

# S-B-S block copolymer-polystyrene blends: 1. Morphology and swelling properties

M. J. Folkes and P. W. Reip

Department of Materials Technology, Brunel University, Uxbridge, Middlesex, UB8 3PH,  
UK

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The microstructure of extruded samples of block copolymer-homopolymer polystyrene blends has been studied using light microscopy and electron microscopy. For some compositions, the homopolymer polystyrene phase is in fibrillar form. These fibrils are dispersed throughout the block copolymer matrix with a surprisingly high degree of spatial ordering. Imbibition of a selective swelling agent results in anisotropic dimensional changes in the blends and these changes are fully consistent with the observed microstructure.

(Keywords: copolymer; polystyrene; blend; extrusion; microstructure; swelling)

## INTRODUCTION

It is now widely accepted that the segregated microphases in block copolymers can be in the form of spheres, cylinders or lamellae, which can form regularly organized periodic structures or macrolattices. In addition, it has been shown that when specimens having a cylindrical or lamellar morphology are prepared from the melt, the flow processes involved in the fabrication of the specimens can lead to pronounced orientation of the microphases. Under appropriate conditions, 'single crystal' samples can be prepared<sup>1,2</sup> which exhibit a very pronounced mechanical anisotropy<sup>3,4</sup>. Anisotropy can also easily develop in samples prepared using normal technological processing routes, e.g. injection moulding<sup>5</sup>. In this latter case, it was found that the anisotropy was little affected by processing conditions but significantly so by the geometry of the injection mould cavity. The anisotropy that is developed may, of course, be inappropriate for a particular application and accordingly an alternative method of microstructural modification is called for. The mechanical blending of two or more homopolymers to achieve new properties is of widespread interest and the potential of blending block copolymers with homopolymers to produce materials of commercial importance has been noted<sup>6,7</sup>. In general, when an S-B-S block copolymer is blended with a commercial homopolymer, e.g. polystyrene, a three-phase structure is produced. If the polystyrene is in the lesser proportion, then it will form a dispersed phase of roughly spherical particles in a matrix of the block copolymer, which itself is two-phase. In principle, this blend should produce a near isotropic material, due to the disruption of the orientation in the block copolymer, thereby providing additional control of the anisotropy of a moulded component. In the case where the block copolymer is in the lesser proportion, the blend manifests many of the characteristics of commercial high impact polystyrene<sup>6</sup>.

The main features of block copolymer-homopolymer blends have been established through work on solvent cast films. Kawai and coworkers<sup>8,9</sup>, Skoulios<sup>10,11</sup> and Shen and coworkers<sup>12,13</sup> have shown that when the

molecular weight of the added homopolymer is less than or comparable with that of the corresponding block of the copolymer solubilization of the homopolymer into the microphases of the block copolymer takes place. In such cases, the dimensions of the microphases increase in relation to the amount of the added homopolymer and in some cases, the morphology of the microphases may also change. However, when the molecular weight of the added homopolymer is larger than that of the corresponding block copolymer, the block copolymer behaves as if it were largely incompatible with the corresponding homopolymer and a three phase structure is produced. However, in such cases, the blocks in the interfacial region between the homopolymer and block copolymer are preferentially anchored in the homopolymer phase and thus help to form a stable interface. This is an important contributory factor to the success of these types of material as high impact polymers.

The surfactant properties of block copolymers when incorporated into homopolymers is well established. However, during melt processing of block copolymer-homopolymer blends, large stresses will be imposed on the two constituents and these will be additional to any interfacial interactions. The microstructure and properties of melt processed blends of homopolymers have been studied extensively (see e.g. ref. 14) and it has been shown that under appropriate conditions, the dispersed phase can deform during processing to produce fibres. The micro-rheological interpretation of this has been reported by Han and coworkers<sup>15</sup> and by Lyngaae-Jorgensen<sup>16</sup>. The corresponding studies using a block copolymer-homopolymer blend are far less numerous. Nandra *et al.*<sup>17</sup> have reported the microstructure and mechanical properties of blends of the Shell copolymer TR4113 and polystyrene resulting from a process of milling followed by injection moulding. They show that a three phase structure exists in which the homopolymer polystyrene phase has deformed into ellipsoidal shaped particles. Continuous polystyrene fibres were not observed. Although there are good reasons to expect improved stabilization of the drawing process to occur in

the dispersed phase due to the presence of the block copolymer<sup>18</sup>, it would seem likely that this cannot be achieved at the very high flow rates in injection moulding.

Our own particular studies, which we will be reporting in this paper, have shown that under appropriate conditions, block copolymer-homopolymer blends can be produced in which the homopolymer phase can be present as well developed fibres. Furthermore, anisotropic dimensional changes occur in samples which have been swollen in selective swelling agents and this anisotropy is completely consistent with the morphology of the blends as deduced from a variety of microscopical examination techniques. Part 2 will report on the mechanical properties of the blends at both low and high strains and discuss the relationship of these properties to the observed morphology of the blends.

