Fine Structures of Styrene–Butadiene Block Copolymer Films Cast from Toluene Solution

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A description is given of the preparation and examination of series of styrene–butadiene block copolymers cast from toluene solution. Regular structures were observed under the electron microscope and it appears that particular solvents may give rise to characteristic structures.

WITH the aid of a staining and hardening method[1], fine structures of block copolymers composed of rubber and glassy polymers can now be observed under the electron microscope[2,3].

The relationships of the fine structures and the mechanical properties of compression-moulded sheets of several types of block copolymer composed of polystyrene (block S) and polybutadiene (block B) have been reported[4].

In the present study, attempts have been made to observe the fine structure of films cast from toluene solution of these same block copolymers. It is of particular interest to note rather regular patterns in these films. Differences in patterns with the differences in block chain arrangement and block chain length were demonstrated.

EXPERIMENTAL

Samples

Block copolymers used in this study were the same as those previously used[4]. Varieties of samples and their characterizations with additional data are shown in *Table 1.*

Table 1. Characterizations of block copolymers

Samples	ST/BD *mole ratios*	$\overline{M}_n$ *by osmotic press.*	$\overline{P}$ ($\overline{M}_n \times 10^{-4}$) *of each one of sequences*			
			S	B	S	B
SB	60/40	$4{\cdot}21 \times 10^5$	2940(30·6)	2130(11·5)		
BSB	60/40	$2{\cdot}86 \times 10^5$		685(3·7)	2040(21·2)	685(3·7)
SBSB ionic copolym.	60/40	—				
	60/40	$2{\cdot}84 \times 10^5$				
SBS–1	80/20	$1{\cdot}69 \times 10^5$	720(7·5)	350(1·9)	720(7·5)	
SBS–2	70/30	$2{\cdot}02 \times 10^5$	790(8·3)	685(3·7)	790(8·3)	
SBS–3	60/40	$5{\cdot}14 \times 10^5$	1840(19·1)	2450(13·2)	1840(19·1)	
SBS–4	50/50	$4{\cdot}08 \times 10^5$	1300(13·5)	2580(13·9)	1300(13·5)	
SBS–5	40/60	$2{\cdot}75 \times 10^5$	740(7·7)	2240(12·1)	740(7·7)	

Preparation of cast film

The copolymers were gradually cast into films about 0·2 mm thick from an approximately one per cent toluene solution in a small glass vessel at

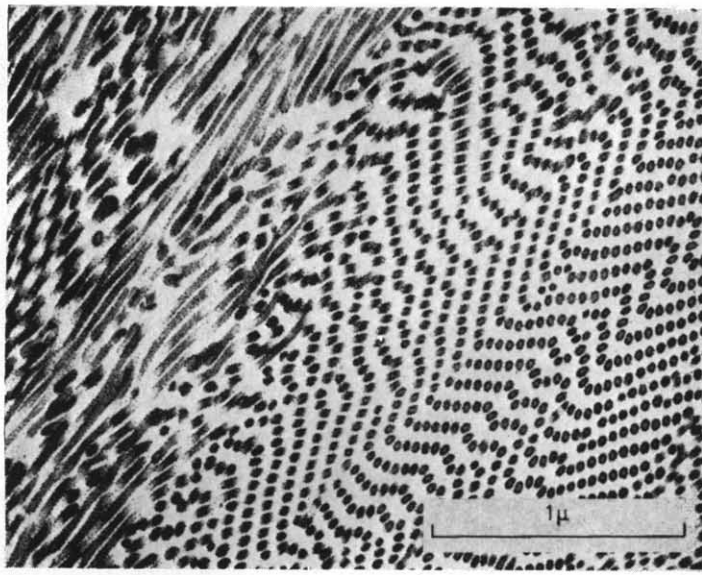

Figure 1(a)

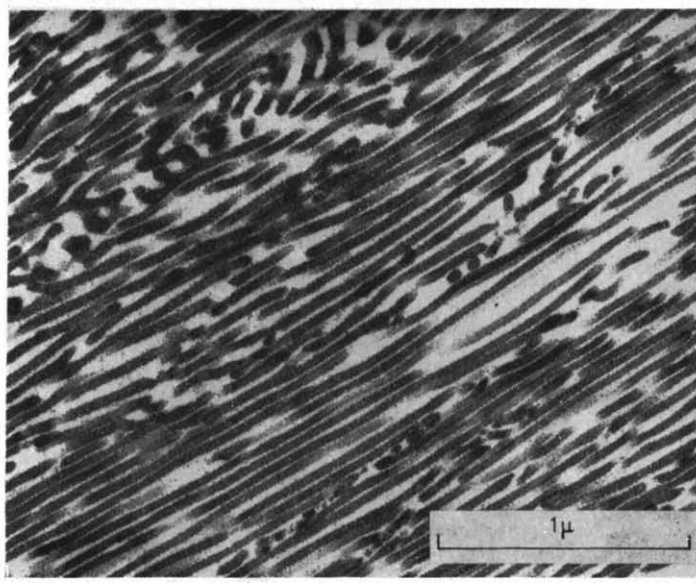

Figure 1(b)

