

Rheological Investigation of Shear-Induced Structure Changes in Multiblock Copolymers

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SYNOPSIS

Styrene-butadiene multiblock copolymers were examined with both newly introduced and established rheological techniques and by transmission electron microscopy (TEM) to evaluate shear-induced structural changes in these polymers. Transient rheological tests (based on superposed flow principles) were developed which probed structural changes that occur in the copolymers during and at the cessation of steady shear. Data from these tests indicated that for the cylindrical morphology copolymer (SB1) there were structural changes occurring during steady shear that were recovered upon cessation of shear. The recovery process took place on time scales that could be significant in processing. The lamellar morphology material (SB2) did not exhibit this recovery behavior. Longer-term structure changes were investigated using established techniques and showed differences between the cylindrical and lamellar copolymers. When tested at 210°C, peaks in $\tan \delta$ occurred at 30 rad/s for SB1 and at 0.5 rad/s for SB2 with saturation strain levels of 150 strain units (SU) for SB1 and 80 SU for SB2. TEM analysis of SB2 indicated that, although rheological changes are significant up to 80 SU, better alignment of the domain morphology can be achieved at moderately low strains of 7 SU. This indicates that the copolymers' rheological changes, which occur as a result of steady shearing, may not be due entirely to domain alignment, but may also be due to more local molecular rearrangements (e.g., chain disentanglement). © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Microphase-separated block copolymers are used in a variety of applications. Styrene-butadiene block copolymers have found use as elastomers when the copolymer is rich in butadiene. When styrene is the major component, it is used as a high-clarity, high-impact thermoplastic. Some of the unique physical and optical properties of these polymers may be attributable to their morphology. Because the morphology can be altered significantly by shearing deformation, it is of interest to understand the mechanisms by which these materials' morphologies depend on shear. With this knowledge, it may be

possible to adjust the conditions of fabrication to obtain the morphology of the material which optimizes the desired properties.

Considerable work has been presented in the literature addressing the possible mechanisms of the flow of block copolymers.¹⁻⁸ Model systems of diblock and triblock copolymers are typically the subjects of these studies. Under specific conditions of shearing, it has been found that alignment of the domain structure on a global length scale can be achieved. The conditions for alignment vary depending on the polymer system and the mode of shearing. For instance, Scott et al.⁴ found that optimal alignment for their cylindrical morphology styrene-butadiene triblock copolymer occurred at a shear strain of 12 strain units (SU) under steady shearing. In contrast, Winey et al.⁷ found that alignment could be achieved with their lamellar styrene-isoprene diblock copolymer with shear strains

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as low as 0.05 SU in a nonlinear dynamic oscillatory flow. Proposed mechanisms of alignment of structure include microdomain destruction/reformation, grain rotation, and combinations thereof.

Also, for some systems, it has been found that accompanying the alignment of the domain morphology is an observed change in the rheological properties of the polymer.^{1-3,5,6} Typically, this has been manifested in a reduction of the dynamic moduli (measured over certain frequency ranges) of the aligned polymer relative to the unsheared state. This was not the case for Winey et al.,⁷ however, who found that for their well-aligned polymer there were no changes in the linear viscoelastic properties over the frequency range probed. However, if it is true that for some systems that rheological properties do change with morphological alignment, then it is of interest to determine if rheological measurement techniques can be developed which reflect the changes which are occurring to the morphology of the polymer as a result of shearing deformation.

Established rheological techniques exist which reflect the long-term structural changes (those that persist for long times after deformation has ended) that occur upon shearing.^{1-3,5} These are based on the measurement of linear viscoelastic properties undertaken at a finite period of time after a specified amount of shear strain has been applied to the polymer. Depending on the polymer system studied and the temperature/frequency range probed, various results have been obtained. In this work, we applied these techniques to study polystyrene-rich styrene-butadiene multiblock copolymers in order to observe how the rheological properties reflect its morphological changes. These are nonmodel systems of overall composition of 75% polystyrene and 25% polybutadiene with multiblock chains of various block lengths. By maintaining this composition ratio, it is possible to produce polymers which exhibit cylindrical or lamellar structures. It is of interest to determine what differences the rheological techniques will indicate for the different morphologies and to what extent they will reflect morphological changes that occur when the polymers are subjected to shearing deformation. If the rheological properties do indeed reflect morphological changes, then the rheological techniques could possibly be used to predict the influence of processing on morphology and, therefore, the physical and optical properties of these materials.

