Structural Changes upon Annealing in a Deformed Styrene–Butadiene–Styrene Triblock Copolymer As Revealed by Infrared Dichroism

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ABSTRACT: Structural and morphological changes in a deformed styrene–butadiene–styrene (SBS) triblock copolymer were usually studied by means of small-angle X-ray scattering techniques through analysis of scattering patterns which are related to rigid polystyrene (PS) microdomains. In the present study, a different approach was demonstrated. Infrared dichroism was used to elucidate these changes induced by annealing through measurements of molecular orientation of rubbery polybutadiene (PB) chains. This was made possible by the fact that (1) structural rearrangements of PS microdomains are inevitably associated with changes of the PB orientation and (2) strain-induced orientation of the PB chains depends on the arrangement or orientation of the PS microdomains which act as cross-links. Infrared dichroism analysis showed that the relaxation of rigid PS microdomains, which occurs even at annealing temperatures (T_a) below the glass transition temperature (T_g) of PS, can be studied by observing the relaxation of the PB orientation and that the remaining PB orientation under constant strain at long annealing time (>30 min) characterizes the orientation of rubbery chains required for activating PS plastic flow. Furthermore, it was found that the loss of PB orientation under strain with annealing time is not equally associated with the lost recovery of the sample length after removal of the extensional stress, suggesting the existence of different mechanisms of PB orientation relaxation. Finally, an anisotropic morphology in annealed SBS polymer was revealed by a strain-induced PB orientation which depends on the redrawing direction with respect to the initial stretching direction (SD). These measurements indicate that, at $T_a \lesssim T_g$ of PS, the PS rearrangement involves essentially rotation of cylindrical microdomains, with the interdomain vector connecting the centers of the cylinders remaining preferentially parallel to the SD; while, at $T_a > T_g$ of PS, the rearrangement process involves more displacement of the PS cylinders, with the interdomain vector oriented perpendicularly with respect to the SD.

I. Introduction

The particular "two-phase" structure in a styrene–butadiene–styrene (SBS) triblock copolymer is a consequence of microphase separation due to the incompatibility between polystyrene (PS) and polybutadiene (PB) chains. The morphology and its relationship with mechanical properties of SBS polymers have been extensively studied.[1-4] It is now known that these polymers are characterized by a highly heterogeneous and ordered morphology, which is responsible for their peculiar mechanical properties, and depending on the content of one component, different microdomain structures (spherical, cylindrical, and lamellar) can be obtained.

More attention has been given to the SBS polymer having a structure of PS cylindrical microdomains embedded in a PB matrix. The typical PS content for such a structure is around 28% by weight. When this polymer is stretched at temperatures below the glass transition temperature (T_g) of PS, a plastic-to-rubber transition is generally observed, like for most SBS polymers. The sample first behaves as a plastic, but after the yielding point it exhibits elasticity with a high elastic deformation. Investigations[1-4] showed that the yielding process involves breakdown or fragmentation of long, glassy PS cylinders, giving rise to short PS cylinders. As the stretching continues, PS cylinders, which are interconnected by PB chains, act as reinforcing fillers and cross-links supporting the stretched rubbery matrix. This high elasticity disappears when the sample is stretched at temperatures above T_g of PS.

Using small-angle X-ray scattering (SAXS) techniques, a series of elegant experiments have been performed by Hashimoto and co-workers on the deformation mechanism upon stretching[5] and the effects of annealing at the highly deformed state on the structure and morphology[6]

for the SBS polymer having cylindrical microdomains of PS. The main points with which we are concerned are schematically illustrated in Figure 1. For solution-cast samples before the first stretching, the characteristic regions, in which PS cylinders are spatially ordered, are randomly oriented (Figure 1a). It has been pointed out[5] that the deformation behavior upon stretching is different for regions having different orientations of the PS cylinders with respect to the stretching direction (SD), and the macroscopic mechanical response is a result of the combination of contributions from all regions. But at high deformations (several hundred percent), as depicted in Figure 1b, essentially all short PS cylinders, resulting from fragmentation of initially long cylinders, are ordered with the cylindrical axis inclined at an angle and the interdomain vector connecting the centers of the cylinders parallel to the SD. Such a morphology is controlled by the orientation of the PB chains. When the sample is relaxed, i.e., after removal of the extensional stress, it recovers a macroscopically random morphology state, but with broken PS cylinders in the ordered regions, as shown in Figure 1c.

As for the annealing effects on structural changes in the SBS polymer when annealed at the highly deformed state, Hashimoto et al.[6] showed that, even at temperatures below T_g of PS, relaxation of the PS microdomains, essentially plastic flow of PS block chains within their own phase, takes place. Depending on the annealing temperature, the nonrecoverable rearrangement of the PS cylinders, combined with the remaining elastically coverable orientation of the PB chains, controls the final morphology after the stress is released.

