB-2, ST content: 41.0%. ST block: 33.0%. Rubbers were crosslinked with 0.3% dicumyl peroxide

polystyrene block unable to be viewed by the electron microscope.

The polystyrene sequences of the copolymer SB-3 form sphere-like domains. However, the dynamic mechanical measurements of SB-3 (Figure 9) show only one glass transition, and at the same time, a variation in the intramolecular composition distribution, as is discussed in the next section. Bearing in mind that the electron micrographs have been taken from sections of the uncrosslinked samples, it could be suggested that crosslinking joins together segments of different composition and thus tends to freeze in the single phase morphology.

The electron micrographs of SB-7 copolymer show uniform-sized, well-oriented rod-like domains. However, in the light of the n.m.r. results the block styrene content is about 12%. Hence the rod-like structure should be understood as rows of polystyrene spheres on which microphase separation is incomplete. Because of variation in the intramolecular composition distribution (the pronounced shoulder in the  $\tan \delta$  peak in Figure 10) and crosslinking effect, the dynamic mechanical measurements of SB-7 show an 'over-randomization'.

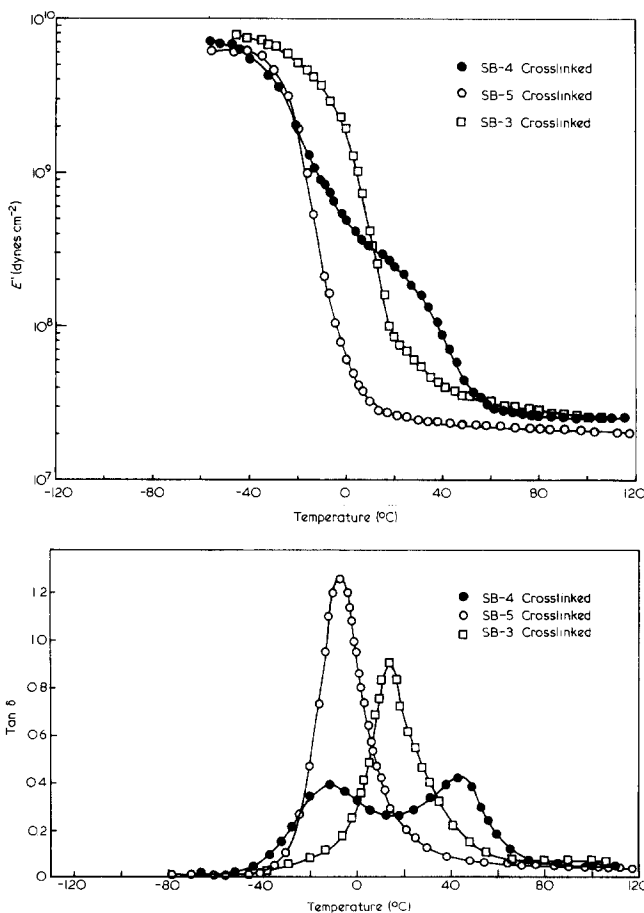
*Dynamic mechanical properties*

Dynamic Young's modulus ( $E'$ ) and loss tangents ( $\tan \delta$ ) of uncrosslinked and crosslinked samples of the copolymers measured on a Rheovibron are shown in

Figures 8-11. Young's moduli of the uncrosslinked randomized copolymers could not be calculated due to the samples' softness.

These figures show how the dynamic mechanical properties of the copolymers change with the degree of crosslinking. The modulus ( $E'$ ) in the rubbery region increases as the degree of crosslinking increases. In addition, two other effects are observed. Firstly, the glass transition temperature is increased and thus the drop in the modulus is shifted to higher temperature. Secondly, the transition region is broadened, and the fall in modulus lessens as the density of crosslinks increases. The broadening of the transition region is due to the heterogeneity in the molecular weight between crosslinks<sup>19</sup>. Widely spaced crosslinks produce only slight restrictions on molecular motions, so the  $T_g$  tends to be close to that of the uncrosslinked polymer. As the crosslinked density is increased (by increasing the amount of crosslinking agent), molecular motion becomes restricted and the  $T_g$  of the crosslinked polymer rises.