In addition to probing long-term structural changes, new methods are presented for probing transient structural changes which occur during shear and immediately upon cessation of flow. These

methods were developed using the principles of parallel superposed flow. Traditional parallel superposition methods have been described elsewhere^{9,10} and have been used recently to investigate microstructural changes in liquid crystalline polymers.¹¹ However, in this study, the superposition provides a transient probe which may be used to investigate structural changes that occur as the shearing deformation is taking place.

Finally, transmission electron microscopy (TEM) results are presented for the lamellar material to determine to what extent long-term morphological changes are reflected in the rheological data. Unfortunately, imaging techniques were not available for studying transient structural changes. However, results of the rheological measurements indicate that imaging the transient structural behavior of these materials could provide useful insight.

EXPERIMENTAL

The two polymers used in this work were both styrene-butadiene multiblock copolymers with an overall composition by weight of approximately 75% polystyrene and 25% polybutadiene. The polymers were synthesized by anionic polymerization of multiple monomer charges. Block length and number were variable and thus allowed one of these materials, SB1, to exhibit a cylindrical morphology and the other polymer, SB2, to have a predominantly lamellar morphology. The polymers contained no processing wax and, therefore, required no cleaning by precipitation. The material already contained a proprietary stabilization package allowing films to be cast directly from a 10% toluene solution of the as received polymer. Films were dried under vacuum at 110°C for 24 h. A longer drying time of 48 h was required for the thicker 1 mm films used for TEM analysis. The morphologies of SB1 and SB2 are shown in Figure 1 (a) and (b), respectively. For SB2, the micrograph represents the initial state of the as-cast sample and shows its lamellar morphology. However, for SB1, the micrograph is of a sample which has been sheared to a low level of strain (~ 7 SU). This micrograph of a sheared sample, taken in the 2-3 plane (see Fig. 2 for plane orientation), is shown because it provides a clearer indication of the cylindrical morphology of SB1.

A Rheometrics RMS-800 with the RHIOS operating software and the arbitrary wave-function generator option was used for all rheological testing. Testing was done in nitrogen at 210°C using parallel-plate geometry. The plate diameter was 25 mm