## FORMULATION AND COMPOUNDING OF BLENDS

### Materials

The materials used for these investigations were a Shell clear general purpose polystyrene (PS) and Shell Cariflex TR1102 block copolymer. The former was available in granular form and had a molecular weight  $M_w$  of  $2 \times 10^4$ . The three block copolymer consists of chains of the form polystyrene-polybutadiene-polystyrene (S-B-S) and the particular grade used in our experiments has already been the subject of extensive investigation (see e.g. refs. 1-3). The molecular weight of the polystyrene (S) block is  $10^4$  and the polybutadiene (B) block  $5.5 \times 10^4$ , giving a volume fraction of polystyrene in the block copolymer of between 20 and 25%. Three blends were used throughout our studies and contained 10%, 30% and 50% by weight of polystyrene.

### Preparation of blends

The appropriate blends were initially compounded using a Robinson two-roll mill at a temperature in the range  $130^\circ\text{C}$ - $170^\circ\text{C}$ . The hides so produced were opaque, in contrast to the transparent samples obtained when the block copolymer is milled on its own. After milling, the material was granulated and then extruded using a Reifenhäuser single screw extruder fitted with a general purpose screw. The barrel temperature varied from  $135^\circ\text{C}$  at the feed hopper to  $180^\circ\text{C}$  at the die. A schematic diagram of the die is shown in Figure 1. A significant feature of this die is the presence of a spider consisting of a simple plate containing 18 circular holes. Although this is commonly used as a means of removing the rotational memory of the melt when in the screw, the melt will be subjected to elongational flow in its passage through each hole. It appears that this is important for the development of the particular microstructure to be described.

## STRUCTURAL EXAMINATION OF THE BLENDS

The choice of examination method that can be used to determine the structure of a particular blend system is dependent upon the physical properties of the component materials, as well as the extent to which they have been blended. It will be shown that as a result of the particular choice of compounding route chosen, together with the elastomeric nature of the S-B-S block copolymer, a single

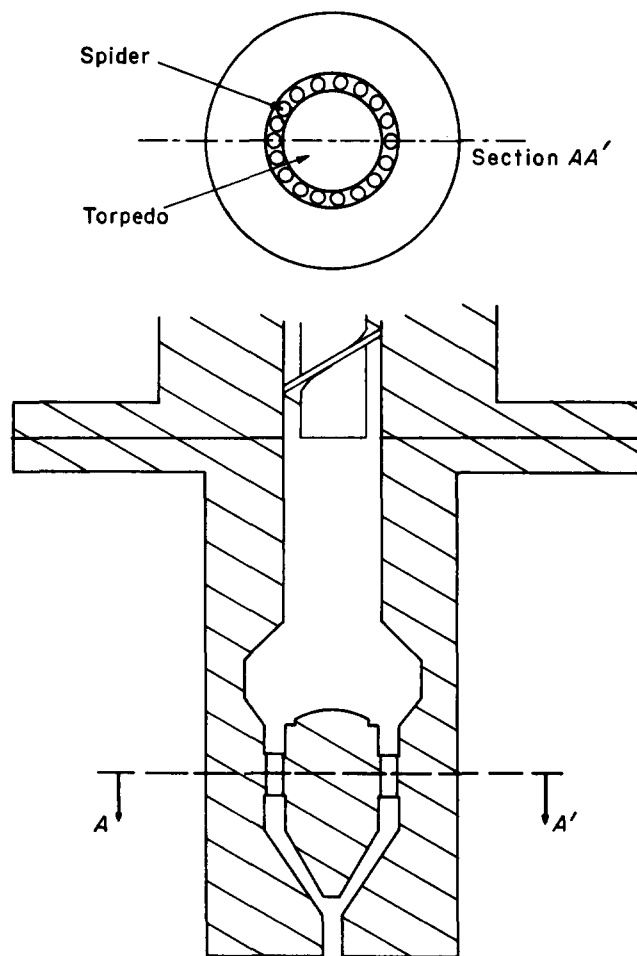


Figure 1 Diagram of the extrusion die used for the blend studies

investigative technique, e.g. optical microscopy, could not effectively reveal all the structural detail necessary to produce an accurate model of the blends. Accordingly, a range of techniques was used including optical microscopy, scanning electron microscopy and transmission electron microscopy.

### Experimental

**Optical microscopy.** Initial examination of the blends was carried out using transmission light microscopy. For this, thin sections of constant thickness (and free from surface defects) are desirable. However, even for those blends containing 50% PS, the cutting of thin sections was made difficult owing to their elastomeric nature. Accordingly, a technique was developed to enable sections to be cut at low temperatures using liquid nitrogen as coolant. This enabled satisfactory sections of minimum thickness  $10\ \mu\text{m}$  to be cut using a sledge microtome. After mounting on glass slides, the sections were examined using a Reichert Jung Microstar microscope. In addition, where necessary a limited amount of reflection microscopy was carried out using a Wild stereomicroscope.