In these studies which have been proven to be important for understanding the deformation mechanism, structural relaxation, and morphology control on the molecular scale,
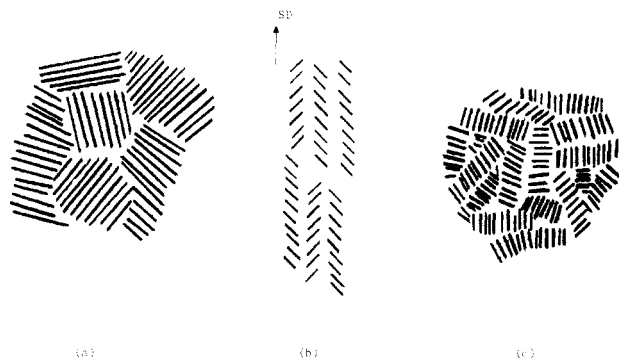
Figure 1. Schematic representation of structures of PS cylindrical microdomains interconnected by PB chains: (a) solution-cast sample before the first stretching, (b) at the highly stretched state; (c) after removal of the extensional stress.

the tool of investigation is the SAXS technique. The SAXS analysis is based on the fact that the shape of the scattering patterns is related to the shape, size, and orientation of individual PS cylindrical microdomains and the arrangement of all PS cylindrical microdomains. In other words, these studies were rendered possible by observing changes in rigid PS cylinders as revealed by scattering patterns. Now, the other molecular process involved in the deformed SBS polymer is the molecular orientation of rubbery PB chains. Although some birefringence measurements were made to see PB orientation,[6] only limited and qualitative information can be obtained because the birefringence analysis is complicated by the contribution from the form birefringence that does not arise from PB chain orientation and may change depending on the orientation of PS microdomains.[1]

In this paper, we present a different approach. An analysis of annealing-induced structural and morphological changes in the deformed SBS polymer was made, based on infrared dichroism orientation measurements. The basic idea is to detect and elucidate these changes by observing the orientation of the PB chains. Why is it possible to do so? First, it is easy to picutre that changes in terms of reorientation or rearrangement of the PS cylinders are inevitably associated with changes in PB orientation. For example, a decrease in the distance between two neighboring PS cylinders implies an orientation relaxation of the PB chains connecting them. Second, unlike "point" (or spherical) cross-links, whose response upon stretching should be isotropic, for the cross-links played by the PS cylinders, the strain-induced PB orientation should be influenced by their arrangement and orientation. For instance, focusing on a locally ordered region as shown in Figure 1c, the orientation of the PB chains should be greater when the SD is perpendicular to the PS cylinders than when it is parallel to them. In the former case, the extensional forces are more efficiently transferred, through PS cylinders, to PB chains, whose alignment along the SD mostly contributes to the sample's deformation, while in the latter case, more positional changes of the PS cylinders (rotation, displacement) are expected to occur, with a smaller extension of the PB chains. Qualitatively, this situation was confirmed by SAXS measurements[5] which showed a greater increase in the distance between PS cylinders, thereby a higher orientation of the PB chains, for samples with PS cylinders oriented perpendicularly to the SD compared to samples having cylinders parallel to it. On the basis of the above considerations, we show, in the present study, that infrared dichroism analysis allows us to get useful information on structural and morphological changes in the SBS polymer

induced by annealing at the deformed state, which are complementary to those derived from SAXS study.

II. Experimental Section

II.1. Sample Preparation. The SBS polymer studied in this work is a commercial product purchased from Aldrich. It contains 30% PS and has a total molecular weight of about 140 000 (GPC value). Film samples of about 250 μm thick were prepared by casting a 12% polymer solution of toluene onto glass plates. They were dried under vacuum at 50 °C for several days. The morphology of cylindrical PS microdomains was confirmed by transmission electron microscopy.

All films used in this study were first stretched, just before an experience, until the yielding process was completed and then relaxed. This means that the starting SBS polymer has a structure of glassy, short cylindrical microdomains of PS (Figure 1c) dispersed in a rubbery PB matrix. The purpose of this treatment is to ensure a homogeneous deformation upon further stretching, which is important for orientation measurements.

Stretching of the samples was performed on a hand-driven device designed and constructed in our laboratory. It is capable of effecting a simultaneous extension of both ends of the film (10 mm in length and in width before stretching) and thus ensures a homogeneous elongation development along the sample. Furthermore, this stretching device can be mounted in the sample compartment of the spectrometer, with the same central part of the film remaining in the infrared beam for all extensions. Small ink marks were put on the film surface to measure the draw ratio λ (where $\lambda = l/l_0$, with l_0 and l being the sample length before and after stretching, respectively).

Unless otherwise stated, the samples subjected to annealing were stretched to a draw ratio of $\lambda = 5$. For annealing at temperatures below 65 °C, the stretched sample fixed on the device was placed in an oven with a well-controlled temperature for the annealing time wanted. But at higher temperatures, the films annealed under tension broke due to fast structural relaxation. In this case, the stretched film was clamped between two copper plates and then subjected to annealing. The sample deformation was kept under compressional forces. After annealing, the samples were rapidly cooled before orientation measurements at room temperature.

II.2. Infrared Dichroism Measurements. The infrared dichroic ratio R is defined as $R = A_{\parallel}/A_{\perp}$, where $A_{\parallel}$ and $A_{\perp}$ are the measured absorbances with the infrared beam polarized parallel and perpendicular, respectively, to the stretching direction. The infrared dichroism allows one to determine the second moment of the orientation distribution function $\langle P_2(\cos \theta) \rangle$ which is related to R through

$$\langle P_2(\cos \theta) \rangle = (R_0 + 2)(R - 1)/(R_0 - 1)(R + 2)$$

in which θ is the angle between the chain axis and the stretching direction, and $R_0 = 2 \cot^2 \alpha$, α being the angle between the chain axis and the transition moment of the infrared vibration considered. $\langle P_2(\cos \theta) \rangle$ represents the average orientation of all the chain segments involved and ranges from 0 for the random orientation to 1 for the perfect parallel orientation. $\langle P_2(\cos \theta) \rangle$ of negative values corresponds to the orientation perpendicular to the stretching direction (–0.5 for perfect orientation).