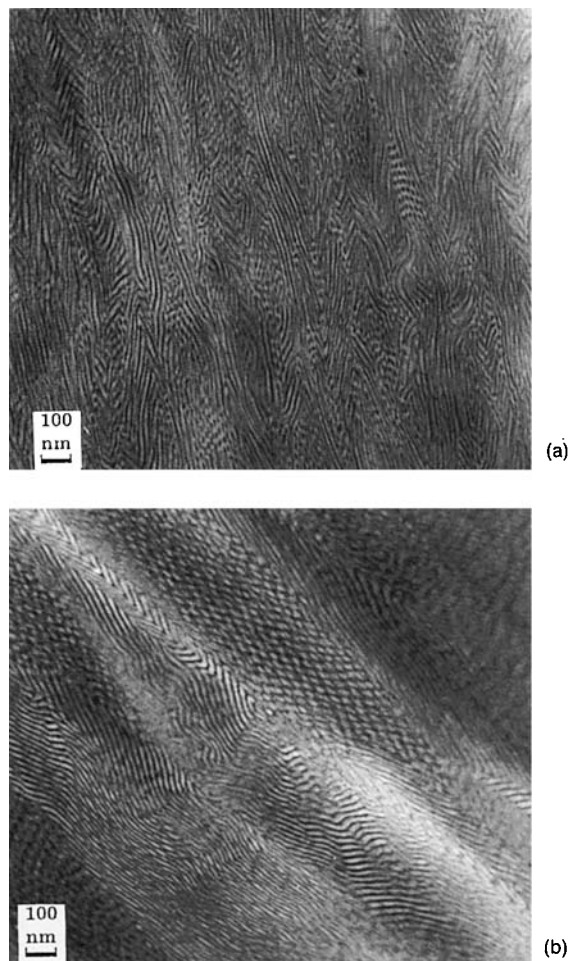


Figure 1 TEM micrographs of sample morphology: (a) SB1 (cylindrical), sheared 7 SU at 0.03 s^{-1} and $T = 210^\circ\text{C}$; (b) SB2 (lamellar), initial state.

and gaps were $\sim 0.4\text{--}0.6 \text{ mm}$ for rheological measurements and $\sim 1 \text{ mm}$ for TEM samples. Measurements of complex viscosity as a function of time were made to ensure that adequate stability was maintained over the duration of the tests.

Sheared samples for TEM were prepared by applying a fixed amount of steady shear strain to the polymer in the parallel plates and then cooling rapidly well below the T_g of polystyrene. (The time required to cool the sample to T_g was approximately 60–90 s.) The sample and plates were then removed from the rheometer and the sample was removed from the plates as it continued to cool to room temperature. The specimens were cryomicrotomed at -110°C to obtain sections giving views in the 1–2 and 2–3 planes (see Fig. 2). The polybutadiene domains of the sections were selectively stained with the vapors of an aqueous solution of OsO_4 . The mi-

croscope used was a Philips 420T STEM operating at 120 kV.

RHEOLOGICAL TESTS

Three primary rheological tests were performed in this study to investigate structural change as a function of shearing deformation. In all three tests, phase angle (or $\tan \delta$) was used as the probe of structural change. (This choice was made because of the better reproducibility of the phase angle as opposed to stress-dependent quantities such as the moduli.) In the first test, long-term structural changes were investigated. These were changes to the polymer structure, due to shearing deformation, that were either permanent or at least persistent for long time scales even when the material was held at the test temperature. This test is similar to that described by others^{2,3,5,7} and involves applying a fixed amount of shear strain to the sample in the steady shear mode. Shear rates of 0.03 and 0.1 s^{-1} were used to achieve strain levels up to 320 SU. The test mode is then switched to dynamic and a measurement is made of the linear viscoelastic properties of the sheared polymer over a frequency range of $0.03\text{--}100 \text{ rad/s}$. Strain-dependence measurements indicated that our materials were in the linear viscoelastic regime for strains up to 0.04 SU. Therefore, all small amplitude oscillatory shear measurements were done at strains $\leq 0.04 \text{ SU}$.

In addition to long-term structural changes, it was also of interest to investigate the possibility of transient structural changes. Two tests were developed to address this concern: The first was to probe structural changes that might occur as the steady shear deformation was taking place. The second was

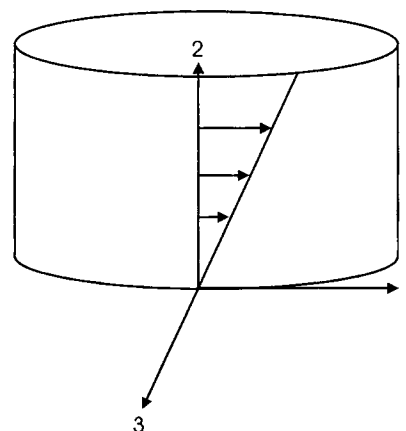


Figure 2 Coordinate system for sheared samples.

to probe any short time scale recovery of structure immediately at the end of shearing.

To investigate structural changes during shearing, use was made of parallel superposition techniques. Parallel superposition involves the combination of a steady shear strain component with a dynamic shear strain component acting in the same direction. An example of this strain function is shown in Figure 3(a). It is simply the sum of a steady shear strain function of given shear rate with a small amplitude oscillatory shear strain function of given frequency and strain amplitude. This superposed strain function can then be carried out to the desired level of steady shear strain. The premise is that the steady shear strain will cause the polymer structure to change, but the dynamic strain function, being at a strain level that falls in the linear viscoelastic regime, will not alter the structure, but will provide a probe of structural changes that are taking place due to the steady shear component. In our tests, the steady shear rate was either 0.03 or 0.1 s^{-1} and the probe frequency was 1.8 rad/s with a strain amplitude of either 0.02 or 0.04 SU. Typically, the maximum steady shear strain achieved was ~ 10 SU.