**Scanning electron microscopy.** In order to derive information concerning the structure of the blends using this method, it is necessary for the samples to be prepared or treated to give some form of topographic relief, which is an indication of the internal structure present. Several techniques were developed which fell into two basic categories, namely the study of fracture surfaces and

treated microtomed surfaces. The former approach was comparatively straightforward and specimens could be conveniently prepared by cooling in liquid nitrogen followed by fracturing using 3-point bending or simple tension. In those cases when treated microtomed surfaces were used, it was necessary to subject these to an etching process. The composition of the etch was similar to that previously used for examining the structure of rubber toughened polymers<sup>19</sup>. It consists basically of chromic and phosphoric acids, which give a powerful oxidizing etch which preferentially attacks unsaturated rubber. By adjusting the concentration of the etch and the sample treatment time, a variety of effects occurred in the samples ranging from surface degradation and splitting to total removal of the S-B-S block copolymer from the blends.

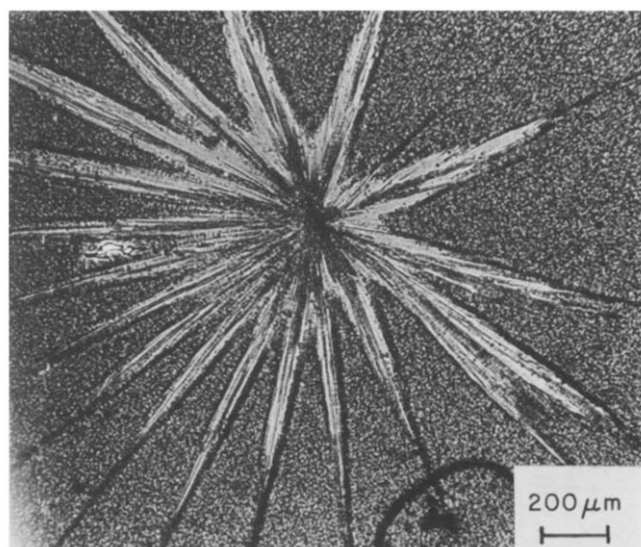
After coating the samples with gold/palladium, the examination of their structure was carried out using a Stereoscan 250 scanning electron microscope.

**Transmission electron microscopy.** The preparation of ultra-thin specimens for the transmission electron microscopy of block copolymers and blends has already been discussed extensively elsewhere<sup>20</sup>. It has been shown that best results are obtained when a combination of osmium tetroxide hardening and cryo-ultramicrotomy are used<sup>21</sup>. However, low temperature microtomy facilities were not available for these particular studies and so the specimen hardening and staining had to be accomplished by prolonged exposure to osmium tetroxide. Nevertheless, sections having thicknesses in the range 50–100 nm were cut successfully and subsequently examined in a Jeol transmission electron microscope.

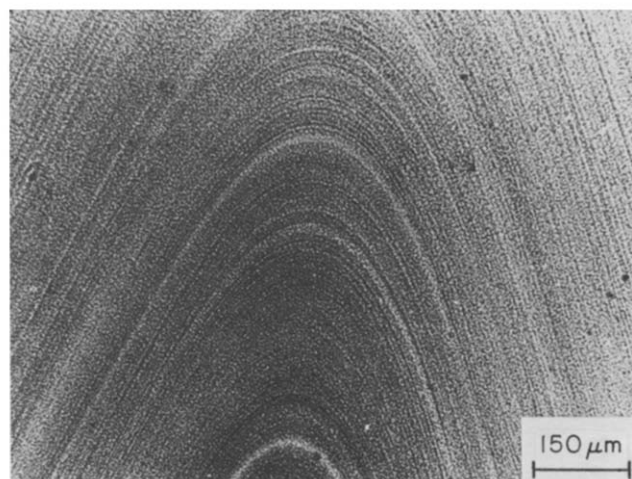
#### Results and Discussion

The results for the 30% PS/70% S-B-S blend will be presented first and a model proposed for the morphology of the blend. The modifications to this morphology when 10% and 50% PS are used will then be presented and discussed.

*Figure 2* shows an optical micrograph of a thin section cut transverse to the extrusion direction for the 30% PS blend. It can be seen that the section is divided into 18 segments, the presence of which must clearly be related to the corresponding number of holes in the spider within



**Figure 2** Optical micrograph of a transverse section cut from a blend of the block copolymer Kraton 102 with 30% homopolymer polystyrene, following the process of milling and screw extrusion