The polarized infrared spectra of a SBS film stretched to $\lambda = 5$ are given in Figure 2. The PB absorption band at 1240 cm^{-1} is not perturbed by any PS bands and is best suited to its orientation measurements. This band is assigned to the CH$_2$ twisting vibration of the cis units in 1,4-polybutadiene[7] and displays high positive dichroism. Although it is known that chain segments of different conformations may have different orientations upon stretching, the high proportion of the cis units in these SBS samples ($\sim$50%) ensures that its orientation is representative of the orientation over all PB chains and, more importantly, offers the basis for the analysis of structural changes in this polymer. As the angle α for the 1240-cm^{-1} band is unknown, the PB orientation was characterized by the infrared dichroic function F:

$$F = (R - 1)/(R + 2)$$

Nevertheless, F of the 1240-cm^{-1} band represents a quantitative
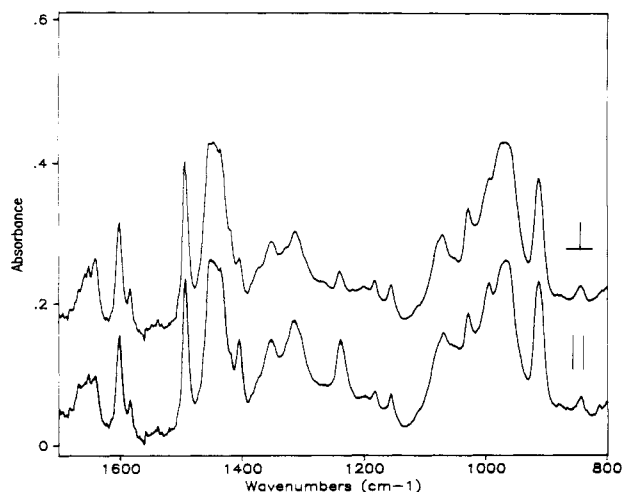
Figure 2. Polarized infrared spectra, in the 800–1700-cm^{-1} region, of a SBS sample stretched to a draw ratio $\lambda = 5$ with the electric vector parallel ($\parallel$) and perpendicular ($\perp$) to the stretching direction.
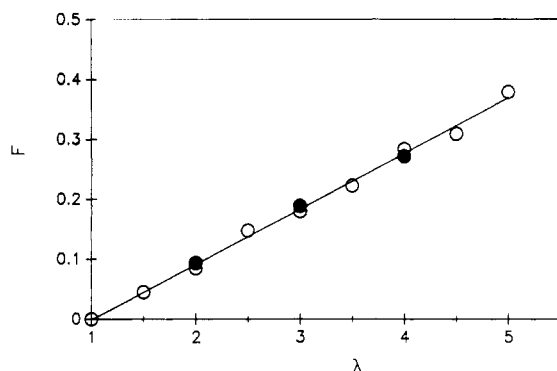

Figure 3. Infrared dichroic function vs draw ratio for as-cast SBS samples: extension increase (O) and extension decrease (●).

estimation of the PB orientation in the sense that, as the transition moment associated with this band is perpendicular to the plane of the methylene group, it is reasonable to assume that α is near zero and $\langle P_2(\cos\theta)\rangle$ is equal to or only slightly greater than F. The PB absorption band at 1314 cm^{-1} can also be used to estimate its orientation. This band has a much smaller parallel dichroism compared to the 1240-cm^{-1} band and is ascribed to the CH bending of the cis units.[8] However, except where otherwise mentioned, F of PB was determined from the 1240-cm^{-1} band in this study.

On the other hand, it is worth while to mention that several PS absorption bands, such as those located at 1496 and 1602 cm^{-1}, can be well used to measure the orientation of the PS chains in the SBS polymer. But throughout this study no molecular orientation of PS was detected within experimental error, indicating a negligible PS orientation. It should be noted that the possible PS orientation arising from the plastic deformation occurs before the yield point, and it could not be observed in this study for samples whose yielding process was completed before subsequent stretchings for orientation measurements.

For infrared dichroism measurements, the polarized spectra were recorded on a Bomen MB-102 Fourier transform infrared (FTIR) spectrometer at a resolution of 4 cm^{-1} from a total of 50 interferograms. Polarization of the infrared beam was performed with a wire-grid polarizer placed between the stretching device and the DTGS detector. The polarizer was rotated 90° between the two polarization measurements, and no instrumental effect resulting from a different orientation of the polarized radiation was observed.

III. Results and Discussion

III.1. Orientation Behavior of As-Cast Samples.
The strain-orientation behavior of as-cast SBS films is shown in Figure 3, where the dichroic function F is plotted as a function of draw ratio λ. Both a linear increase upon
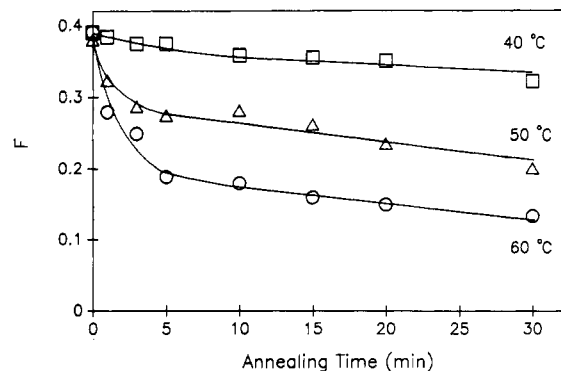