After the superposed flow test was performed, it was necessary to use signal processing techniques to extract the information provided by the dynamic probe. A typical stress response curve is shown in Figure 3(b). The first step in analyzing the data was to remove the dynamic component to obtain the steady component. This was done using a Butterworth notch filter which was available through the MATLAB software package. The filtering produced the smooth curve shown through the data in Figure 3(b). This filtered response was then subtracted from the data to obtain the dynamic component alone. The same procedure was then applied to the measured strain to obtain the dynamic component of the strain. The dynamic components of the stress and strain were then processed using a separate code to determine the phase shift as a function of strain.

To investigate structural changes that might occur at the cessation of shear, similar strain function generation and data analysis techniques as described above were used. In this test, a prescribed amount of steady shear strain was applied to the sample, and then immediately after the strain level was achieved, a dynamic probe (with the same frequency and strain amplitude as described above) was begun. This was accomplished by generating a single, continuous strain function wave form. Therefore, there was no interruption during the transition from steady to oscillatory

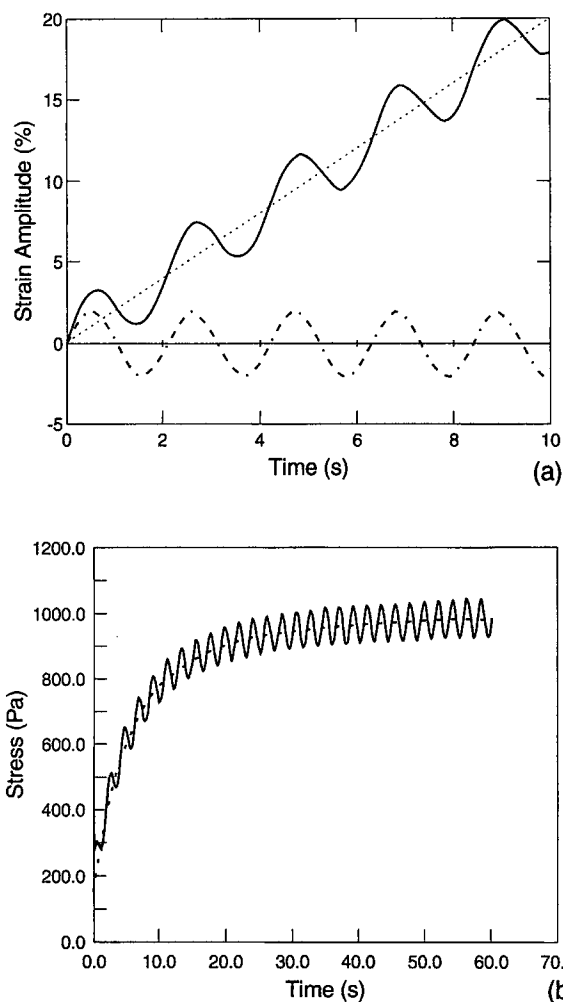


Figure 3 Superposed flow experiment: (a) strain input functions for (----) steady shear; (-·-·-·) oscillatory shear; and (—) superposed shear; (b) (—) stress output and (----) filtered stress for superposed shear.

deformation. A typical wave form is shown in Figure 4(a). Again, the steady shear component could be carried out to the desired strain level before the oscillatory probe began.

To obtain information from the dynamic probe, similar signal processing techniques to those described above were used. A typical stress response for this test is shown in Figure 4(b). The first step in obtaining the recovery data is to remove the data corresponding to the steady shear. Then, the remaining data, which is a combination of both stress relaxation and the dynamic probe, can be analyzed using the filtering technique described previously. From this procedure, plots of the phase angle vs. time can be generated corresponding to the recovery part of the test.