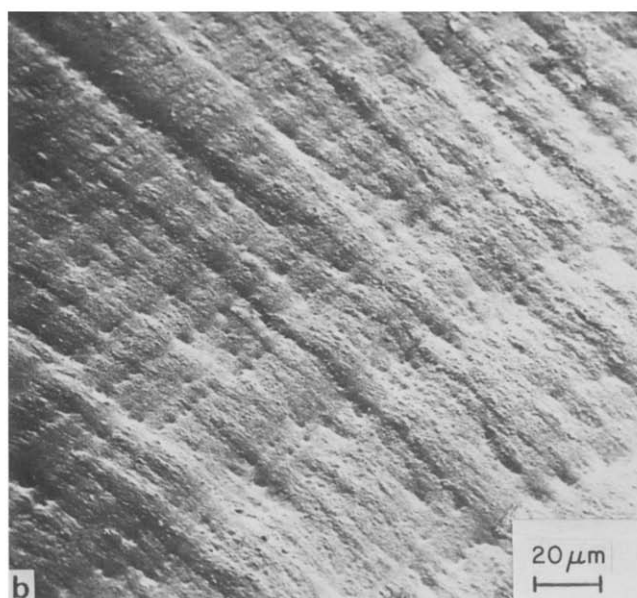
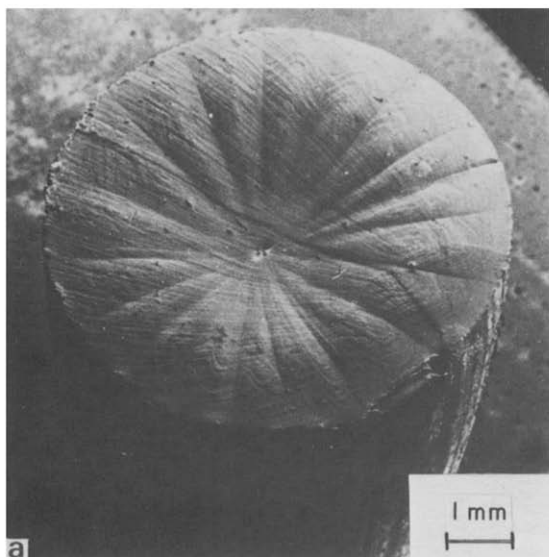


**Figure 3** As *Figure 2*, but different region of the same sample showing the existence of a striated two phase structure

the extrusion die. Rather surprisingly, a closer examination shows that a two phase structure exists on the scale of 1  $\mu\text{m}$ , as revealed in *Figure 3*. The fact that such a structure can be observed without resort to any of the normal methods used for revealing the dispersed phase in two-phase systems, e.g. toughened plastics, is also surprising in its own right. The dimensions of the dispersed phase being 0.5–5.0  $\mu\text{m}$  suggests that the contrast between the dispersed homopolymer polystyrene and the block copolymer arises from scattering of the light at the PS-copolymer interface. Furthermore, since this structure was observed in sections much thicker than the size of the dispersed homopolymer polystyrene phase, it follows that there must be some continuity of this phase parallel to the extrusion direction, i.e. the polystyrene phase should be essentially fibrillar in nature.

*Figure 3* also shows that the PS phase is arranged along well-defined layers. This is very unexpected, since it implies a high degree of transverse ordering of the dispersed phase—an observation which to the best of our knowledge has not featured in earlier rheological studies of two phase fluids. Indeed it would be difficult to visualize a flow mechanism that would alone account for this structure. Longitudinal sections from the extrudates failed to show any two-phase structure except in the case of very thin sections (5  $\mu\text{m}$ ), when a striated structure could be seen occasionally. The difficulty encountered suggests that although transverse ordering of the PS phase exists, it is not long-range.

The 18 segments present in the extrudate were also apparent in scanning electron micrographs of high speed tensile fracture surfaces, as shown in *Figure 4*. Closer examination of these fracture surfaces shows the transverse layering effect consisting of lines of small pits lying in the layer planes. The pits would seem to be associated with the proposed PS fibrils and probably form as a result of the necking and fracture of these fibrils followed by their partial recovery after sample failure. If the specimens are fractured using 3 point bending at a temperature slightly above the  $T_g$  of the polybutadiene phase ( $-80^\circ\text{C}$ ) the process of fracture is characteristic of a composite material. The fracture initiates at the sample surface and as the crack propagates into the material it is redirected parallel to the axis of the PS fibrils. Longitudinal fracture surfaces produced in this way confirm the fibrillar nature of the blend (see *Figure 5*).



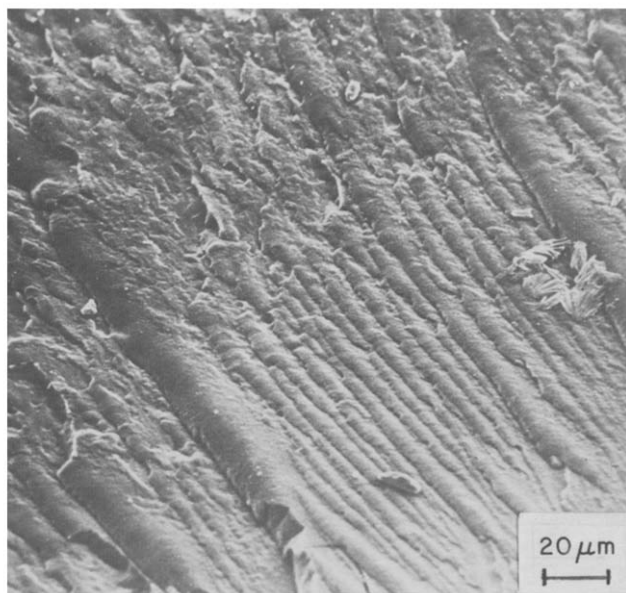
**Figure 4** (a) Scanning electron micrograph of a high speed tensile fracture surface for the blend of Kraton 102 with 30% homopolymer polystyrene. (b) Enlargement of (a), showing the existence of lines of small pits, related to the two phase microstructure

More direct evidence for the presence of PS fibrils in this blend comes from scanning electron microscopy of etched surfaces. Using the etch described previously above, it was found that longitudinal samples revealed a fibrous structure as shown in *Figure 6*, whereas transverse etched surfaces show clearly the irregular break-up of the blend (see *Figure 7*). Examination of the edges and sides of the blocks shown in this Figure suggests that the PS fibrils are reasonably continuous.