Figure 1—Ultrathin section of SB type block copolymer film cast from toluene solution, showing rod structure orienting almost parallel to the film surface: (*a*) normal, (*b*) parallel section. ST/BD=60/40

room temperature. The remaining solvent was removed under vacuum of about 10^{-4} mm Hg at 50°C for a few days.

Ultrathin sectioning

The films obtained as above were exposed to osmium tetroxide vapour for a few days. The longer the staining period, the deeper will the osmium tetroxide penetrate below the surface of the specimen. As pre-sectioning, recommended by Kato[1], was not used, deeper penetration was necessary to obtain well stained sections. In this way, the polybutadiene phase was selectively stained and hardened to a depth of several microns from the surface. The stained films were then embedded in epoxy resin and ultrathin sectioning carried out by an LKB ultramicrotome to a thickness of about 400 Å. Sections were cut in three directions so as to determine their structures in three dimensions—parallel to the film surface and the others perpendicularly crossed in two directions normal to the film surface. As the patterns of the last two sections were found to be completely identical, however, micrographs of the parallel and of one of the normal sections only are given.

RESULTS

Figure 1(a) shows the electron micrograph of an ultrathin section of SB type block copolymer cut normal to the film surface. The black portions in the micrograph represent the block B phase stained selectively by osmium tetroxide. The figure seems to be composed of two kinds of patterns: regularly arranged, well defined particles and oriented stripes of various lengths.

The section cut parallel to the film surface in the vicinity of it is shown in *Figure 1*(b), where only oriented stripes are observable. The patterns did not vary much even when the cutting position was far from the surface.

It can be seen from these figures that the block B phases agglomerate in the form of a rod, which assembles regularly to form a bundle with a certain size. The bundles are arranged almost parallel to the film surface, curving in various directions. The regularly arranged, well defined particles and the oriented stripes have now been found to represent the cross sections and the almost parallel sections, respectively, of the regularly assembled rods. The average diameter of the rod ($2R$) and the average distance separating the axes of two adjoining rods (d) were about 330 Å and 550 Å, respectively. The fine black dots that appeared inside the dark phases were possibly due to deposits of metal osmium.

The patterns of BSB were almost the same as those of SB in both sections. Only the normal section is shown in *Figure 2*. Dark bands like a Moiré pattern observed in the portion of oriented stripes in *Figure 2* were attributable to the interlocks of the ends of the stripes.

Patterns similar to those above were also observed in SBSB. These results indicate that such rod structures are also realized in BSB and SBSB. The average values of $2R$ and d, however, were much smaller than for SB: $2R = 200$ Å, $d = 400$ Å for BSB, and $2R = 140$ Å, $d = 270$ Å for SBSB.

For the ionic copolymer prepared by polymerizing a mixture of the two

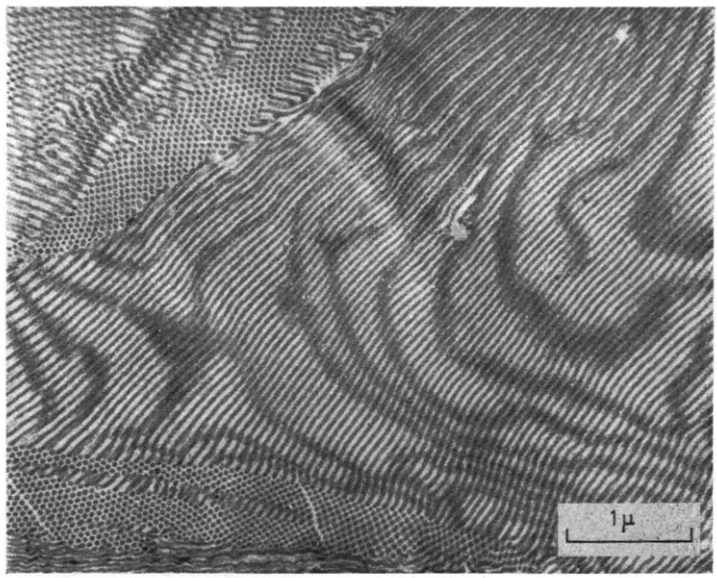

Figure 2—Ultrathin, normal section of BSB type block copolymer film cast from toluene solution. Rod structure similar to that in *Figure 1* is seen. ST/BD=60/40