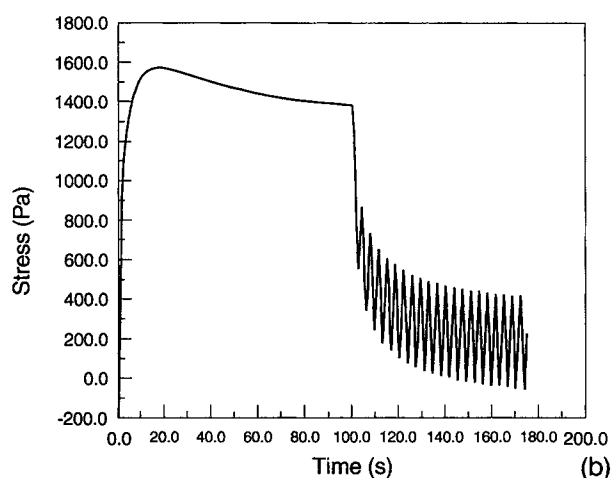
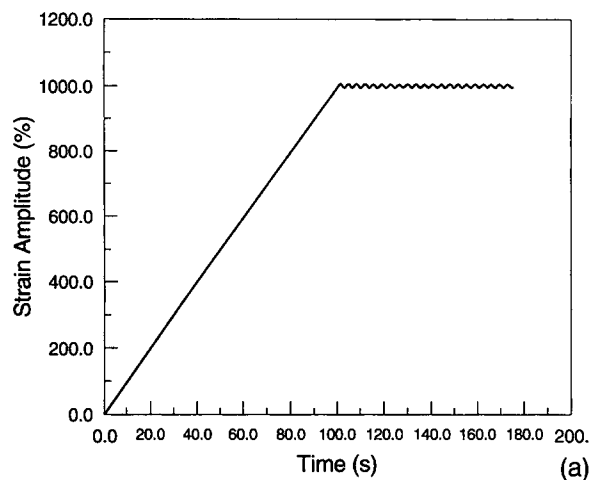


Figure 4 Cessation of flow experiment: (a) strain input function; (b) stress output.

RESULTS AND DISCUSSION

Rheological Characterization

Results from applying the three rheological tests to material SB1, the cylindrical morphology material, are presented in Figures 5–7. Beginning with the long-term structural changes (Fig. 5), it can be seen that significant changes in the linear viscoelastic properties result due to the application of steady shear strain to this polymer. Within the frequency range of 0.3–100 rad/s, significant increases in $\tan \delta$ are observed with increasing levels of applied strain with a peak occurring at ~ 30 rad/s. Below 0.3 rad/s, it appears that phase angle is not influenced by the applied strain. Also, based on the higher-frequency data, it is likely that at some frequency beyond the measurable limit of 100 rad/s $\tan \delta$ will not be influenced by the applied strain. However,

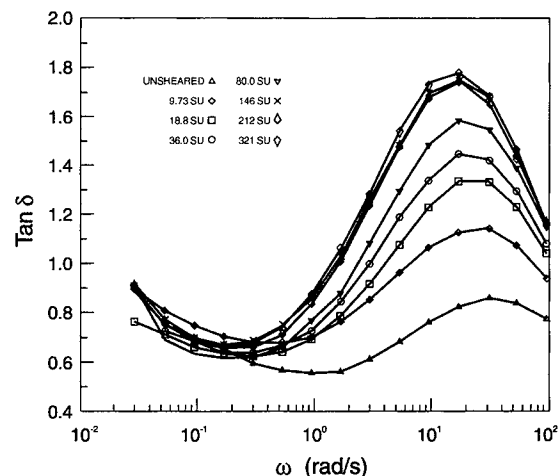


Figure 5 $\tan \delta$ of SB1 sheared to various levels of strain (given in strain units, SU) at $T = 210^\circ\text{C}$.