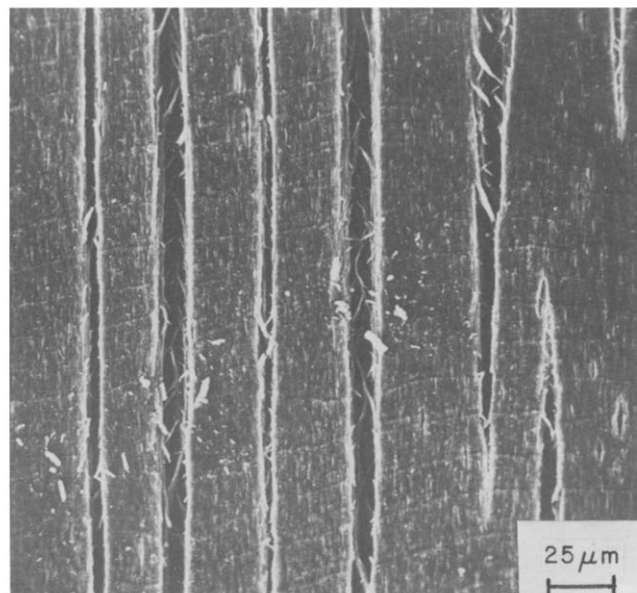
The high degree of transverse ordering of the PS fibrils along well-defined layers is reminiscent of that observed by Dlugosz *et al.*<sup>22</sup> when a block copolymer exhibiting a lamellar morphology is subjected to an extrusion process. The layer periodicity, of course, is on a vastly different scale in the two cases. Nevertheless the driving force required to develop transverse ordering in the blend could partly arise if the block copolymer matrix undergoes a phase transition to a lamellar morphology during the process of blending. Partial confirmation of this has been obtained using transmission electron microscopy using the Kato<sup>23</sup> osmium tetroxide staining

technique. *Figure 8* is a micrograph of a transverse section cut from the blend showing alternating light and dark bands present around the fibrils and stretching between them to give a 'webbed' effect. The periodicity of these striations is 20–40 nm, which is a typical figure for the periodicity of the microphases in a block copolymer. A striated structure was also observed in longitudinal sections and is consistent with a phase transition from a rod-like to a lamellar morphology in the S-B-S block copolymer matrix.

The phase transition is believed to occur by the solubilization of a low molecular weight fraction of the homopolymer PS by the dispersed microphases in the block copolymer. The required volume fraction of low molecular weight material is either naturally present in the homopolymer or is additionally generated by chain scission during the compounding and screw extrusion processes.



**Figure 5** Scanning electron micrograph of a longitudinal fracture surface for the blend of Kraton 102 with 30% homopolymer polystyrene



**Figure 6** Etched longitudinal fracture surface for the blend of Kraton 102 with 30% homopolymer polystyrene

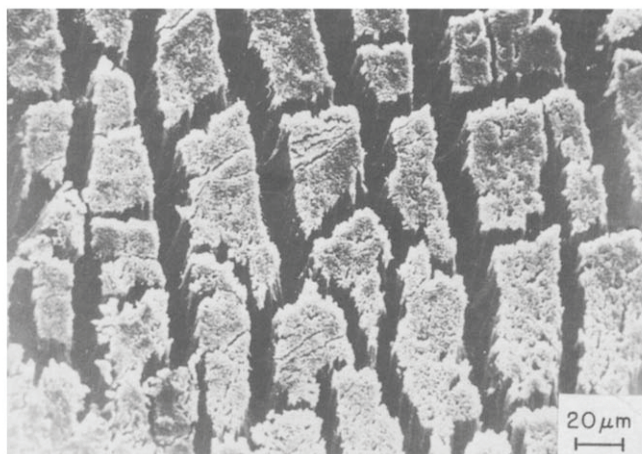


Figure 7 Etched transverse fracture surface for the blend of Kraton 102 with 30% homopolymer polystyrene

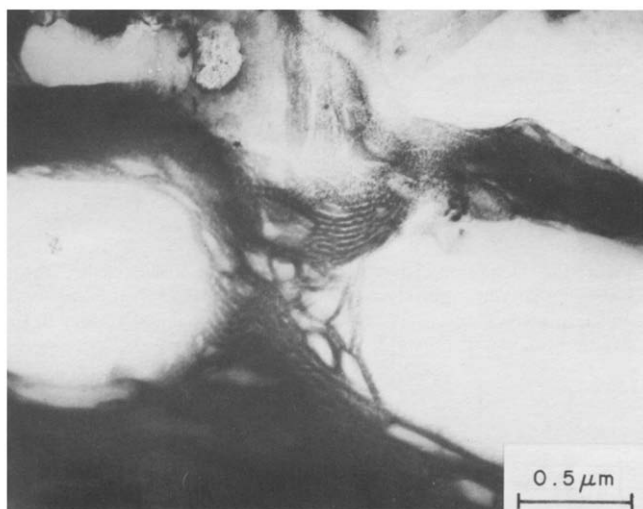


Figure 8 Transmission electron micrograph of a thin section cut transverse to the extrusion direction for a blend of Kraton 102 with 30% homopolymer polystyrene. White areas are the unstained polystyrene phase