Figure 4. Infrared dichroic function vs annealing time for SBS samples annealed under constant strain ($\lambda = 5$) at temperatures indicated in the figure.
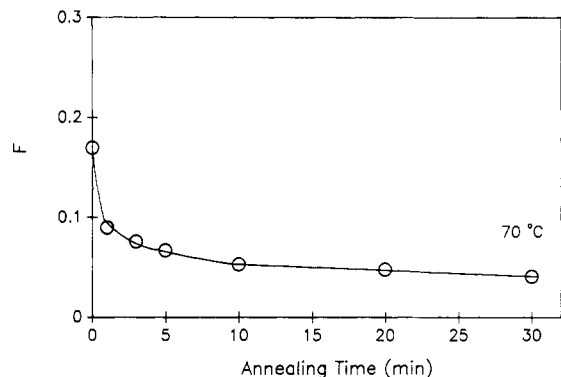

Figure 5. Infrared dichroic function vs annealing time for a SBS sample annealed under constant strain ($\lambda = 3$) at 70 °C.

stretching and a linear decrease when relaxed for the PB orientation are observed, and the orientation is reversible. Moreover, further repeated cycles of stretching increase and decrease resulted in negligible changes in PB orientation, and the sample recovered its length before stretching when the extensional stress was removed. This result indicates that the sample deformation is governed by the elastically oriented PB chains, and the short PS cylindrical microdomains do not undergo significant changes upon repeated stretching at room temperature. At the relaxed state, the morphology before the first stretching is recovered with randomly oriented regions, in which the PS cylinders are ordered.

III.2. Orientation Relaxation under Constant Strain.
Using the stretching device described above, we can treat highly stretched SBS samples at temperatures up to 65 °C and then measure the orientation of PB chains under constant strain. This makes it possible to see the effects of annealing time and temperature on the structure of the deformed SBS polymer, through measurements of changes in PB orientation.

In Figure 4, the dichroic functions are given of stretched samples annealed at three temperatures below T_g of PS for different times. It is seen that even at 40 °C a decrease of chain orientation occurs. The orientation relaxation becomes fast as the temperature increases. A striking feature in this figure is that, similar to the chain relaxation of oriented thermoplastic polymers above T_g,[9] a rapid decay of orientation is observed at short times (within the first 5 min), and then this decrease is slowed down. As shown in Figure 5, a similar result is obtained for a sample annealed at a higher temperature, 70 °C, and stretched to $\lambda = 3$ (the film broke with $\lambda = 5$).

It is important to keep in mind that the structure of the highly oriented SBS polymer is essentially like that depicted in Figure 1b. As both ends of the PB chains are

fixed on rigid PS cylinders, it is obvious that the loss of PB orientation in samples under constant strain is a consequence of a structural rearrangement of the PS microdomains; otherwise, the PB orientation should essentially be constant at a given strain. The key molecular process involved in such structural rearrangement, suggested by Hashimoto et al.,[6] is a plastic flow of PS block chains within their own phase, essentially the displacement parallel to the interface between the PS and PB domains. It was shown that this plstic flow below T_g of PS could be activated by the mechanical stress arising from the PB orientation and leads to a decrease in the end-to-end vector of the PB chains, which is necessary for their orientation relaxation. The results in Figures 4 and 5 confirm PB orientation relaxation associated with these changes and indicate that structural rearrangement of glassy PS cylinders is favored at higher temperatures, giving rise to fast orientation relaxation of the PB chains.

The other feature revealed in Figures 4 and 5 is that the relaxation of PB orientation attains a plateau at long annealing times, and this remaining PB orientation under strain decreases as the temperature increases. Indeed, no further significant decrease of PB orientation was observed at times longer than 30 min. This can be understood by the fact that PS plastic flow is activated by PB orientation, and, in turn, PB orientation relaxation is allowed by PS plastic flow. This means that, as PS structural rearrangement progresses, the PB orientation will be too small to supply a local mechanical energy which is high enough to overcome the free energy involved in the PS plastic flow. When the PS plastic flow is stopped, no more PB relaxation takes place. Obviously, at higher temperatures the minimum mechanical energy required to activate PS plastic flow decreases due to thermal contribution. So, the remaining PB orientation at long annealing time (>30 min) characterizes the orientation of rubbery chains required to start the process of PS rearrangement at temperatures below its T_g.

Macroscopically, the annealing-induced orientation relaxation of the PB chains was reflected by unrecoverable deformation of the sample; i.e., it could not recover its initial length after removal of the stress. Now, the question raised is, what is the relation between the lost molecular orientation of the PB chains under strain and the lost recovery of the sample after release of the stress? We can define

$$\text{lost orientation} = (F_0 - F_t)/F_0$$

$$\text{lost recovery} = (\lambda_r - 1)/(\lambda_i - 1)$$

in which F_0 and F_t are dichroic functions measured before annealing and after annealing for a time t, respectively; λ_i is the initial draw ratio and λ_r the residual draw ratio at a given annealing time. Figure 6 shows the plot of lost recovery vs lost orientation (in units of percent) for samples annealed at 60 °C with λ_i = 5 and at 70 °C with λ_i = 3. The first observation that can be made is that the lost reocovery of the sample length is directly proportional to the lost PB orientation. However, at the same lost orientation the lost recovery is greater for higher temperatures. More interestingly, it seems that two different regions can be distinguished in Figure 6. At lost orientations below about 50%, the lost recovery develops with increasing lost orientation in a less sensitive way than in the region where the lost orientation is above 50%. Moreover, at high lost orientations, a similar slope for the increase in lost recovery is observed for both temperatures.
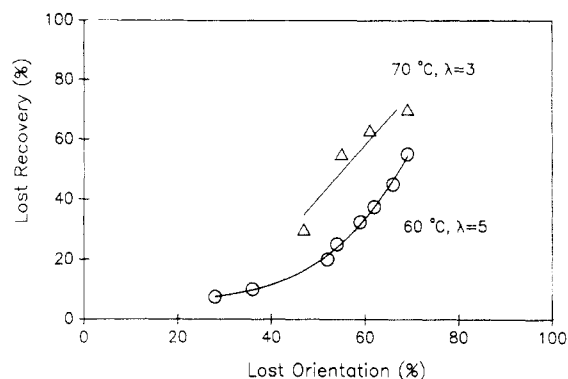