within this frequency window, there is a significant increase in the phase angle as one goes from the unsheared state to higher levels of strain. Increases in $\tan \delta$ are large initially (as in going from 0 to 10 SU) but diminish as the strain level increases. Ultimately, at ~ 150 SU and beyond, there are no further changes in the magnitude of $\tan \delta$. These observations are consistent with those found by others for triblock copolymers.^{1,3} In these studies, it was found that the storage and loss moduli decrease with increased applied strain levels and that, over certain frequency ranges, the decrease in the storage modulus is greater than is the decrease in the loss modulus. These large changes in $\tan \delta$ with strain would seem to indicate significant structural changes

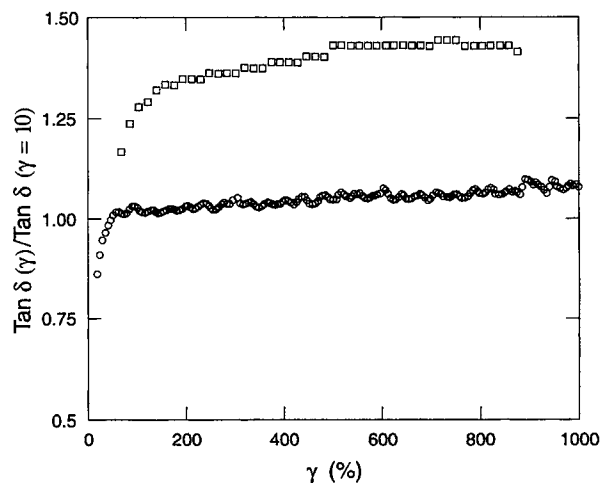


Figure 6 $\tan \delta$ of SB1 measured during shear (superposed flow). Probe frequency = 1.8 rad/s, $T = 210^\circ\text{C}$, shear rate: (○) 0.03 s^{-1} ; (□) 0.1 s^{-1} .

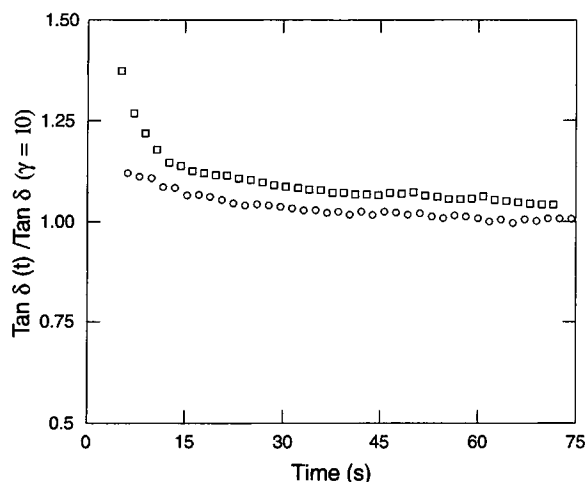


Figure 7 $\tan \delta$ of SB1 measured at cessation of steady shear. Probe frequency = 1.8 rad/s; $T = 210^\circ\text{C}$; shear rate: (○) 0.03 s^{-1} ; (□) 0.1 s^{-1} .

in SB1 that may be attributable to morphological or molecular rearrangement (e.g., chain disentanglement).

In addition to the long-term structural changes described above, we would like to investigate the possibility that there are also short-term, transient structural changes occurring that are missed by the long-term test. Results from the two transient tests (Figs. 6 and 7) provide insight to this possibility. Results of the superposed flow test for SB1 are given in Figure 6. Results are presented for two steady shear rates at a given probe frequency. The data are plotted as $\tan \delta(\gamma)/\tan \delta(\gamma = 10)$ vs. strain where $\tan \delta(\gamma = 10)$ was obtained from the long-term test data. Therefore, the transient data should ultimately approach a value of unity. From this plot, it can be seen that after an initial start-up transient there is a steady growth in the value of $\tan \delta$ as strain increases. This is to be expected based on the long-term test results. However, there are two points of interest in the superposed flow data that would not have been anticipated based on the long-term test data. First, there appears to be a rate dependency to the data. At the higher steady shear rate of 0.1 s^{-1} , there is a significantly higher level of $\tan \delta$ at any given strain, indicating greater structural changes occurring at the higher shear rate during steady shearing. The second point of interest is that the magnitude of the data is greater than unity nearly from the beginning of the test. Also, in the case of the higher shear rate, the data are significantly higher than unity. These data would seem to indicate that during shearing there are structural changes occurring that must recover upon cessation

of flow in order for the superposed flow data to be in agreement with the long-term test data.