A schematic diagram of the proposed microstructure of the 30% PS/70% S-B-S blend is shown in Figure 9. The microstructure arises from a combination of factors namely the process of phase transition in the block copolymer and the significant lowering of the surface energy of the dispersed homopolymer PS by the block copolymer. The latter aids the formation of the large fibrils by the process of elongational flow through the 'spider' holes. Finally, the fibrils are ordered by their association with the block copolymer.

It is interesting to note that the formation of this microstructure depends on a delicate balance of the factors just described, and that it is partly fortuitous that the screw extrusion process can generate this. For example, alterations to the volume fraction of added PS have a marked effect on the blend microstructure as described below.

For the case of a 10% PS/90% S-B-S blend, light microscopy of thin sections did not reveal any apparent internal structure. However, an SEM examination of etched microtomed surfaces showed evidence of a fine, almost interconnected particulate structure, as shown in Figure 10. The particles have a diameter of approximately  $0.2\ \mu\text{m}$  and seem well dispersed, as judged from the transverse section. Longitudinal sections suggest that to some extent these particulate structures are aligned in the

extrusion direction. No evidence for a fibrillar structure could be found.

These results contrast markedly with the observed microstructure for a 50% PS/50% S-B-S blend. An optical microscopic examination of thin transverse sections cut from this blend revealed a similar structure to that shown in Figure 3 for the 30% PS blend. However, when etched microtomed surfaces were observed in the scanning electron microscope, it was found that the microstructure of the blend consisted predominantly of very well developed polystyrene fibrils, of diameter in the range  $0.5\text{--}1.0\ \mu\text{m}$ , and highly aligned parallel to the extrusion direction (see Figure 11). Since the etch used in these studies attacks the S-B-S phase quite vigorously, the polystyrene fibrils shown in the transverse section tend to collapse, owing to the lack of support from the matrix phase.

Summarizing, if we take the results for the three blend systems, it appears that the microstructure is directly related to the concentration of homopolymer polystyrene. For low polystyrene content (10% vol), a particulate structure is present. For higher concentrations, an increasing proportion of this added polystyrene appears

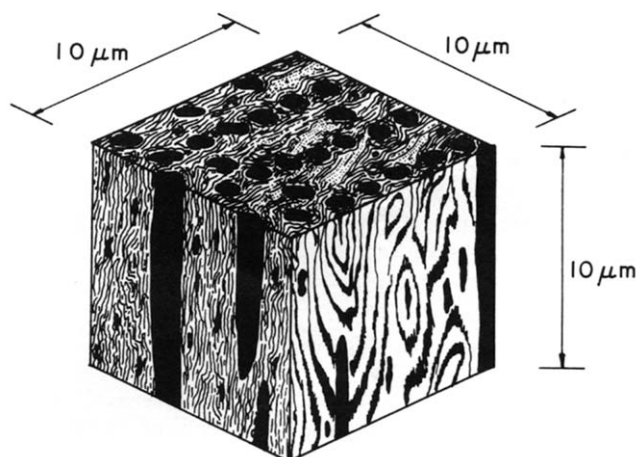


Figure 9 Schematic diagram of the microstructure of the Kraton 102-30% homopolymer polystyrene blend. Black areas represent the homopolymer polystyrene

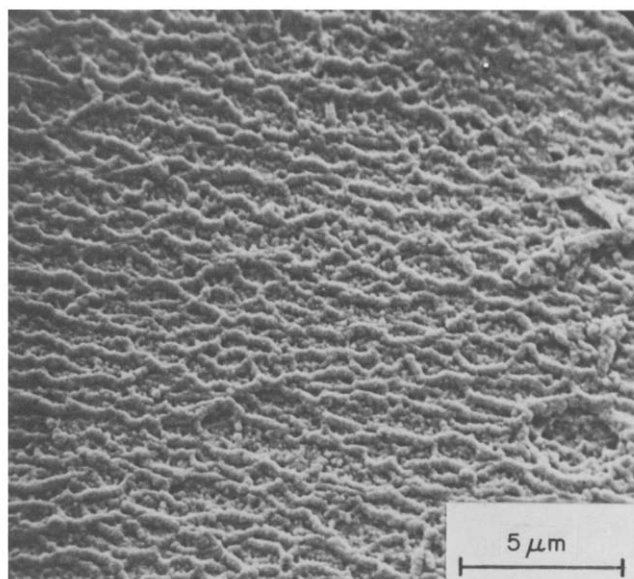


Figure 10 Scanning electron micrograph of an etched longitudinal section cut from a blend of Kraton 102 with 10% homopolymer polystyrene, following the processes of milling and screw extrusion