Figure 8 shows that the copolymerization of the butadiene-styrene mixture has led to block polymers SB-1, SB-2 as has already been demonstrated by the n.m.r. and EM results. The magnitude of the loss tangent peaks of the butadiene and styrene blocks are characteristic of the relative concentrations of the two components in both block polymers. The values of the modulus in the plateau regions between the two glass transitions are also in agreement with the concentrations of the ST:BD. The  $T_g$ 's



**Figure 9** Dynamic Young's modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) of SB-4, SB-5, SB-3 constant composition copolymers with increasing degree of randomness; ST:BD $\approx$ 45:55. Block ST contents: SB-4=27.7%, SB-5=24.8%, SB-3=12.4%. Rubbers were crosslinked with 0.3% dicumyl peroxide

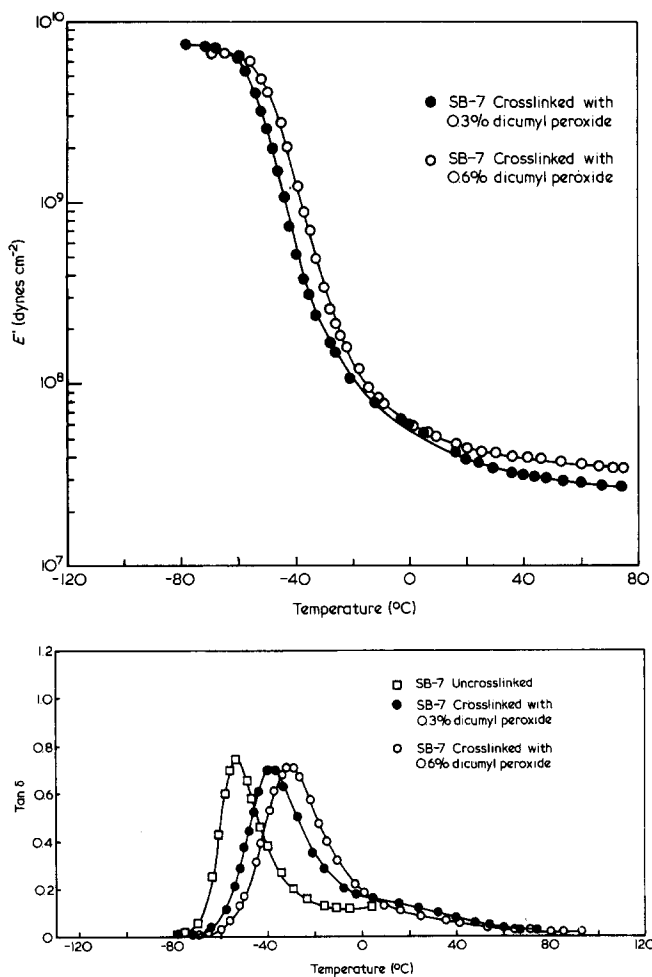


Figure 10 Dynamic Young's modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) of SB-7 randomized copolymer with increasing degree of crosslinking. ST content: 28.6% ST block: 11.5%

of the butadiene block are the same in both copolymers as is expected by the identical microstructure in Table 3.

The randomized butadiene-styrene copolymers SB-4, SB-3 show large changes in both loss tangent peaks and Young's moduli compared to SB-1, SB-2, as is shown in Figure 9. The polybutadiene loss tangent peak moves to a higher temperature and the polystyrene one is displaced towards a lower temperature in SB-4, while the two peaks emerge in SB-5 and SB-3. The shift of the loss tangent peaks of butadiene and styrene blocks is in line with the degree of randomness in the three copolymers. This shift is attributed to some mixing of the block segments in the copolymers as a result of the increased compatibility of the blocks, i.e. the lengths and purity of both polystyrene and polybutadiene blocks decrease from SB-4 to SB-3 (as shown by the n.m.r. results). The increased 1,2 vinyl content also contributes to the shift of the polybutadiene loss tangent peak towards higher temperatures.

The shift of the loss tangent peaks is followed at the same time by a broadening in the transition regions. Kraus *et al.*<sup>7</sup> have suggested that this broadening is due to chain segments of various compositions passing through their glass transitions, each at its characteristic temperature. Since the prepared randomized butadiene-styrene copolymers have uniform intermolecular composition distribution, the broadening of the transition peaks is due to variation in the intramolecular composition distribution (and hence to the

monomer sequence distribution across the sample). The broadening effect persists in the copolymers SB-4, SB-3 and clearly in SB-7. The copolymer SB-7 has a broad transition region with a pronounced shoulder towards higher temperatures while the drop of modulus is less steep indicating a variation in the intramolecular composition distribution. In contrast, SB-6 has a narrow transition region with a steep drop in Young's modulus.