Figure 6. Lost recovery of the SBS sample length after removal of the extensional stress vs lost orientation of the PB chains under constant strain. The annealing temperature and initial draw ratio are indicated in the figure.
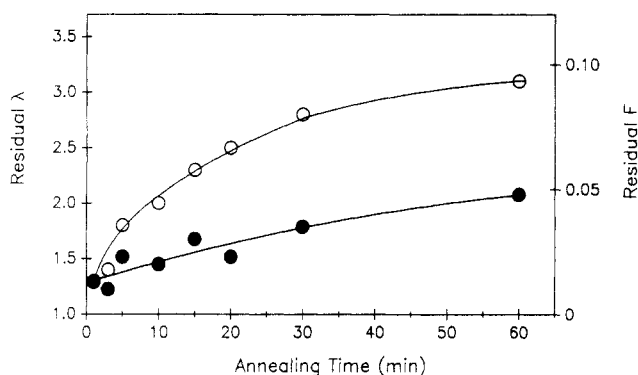

Figure 7. Residual dichroic function (●) and corresponding residual draw ratio (O) vs annealing time for a SBS sample annealed at 60 °C with an initial draw ratio λ = 5.

This result shows that the orientation relaxation of the PB chains with time is not equally associated with the unrecoverable deformation of the sample. This suggests the existence of different mechanisms of PB orientation relaxation, for which the relaxation of the PB chains is related to the plastic flow of PS in a different manner. One tentative explanation is that at the early stage of annealing the loss of PB orientation is essentially arising from the displacement of PS block chains on both sides of the PB chains, without significant changes of the arrangement of PS cylinders, while at the later stage of annealing the relaxation of the PB chains is related to more rotations and changes in position of the cylinders, which are more effective for unrecoverable deformation of the sample after removal of the stress. Further studies are needed in order to get a deeper insight into these molecular processes.

III.3. Residual Orientation. In the studies of Hashimoto et al.,[6] after taking into account the form birefringence arising from orientation of the PS cylinders, it was concluded that residual orientational birefringence of the PB chains exists in relaxed samples.

Infrared dichroism permits direct measurements of the residual orientation of the PB chains in these samples. The residual dichroic functions of a relaxed sample after being annealed under tension at 60 °C for different times are given in Figure 7 with corresponding residual draw ratios. In Figure 8, the residual orientation and corresponding residual deformation are given for samples annealed at different temperatures for 30 min. These results confirm that some PB chain orientation exists in these samples and, more importantly, show that the residual orientation is small, in most cases less than 10% of the orientation in the initially stretched samples.
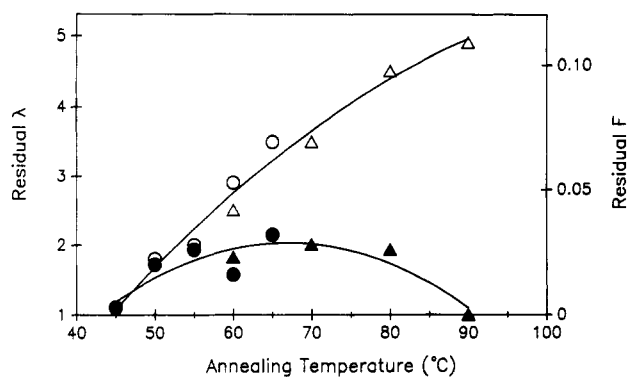
Figure 8. Residual dichroic function (●, ▲) and corresponding residual draw ratio (○, △) vs annealing temperature for SBS samples annealed for 30 min. Circle and triangle symbols refer to samples annealed under tension and under compression, respectively.
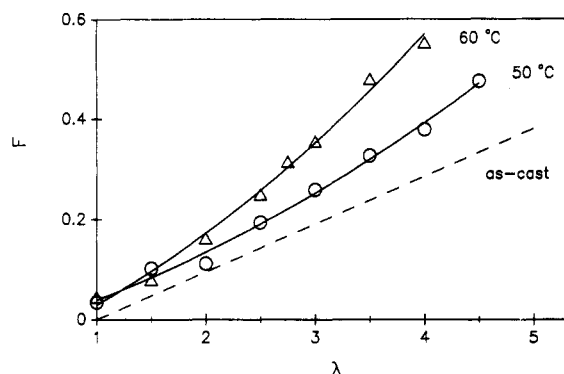