monomers, honeycomb patterns extending throughout the structure were observed for normal sections [*Figure 3*(a)]. The parallel sections resembled to some extent that of the normal one, but differed in the proportion of the peculiar patterns like a terrace-field with white spots, as shown in *Figure 3*(b). It can therefore be concluded from the figures that the block B agglomerates to form sheets that are penetrated by block S phases and that the sheets, alternately separated by block S sheets, extend throughout the film tending to orient their surfaces parallel to the film surface.

Finally, several SBSs with varying styrene/butadiene (ST/BD) mole ratios were investigated. They are designated as SBS–1 to 5 according to the changes of ST/BD mole ratios from 80/20 to 40/60 (*Table 1*). Unfortunately, SBS–2 was not examined because of a lack of samples.

The pattern shown in *Figure 4* is a section of SBS–1 cut normal to the film surface. As the parallel sections are identical with the normal one, it can be assumed that the block B phases form spherical particles and disperse evenly in the block S phase. The average diameter of the particle is about 200 Å.

The structure changed to rod in SBS–3 as was seen by the presence of the stripe and particle pattern in the normal section and the stripe pattern only in the parallel section. $2R$ and d are about 180 and 330 Å, respectively.

Figures 5(a) and *5*(b) show the patterns of SBS–5 cut normal and parallel, respectively, to the film surface. It is clear from the figures that the block B phase forms sheets alternately separated by block S sheets tending to orient their surfaces parallel to the film surface. SBS–4 shows patterns

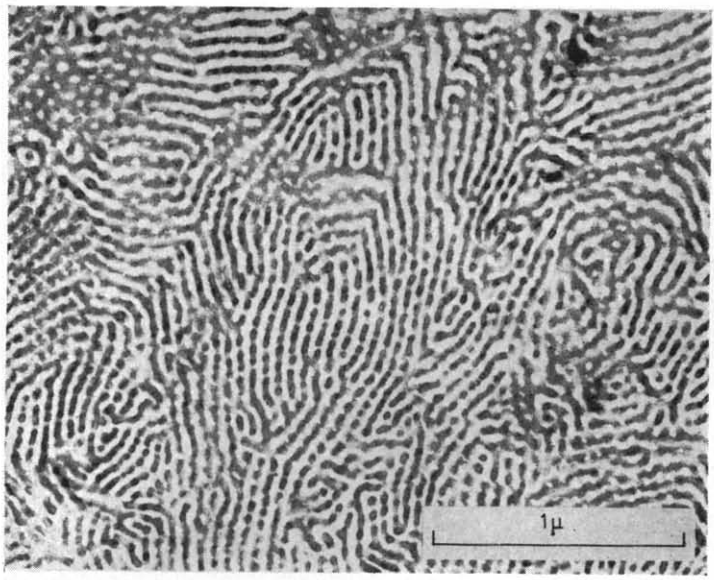

Figure 3(a)

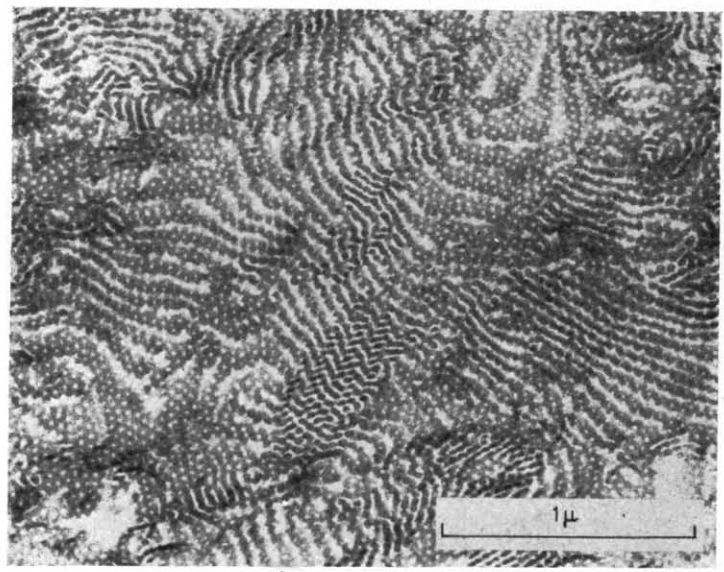

Figure 3(b)