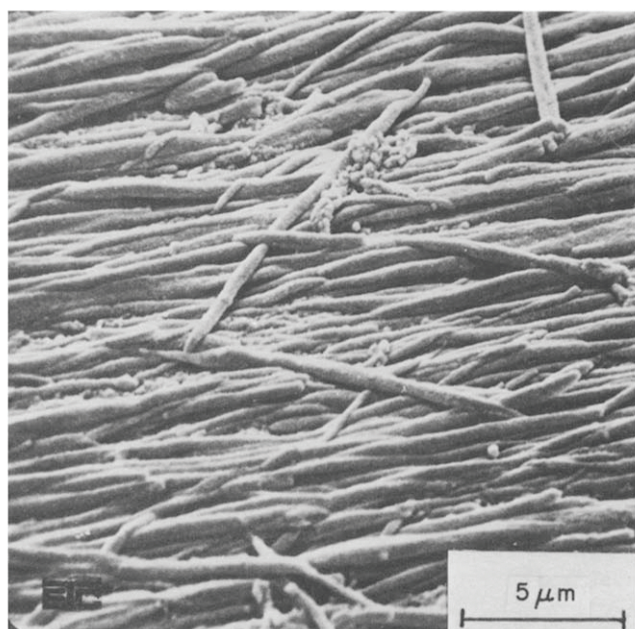


Figure 11 Scanning electron micrograph of an etched longitudinal section cut from a blend of Kraton 102 with 50% homopolymer polystyrene, following the processes of milling and screw extrusion

in the form of fibrils. For 50% PS/50% S-B-S, this conversion from a particulate to a fibrillar microstructure is essentially complete.

These changes in microstructure, together with the model proposed for the blend, as shown in Figure 9, are consistent with some independent results arising from a study of the expansion of the samples when swollen in a preferential swelling agent for the S-B-S phase. These results will now be discussed.

### SWELLING PROPERTIES OF THE BLENDS

Work by Folkes and Keller<sup>24</sup> and Folkes, Keller and Odell<sup>25</sup> was concerned with the effects of imbibing a selective swelling agent on the dimensions of S-B-S block copolymer samples, each possessing a uniformly oriented macrolattice. The changes in sample dimensions were anisotropic and related directly to the alignment of the microphases in the samples. For the purposes of this present study, the swelling properties may be used as a diagnostic method for the qualitative determination of orientation in the blend samples.

#### Measurements

Swelling was achieved by exposing specimens to hexane vapour, which is known to be a preferential swelling agent for the polybutadiene phase of the S-B-S block copolymer. The dimensional changes of the samples were measured using a travelling microscope. The small rectangular specimens required for these studies were cut in a predetermined direction from the extrudates. One axis of the specimen was always parallel to the extrusion direction. Additionally, for the case of the 30% PS and 50% PS blends which show transverse ordering (see Figure 3), the other two principal axes of the specimen were tangential and orthogonal to the striations. The definition of the axes is shown schematically in Figure 12.

#### Results and Discussion

Figure 13 shows the variation of the sample dimensions as a function of time for the 10% PS blend. Although the

dimensional changes in the three directions vary slightly, there are no major differences between the blend and pure copolymer. With this particular blend there is no significant reduction in the degree of swelling in the extrusion direction; the homopolymer polystyrene, although partially ordered along the extrusion direction, is not continuous and is therefore ineffective in constraining the swelling.

The swelling results for the 30% PS and 50% PS blends are shown in Figures 14 and 15. In these cases, the changes in sample dimensions in the three directions are very anisotropic. There is virtually no swelling in the extrusion direction and this, of course, is due to the restraining effect of the aligned homopolymer polystyrene fibrils. For the 30% PS blend, there is also a significant difference in the

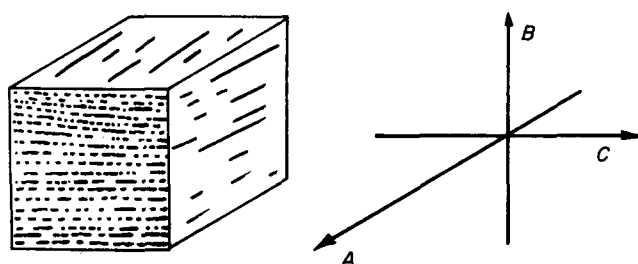


Figure 12 Definition of axes used in the swelling studies of the Kraton 102-homopolymer polystyrene blends. A represents the extrusion direction while B and C are respectively orthogonal and parallel to the striations shown in Figure 3

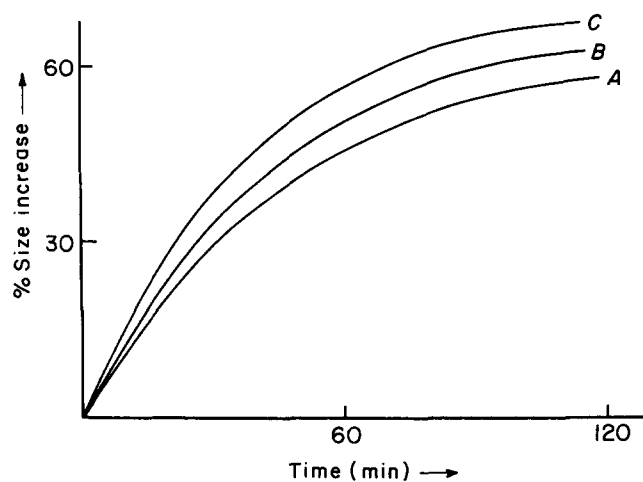


Figure 13 Swelling anisotropy in the blend of Kraton 102 with 10% homopolymer polystyrene