Figure 9. Infrared dichroic function vs redraw ratio for SBS samples annealed under tension at temperatures indicated in the figure for 1 h with a draw ratio $\lambda = 5$ and then relaxed and for an as-cast sample for comparison. The redrawing direction is along the initial stretching direction.
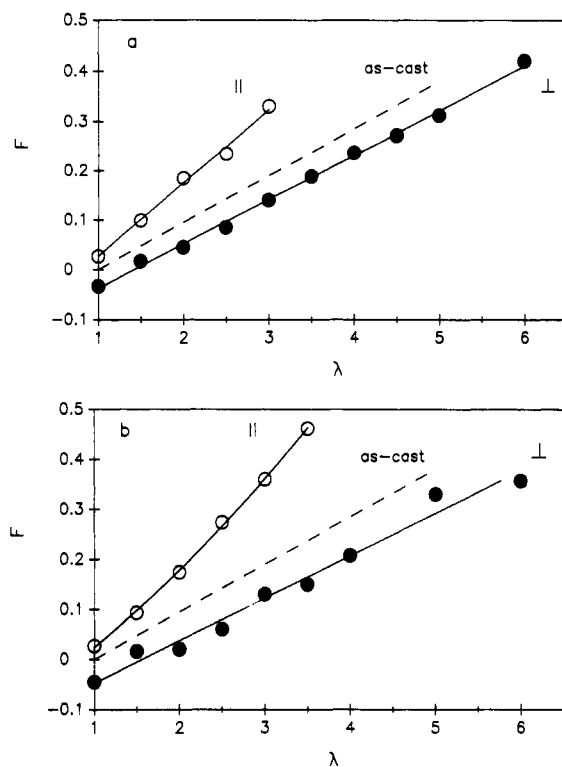

Figure 10. Infrared dichroic function vs redraw ratio for SBS samples annealed under compression at (a) 70 and (b) 80 °C for 1 h with a draw ratio $\lambda = 5$ and then relaxed and for an as-cast sample for comparison. The two redrawing directions, parallel ($\parallel$) and perpendicular ($\perp$) with respect to the initial stretching direction, are indicated in the figure.

On the other hand, despite some scattering of data in Figures 7 and 8, the infrared dichroism measurements clearly show that the residual orientation of the PB chains is related to the final morphology of the annealed sample. In Figure 7, it increases as the structural rearrangement of the PS microdomains develops, which is characterized by an increased unrecoverable deformation (higher residual draw ratio). So it is likely that this residual orientation of the PB chains is imposed by the structural changes of the PS cylinders that occurred during the annealing process. A maximum of residual orientation appears in Figure 8 at about 70 °C because at temperatures near T_g of PS the mobility of the PS chains is high enough to organize the removal of such a memory of the PB orientation along the initial stretching direction.

It must be mentioned that other factors could contribute to the observed residual orientation. One of them is the formation of microvoids that could develop with time in these samples when annealed under strain.

III.4. Morphological Changes upon Annealing.
Strain-induced orientation measurements were performed on samples after being annealed under strain and then relaxed; i.e., they were used as starting samples and redrawn. The purpose was to detect and elucidate the morphological changes induced by the annealing process. Obviously, if no changes in the arrangement of the PS cylinders occurred, the same orientation development should be obtained compared to as-cast samples.

The orientation behavior of two annealed SBS samples upon redrawing is shown in Figure 9,where the infrared dichroic function is plotted as a function of the redraw ratio defined as l_s/l_r (l_s and l_r are, respectively, the sample

length after and before the second draw, and l_r is also the residual length after the initial annealing). Before the second draw, these samples were stretched with a draw ratio of 5, annealed under this strain at 50 and 60 °C, respectively, for 1 h, and then relaxed by removing the stress (the residual λ being 2.2 and 3, respectively). The redrawing was performed along the initial stretching direction, and the nonzero orientation at $\lambda = 1$ in Figure 9 is due to the residual orientation in the annealed samples as shown in section III.3. Also, it was noted that when the stress was released, the sample recovered the length before the second draw.

It is clear, from Figure 9, that morphological changes took place because the PB orientation is greater in annealed samples than in as-cast ones. This increase is higher for the sample annealed at 60 °C compared to that annealed at 50 °C, indicating that the orientation increase is enhanced by more annealing-induced morphological changes. Similar results were obtained for samples annealed under compression.

On the basis of these results, it can be thought that in the annealed samples PS cylindrical microdomains are arranged in a way different from that in as-cast samples, making them act more efficiently as cross-links and leading to higher PB orientation upon redrawing. It is natural to assume that some kind of order of the PS cylinders exists along the initial SD. In other words, an anisotropic morphology may be formed in annealed samples. If this is the case, it should be reflected by an anisotropic orientation behavior of the PB chains when the sample is redrawn along the perpendicular to the initial SD.

Annealed samples having a size large enough for redrawing in the two directions were prepared under compression. The results of the orientation measurements for samples annealed at 70 and 80 °C are given in Figure 10 (the directions of redrawing are indicated in the figure).
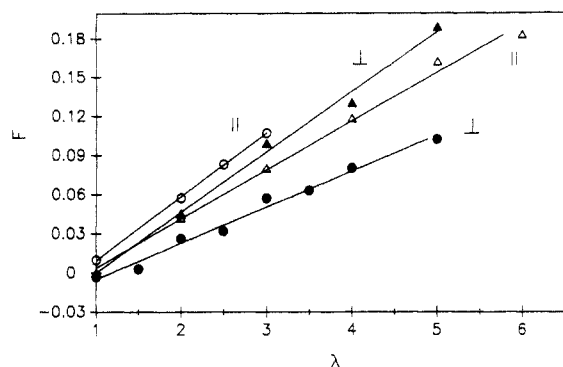
Figure 11. Infrared dichroic function of the 1314-cm^{-1} band vs redraw ratio for SBS samples annealed under compression at 80 °C (circle symbol) for 1 h and 120 °C (triangle symbol) for 30 min with a draw ratio λ = 5 and then relaxed. The two redrawing directions, parallel ($\parallel$) and perpendicular ($\perp$) with respect to the initial stretching direction, are indicated in the figure.