Figure 3—Ultrathin sections of ionic copolymer film cast from toluene solution, showing that block B forms sheets penetrated by block S component: (*a*) normal, (*b*) parallel section. ST/BD=60/40

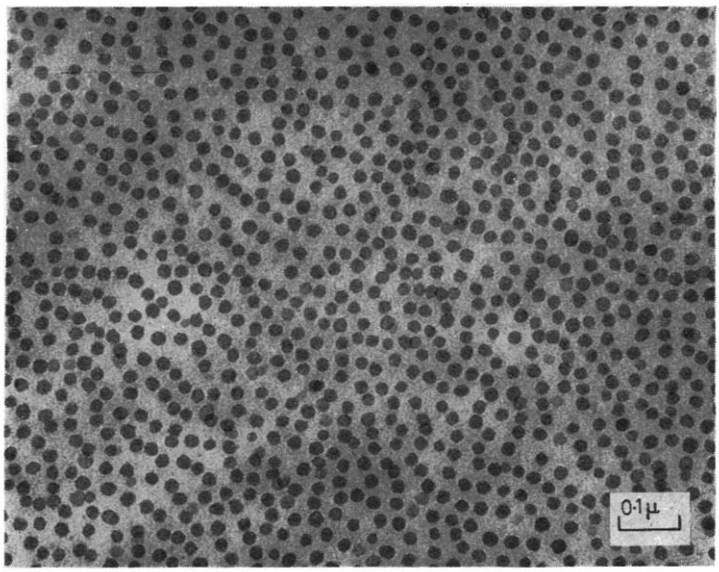

Figure 4—Ultrathin section of SBS–1 film (ST/BD=80/20) cast from toluene solution. The same patterns were observed in both normal and parallel sections, indicating formation of spherical particles

similar to that of SBS–5, but differs in that the sheets are more distinctly separated from each other and they are thinner.

Various structures are schematically illustrated in *Figure 6* and the structure parameters summarized in *Table 2*.

Table 2. Structure parameters of block copolymer films

Samples	ST/BD *mole ratio*	*Structures of block* B *phase*	*Structure parameters, Å*
SB	60/40	rod	$2R=330$, $d=550$
BSB	60/40	rod	200, 400
SBSB	60/40	rod	140, 270
ionic copolym.	60/40	punched sheet	thickness {S:270 B:200
SBS–1	80/20	sphere	diameter: 200
SBS–2	70/30	—	—
SBS–3	60/40	rod	$2R=180$, $d=330$
SBS–4	50/50	sheet	thickness {S:130 B:130
SBS–5	40/60	sheet	—

DISCUSSION

It is important to note that the copolymers of constant overall composition (ST/BD=60/40) all show 'rod' structure, irrespective of their sequence arrangements. On the other hand, under the constant sequence arrangement (SBS), there is clearly a progressive change in structure from 'sphere' through

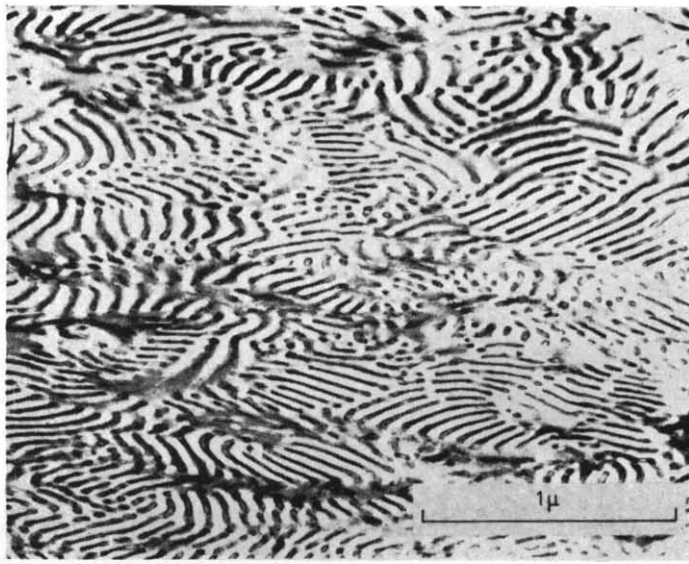

Figure 5(a)