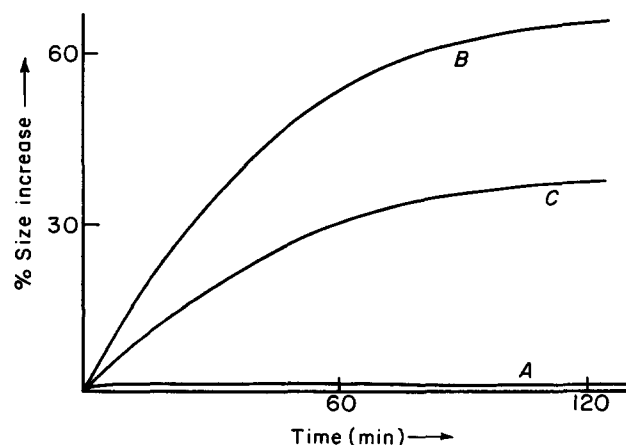


Figure 14 Swelling anisotropy in the blend of Kraton 102 with 30% homopolymer polystyrene

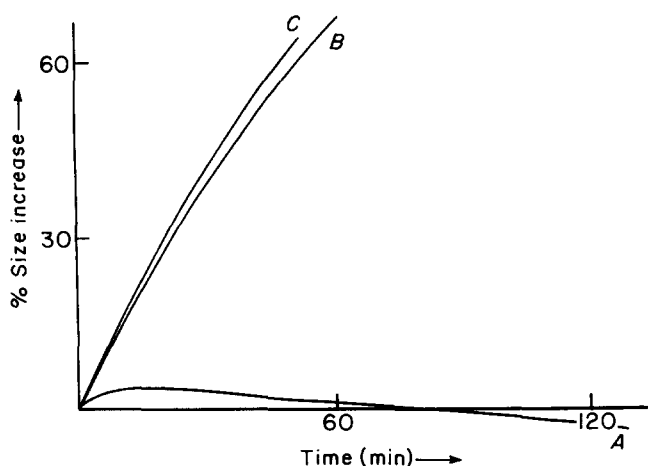


Figure 15 Swelling anisotropy in the blend of Kraton 102 with 50% homopolymer polystyrene

swelling in the *B* and *C* directions. This is associated with a partial alignment of the lamellar microphases in the S-B-S copolymer in the *C* direction, as proposed earlier in the paper. Indeed this result is consistent with the findings of Folkes and Keller<sup>24</sup> regarding the anisotropic swelling properties of an S-B-S block copolymer 'single-crystal' possessing a lamellar morphology. Initially, the sample dimensions perpendicular to the lamellae increased significantly, while no change was observed parallel to the lamellar surface. In structural terms, this swelling process was attributed to an increase in the thickness of the polybutadiene layers due to the imbibition of the selective swelling agent, all other dimensions remaining constant owing to the restraining effect of the polystyrene layers. It is interesting that the anisotropic swelling properties of the 30% PS blend can be satisfactorily interpreted only on the basis of a phase transition from cylindrical to lamellar microphases occurring in the S-B-S copolymer. The swelling results therefore provide supporting evidence for the mechanism of formation of this blend.

The fact that the dimensional changes in the *B* and *C* directions in the 50% PS blend are almost identical is probably associated with a progressive reduction in the alignment of the lamellae in the *C* direction, as the concentration of homopolymer polystyrene increases. Finally, it should be noted that even after prolonged exposure to the swelling agent, no sudden increase in the dimensions of the samples along the extrusion direction was observed, which could have resulted from a break-up of the homopolymer polystyrene fibrils. This does not exclude the possibility that a phase change may occur in the S-B-S copolymer, in line with that previously reported<sup>24,25</sup>. However, this seems unlikely since no permanent change in the dimensions of the blend samples was observed after they had been removed from the swelling agent and then subsequently allowed to dry out.

### CONCLUDING REMARKS

The microstructure of extruded samples of block copolymer-homopolymer polystyrene blends has been studied using light microscopy and electron microscopy. For all of the blend compositions studied, it was found that the homopolymer polystyrene formed a separate

phase, which in some cases was in the form of well developed fibrils aligned parallel to the extrusion direction. Furthermore, a previously unsuspected degree of spatial ordering of these fibrils was observed normal to the extrusion direction. It is proposed that this ordering arises from a molecular association of the homopolymer polystyrene with the block copolymer, which itself undergoes a transformation from a cylindrical to lamellar microphase morphology. The effects of imbibing a selective swelling agent have also been investigated and the anisotropy of the dimensional changes in small samples of the blends was found to be fully consistent with the observed microstructure.

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