Figure 12. Schematic representation of the arrangement of PS cylinders for SBS samples in the deformed state: (a) as-stretched before annealing; (b) annealing at temperatures $T_a \lesssim T_g$ of PS; (c) annealing at temperatures $T_a > T_g$ of PS. The essential difference is the change in the direction of the interdomain vector **r** connecting the centers of the PS cylinders with respect to the stretching direction SD (see text).

Indeed, the strain-induced orientation is very different, depending on the redrawing direction. The PB orientation is much greater when the sample is redrawn along the initial SD than when it is redrawn perpendicular to this direction, with the orientation of the as-cast sample intermediate between them. Moreover, it can be seen that this orientation anisotropy is more pronounced for the sample annealed at 80 °C (Figure 10b) compared to the sample annealed at 70 °C (Figure 10a). These results confirm an anisotropic arrangement of PS cylindrical microdomains in the annealed samples, which is more important at higher temperatures for annealing at $T_a \lesssim T_g$ of PS. This morphology anisotropy is also reflected by very different maximum sample extensions upon redrawing along and perpendicular to the initial SD, as can be seen in Figure 10.

It is of interest to see the temperature effects over a broad range on morphological changes. But at $T_a > T_g$, we could not obtain films good enough for the redrawing experiment in two directions. Nevertheless, we found one way to prepare such films by coating the sample with a sealing film of Teflon before clamping it between the cooper plates. Unfortunately, the 1240-cm^{-1} band is perturbed by absorptions of the trace of Teflon film retained on the surface of the annealed sample. In order to overcome this problem, we used the 1314-cm^{-1} band (see the Experimental Section), which is not affected by the trace of Teflon film, to estimate the orientation of PB chains. Figure 11 shows the dichroic functions of this band upon redrawing in the two directions for a SBS sample annealed at 120 °C for 30 min with λ = 5 and then relaxed (residual λ = 5). For comparison, the results from this band for the sample annealed at 80 °C (Figure 10b) are also shown in this figure. It is seen that contrary to the sample annealed at 80 °C, which has a greater PB orientation when redrawn along the initial SD as observed from the 1240-cm^{-1} band, the sample annealed at 120 °C exhibits a higher PB orientation when it is redrawn perpendicularly to the initial SD. This result indicates a difference in morphological changes in the deformed SBS polymer when it is annealed below and above the glass transition temperature of PS.

It is evident that the observed changes in annealed samples are a consequence of the relaxation of the PS cylinders by the unrecoverable plastic flow. The SAXS analysis of Hashimoto et al.[6] showed that when the SBS polymer is annealed under constant strain, the relaxed PS cylindrical microdomains undergo rotation toward the stretching direction. After removal of the extensional stress, the unrelaxed PS cylinders tend to go back to their initial state before stretching, associated with the elastic
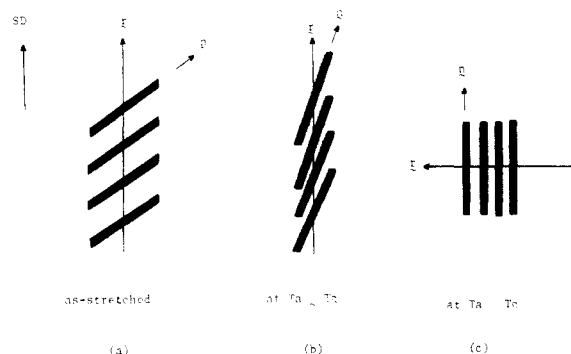
recovery of oriented PB chains, while the relaxed PS cylinders, with relaxed interconnecting PB chains, preserve their domain orientation and arrangement. So, it is clear that the relaxed PS microdomains have a macroscopically anisotropic arrangement, which is responsible for the behavior of PB orientation upon redrawing. The measured orientation of the PB chains is a response averaged over all PS cylinders, i.e., from relaxed and unrelaxed regions, and qualitatively, the magnitude of the orientation difference with respect to as-cast samples is a measure of the importance of the relaxed PS microdomains, which depends on the annealing temperature.

Figure 12 schematically illustrates the interesting information on the relaxation of PS cylinders under strain, which we can derive from the orientation measurements. The arrangement of PS cylinders in a highly deformed state before annealing is depicted in Figure 12a. When annealed at $T_a \lesssim T_g$ of PS (≤ 80 °C), as shown in Figure 12b, the morphological changes involve essentially the rotation of PS cylinders with their long axis **n** aligned more along SD, accompanied by changes in the distance between the cylinders, but the interdomain vector **r** connecting the centers of the PS cylinders remains preferentially parallel to SD. This explains the observed PB orientation (Figure 10) which is greater upon redrawing along the initial SD than perpendicularly to it, because only with such an arrangement PB chains support most of the extensional stress in the direction of the initial SD, giving rise to a high orientation, while extensional forces perpendicular to the initial SD result in more rearrangement of the PS cylinders (rotation, displacement) instead of the PB orientation. Then, at $T_a > T_g$ of PS (e.g., 120 °C), the situation is illustrated in Figure 12c. The morphological changes involve more displacement, combined with further rotation, of the PS cylinders, with the interdomain vector **r** oriented perpendicularly to SD. This change of the direction of **r** causes the observed inverse situation; that is, the PB orientation is greater upon redrawing in the direction perpendicular to the initial SD than along it (Figure 11).