Figure 5(b)

Figure 5—Ultrathin section of SBS–5 film (ST/BD=40/60) cast from toluene solution, showing the alternate sheets of block B and block S: (*a*) normal, (*b*) parallel section

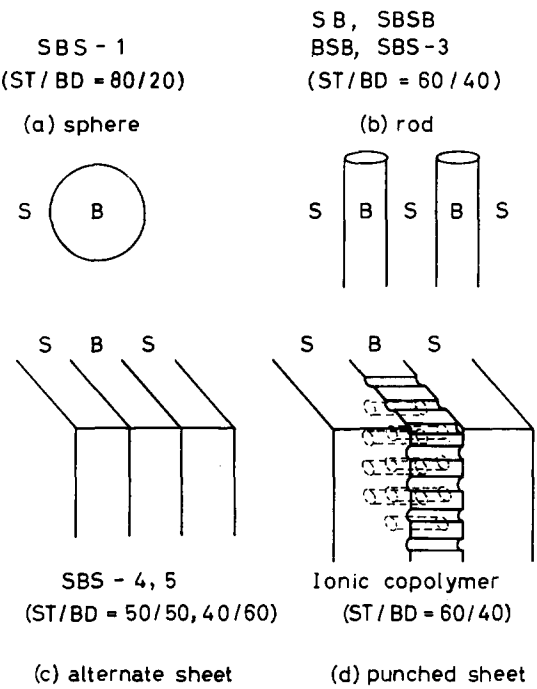

Figure 6—Schematic diagrams of the three types of fundamental structures (sphere, rod and sheet) and one peculiar penetrated sheet structure

'rod' to 'sheet'. These results may indicate that the structures are determined only by the overall composition, not by the type of block chain arrangement.

Similar structure changes were reported recently[3] in a styrene–isoprene series with varying isoprene fractions.

Based on these results, it is expected that the same changes can be observed in every type of block copolymer and that, upon further increase in BD fractions, phase inversion may well occur, thus yielding rod and then sphere block S phases dispersed in block B matrix.

Structure appears to be somewhat peculiar in the ionic copolymer. This may be attributable to the presence of a random portion in the block chains as characterized in the previous paper[4].

As the structure parameters of sphere, rod and sheet, and the sequence length of the two components are known, relationships can be obtained between the size of each structure and of one block chain. It has been calculated that about 130 block B chains exist in one sphere of SBS–1, assuming the density of the block B phase to be 1·00. As two block S chains are stretched out from each one of the block B chains through the surface of the sphere, the area required for one block S chain to protrude from the surface of the sphere can be calculated by dividing the surface area of the sphere by the number of the block S chains which are stretched out (*Figure 7*). If the area is represented by the square of L, it becomes about 21·6 Å for SBS–1.

For rods of SB, BSB and SBS–3, the number of block Bs existing in one

rod 100 Å long was calculated to be 45, 51 and 11, and then the L value became 48·2, 34·9 and 49·1 Å, respectively.

The same calculation was carried out on the sheet structure of SBS–4; then the L value became 42·0 Å.

The L value may represent the minimum distance separating the two adjoining block chains after free agglomeration from a good solvent for

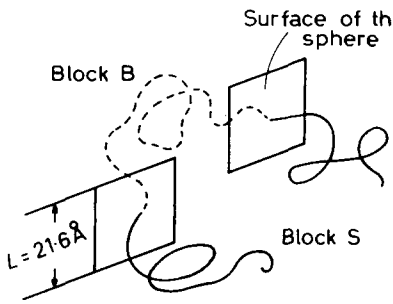

Figure 7—Schematic diagrams of effective area (L^2) occupied by one block chain which protrudes through the surface of the sphere of SBS–1

both components, although it is only an approximate value. It is interesting that the longer the block B length, the larger is the L value, except for SBS–4. It is possibly the size of one block B chain coiled in a solid state.

CONCLUSION

Fairly regular structures of block B phases have now been observed under the electron microscope in ST–BD block copolymer cast films. When compared at the same ST/BD mole ratio (60/40), all of the four types of block copolymer showed a regularly arranged rod structure of block B phase with varying structure parameters, irrespective of their types of block chain arrangement.

An increase in BD fraction in the SBS series resulted in the change of the structure of block B phase from sphere through rod to sheet.

It is thought that different structures are formed by different solvents, and a study on these lines is now in progress, several new structures having already been disclosed. Through such studies, phase structure will be controlled by the 'molecularly designed polymer'.

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