Two kinds of homogeneity, intramolecular and intermolecular, are pertinent to random copolymers. It is therefore important to notice that the copolymers SB-5 and SB-6 prepared with different feed ratios but with the same amount of *tert*-BuOK (0.05 moles/mole *n*-BuLi) are random and tend to be uniform in both aspects, as Figures 1, 9 and 11 show.

### CONCLUSIONS

In graded block and randomized copolymers of butadiene-styrene the 300 MHz <sup>1</sup>H n.m.r. spectra provide a rapid and accurate determination of the monomer composition and microstructure of the polybutadiene sequences. *Cis*, *trans* butadiene contents can be determined in the aliphatic region of the n.m.r. spectra; however, the accuracy of the results appears to depend on the composition and degree of randomness of the copolymers.

Introduction of *t*-BuOK in the butadiene, styrene, *n*-

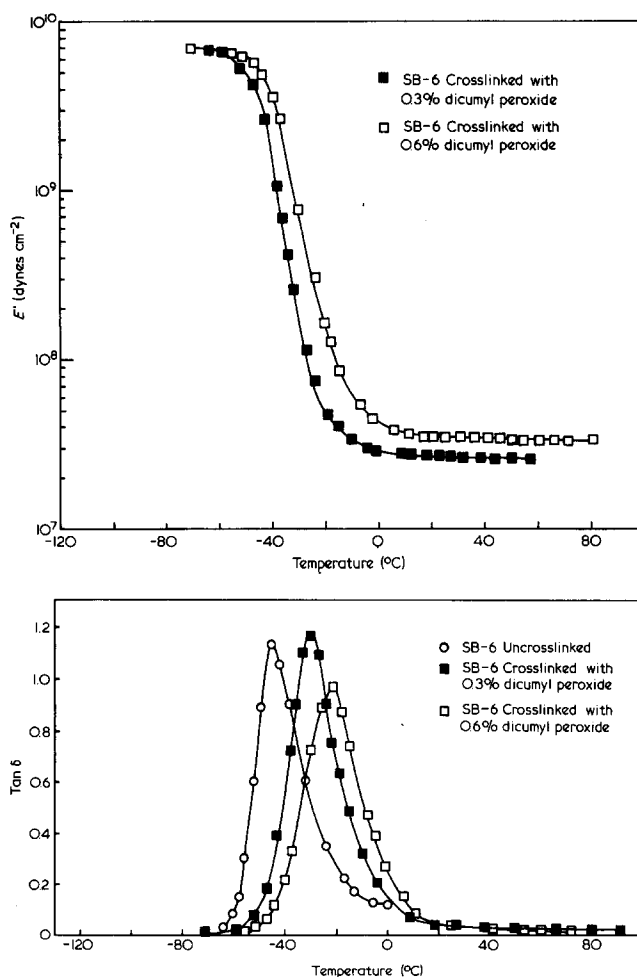


Figure 11 Dynamic Young's modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) of SB-6 randomized copolymer with increasing degree of crosslinking. ST content: 29.6% ST block: 9.7%



BuLi system decreased the length and purity of the polybutadiene and polystyrene sequences of the randomized copolymer chains. The monomer sequence distribution of these complex molecules was successfully investigated by examining their morphology and their dynamic mechanical properties. Both techniques have shown that any variation in the monomer sequence distribution across the sample of the randomized copolymer (and hence in the intramolecular composition distribution) depends on the amount of t-BuOK used. Copolymers prepared with 0.05 moles t-BuOK/mole n-BuLi appear to be random and uniform in both intermolecular and intramolecular composition distribution.

The block styrene content calculated from  $^1\text{H}$  n.m.r. is the total sum of all styrene sequences longer than 2 to 3 units distributed across the randomized copolymer chain. Hence, the determination of the length of the polystyrene end block is uncertain. With hindsight this uncertainty could have been avoided by polymerizing a mixture of butadiene, styrene with n-BuLi in the presence of t-BuOK, followed by addition of a known amount of styrene monomer to form the end block.

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