The point to be emphasized here is that a high orientation of the PB chains will be achieved when the stretching direction is parallel to the interdomain vector **r**, regardless of the angle between the axis of cylinders **n** and SD. For a SBS sample stretched and then relaxed, without being subjected to thermal annealing, the orientation of **r** of all regions is random and the strain-induced orientation of PB chains is the same whatever the re-
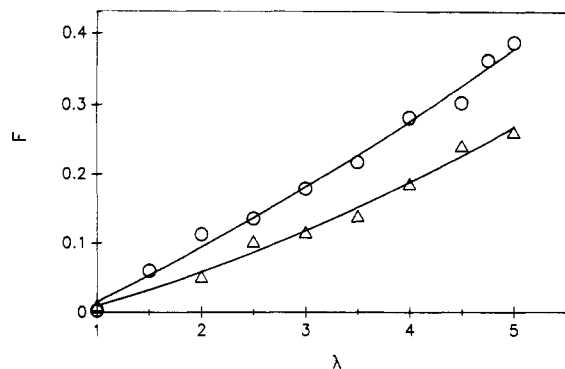
Figure 13. Infrared dichroic function vs draw ratio for SBS samples reheated to 60 °C for 2 h (O) and 100 °C for 30 min (△) after being annealed under tension at 60 °C for 1 h with a draw ratio $\lambda = 5$ and then relaxed.

drawing direction. Now, for samples thermally treated in a stretched state and then relaxed, the orientation of **r** is no longer random. The preferential direction averaged over all **r** is determined by the morphological changes which occurred during annealing and is temperature-dependent. It is recognized that the real situation is complex about the distribution of **r** for the relaxed PS cylinders and its evolution as a function of annealing temperature and time and other factors such as, for example, the initial strain. But essentially, as shown in Figure 12, at $T_a \lesssim T_g$ of PS, the average **r** is oriented along the initial SD, while at $T_a > T_g$ of PS, it is perpendicular to this direction. Noting that at $T_a > T_g$ an orientation of **r** perpendicular to SD is indicated by SAXS analysis.[6]

III.5. Healing Effects. As mentioned in the Introduction, when a solution-cast SBS sample is stretched beyond the yielding point, the long cylindrical microdomains of PS are fragmented into short cylinders. When the sample is relaxed, it can almost recover the initial morphological state but with short cyliners of PS. It is well-known[1-4] that, even at room temperature, the sample tends to re-form the long PS cylindrical microdomains. This healing effect can be accelerated by heating the sample.

A similar healing phenomenon was observed for samples which were annealed under strain and could not recover their initial length after removal of the stress. By heating these samples for a limited time, their length can decrease up to almost the initial value. This morphological recovery can also be examined by strain-induced orientation measurements.

For this purpose, SBS samples were first annealed under tension at 60 °C for 1 h with a draw ratio of 5 and then relaxed. The residual draw ratio λ_r was 3.2. Two of the annealed samples were then reheated to 60 °C for 2 h and 100 °C for 30 min, respectively, and the unrecoverable deformation disappeared at both temperatures with $\lambda_r <$ 1.5. Figure 13 shows the orientation development of the PB chains for both reannealed samples, upon redrawing along the initial SD. It is seen that the PB orientation for the sample healed at 60 °C is the same as that of the as-cast sample (Figure 3), indicating that the morphology is recovered to a similar state as that before annealing. However, the orientation for the sample reannealed at 100 °C is significantly smaller, showing a different morphology in this recovered sample. In light of the discussion in section III.4, it seems likely that the re-formed morphology after reannealing at 100 °C has more local disorder, with smaller regions in which PS cylinders are ordered and correlated by the interdomain vector **r**. This leads to a decreased efficiency of the PS cylinders as crosslinks for the orientation of PB chains.

This result shows the influence of the reannealing temperature, being below or above T_g of PS microdomains, on the morphology recovery.

IV. Conclusions

Infrared dichroism was proposed to investigate the annealing-induced structural and morphological changes in a deformed SBS polymer through measurements of molecular orientation of PB chains. It is shown that the relaxation of glassy PS microdomains can be studied by observing the relaxation of the PB orientation. Furthermore, it was found that the lost PB orientation under constant strain with annealing time is not equally associated with the lost recovery of the sample length after removal of the stress, suggesting the existence of different mechanisms of PB orientation relaxation, and that, in relaxed samples, the residual PB orientation along the initial stretching direction is small but increases with the structural rearrangement of the PS microdomains induced by annealing at $T_a < T_g$ of PS.

On the other hand, the morphological changes which occurred during annealing under strain were studied through strain-induced PB orientation measurements on relaxed samples. An anisotropic morphology was revealed by different PB orientations, depending on the redrawing direction with respect to the initial stretching direction. These measurements indicate that, at $T_a \lesssim T_g$ of PS, the rearrangement of the PS microdomains in terms of the rotation of cylinders toward the stretching direction does not change much the direction of the interdomain vector **r** connecting the centers of the cylinders, which remains preferentially parallel to the stretching direction, while, at $T_a > T_g$, the rearrangement process involves more displacement of the PS cylinders, with the interdomain vector **r** perpendicular to the stretching direction. Qualitatively, it can be expected that the PB orientation in annealed and then relaxed samples will be more effective at the redrawing direction that is parallel to the preferential direction of **r** averaged over all relaxed PS cylinders, which is dependent upon the annealing temperature.

Through this study, we demonstrated that infrared dichroism is a useful and convenient tool for elucidating structural and morphological changes in deformed SBS polymers, and it is complementary to small-angle X-ray scattering techniques. The use of this approach can be extended to other elastomeric block copolymers for studies of the processes in which molecular orientation is involved.

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