Data from the cessation of flow test (Fig. 7) indicate that there is recovery of structure at the end of steady shearing. In this test, samples are sheared to a strain level of 10 SU and then recovery behavior is observed. In Figure 7, it can be seen that there is recovery that occurs rapidly in the first 15–20 s and then more slowly at longer times. Within the time frame of the test, it appears that the data of both shear rates asymptotically approach the value of one at long times. These results indicate that the transient test data are consistent with the long-term test data. More importantly, the data indicate that there are structural changes occurring during and at the cessation of steady shearing (due to either micro-phase or molecular rearrangement) that are missed by just examining the long-term test results. In addition, the recovery of structure at the cessation of flow is occurring on time scales that may be significant in processing.

Significant differences in results are obtained when the three rheological tests are applied to SB2, the polymer with the lamellar morphology. The long-term structure test data (Fig. 8) indicate similar trends for SB2 as for SB1 (i.e., increasing $\tan \delta$ with applied strain, characteristic peak in $\tan \delta$); however, quantitatively they are quite different. The lamellar material is characterized by a $\tan \delta$ peak that occurs at $\sim 0.5\text{ rad/s}$ (vs. 30 rad/s for SB1). Also, the magnitude of applied strain beyond which there are no further changes in $\tan \delta$ is smaller for SB2 at $\sim 80\text{ SU}$ which is almost half that found for SB1 at $\sim 150\text{ SU}$. However, the data do confirm that at sufficiently high frequencies the phase angle is no

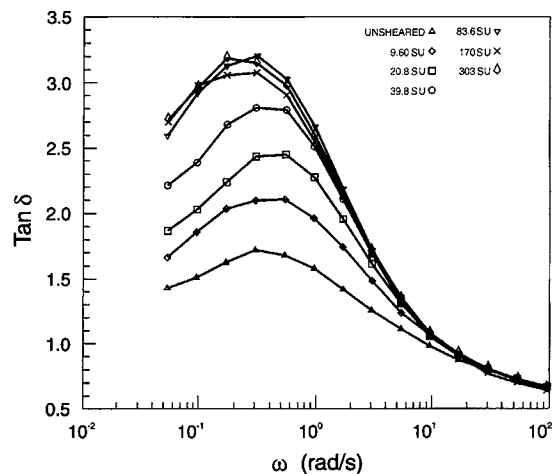


Figure 8 $\tan \delta$ of SB2 sheared to various levels of strain (given in strain units, SU) at $T = 210^\circ\text{C}$.

longer affected by applied strain. In combination with the SB1 data, this would indicate that there is a window approximately four decades wide which reflects structural changes due to applied strain with the location of the window being dependent on the polymer's characteristics.

The transient tests also show differences between the two polymers. In regards to the superposed flow test (Fig. 9), it can be seen that SB2 exhibits much less of a shear rate dependency than does SB1. In addition, over the duration of the test, it can be seen that the data just slightly exceed a value of unity. This would seem to indicate that, unlike SB1, structural changes that occur during shearing do not significantly exceed that which would be expected based on the long-term test results. This is also indicated in the cessation of flow data (Fig. 10) in that negligible recovery is experienced when shearing is stopped.

Morphological Characterization

Although these tests reflect shear-induced structural changes in the polymer, the question remains as to whether the structural changes do indeed reflect morphological alignment, chain disentanglement, or some combination of morphological and molecular rearrangement. Imaging techniques are required to determine to what extent the rheological changes are due to morphological rearrangement. Although it would be interesting to be able to observe the transient behavior of the morphology during and at the cessation of shear, the imaging methods required to achieve this were not available. However, it was

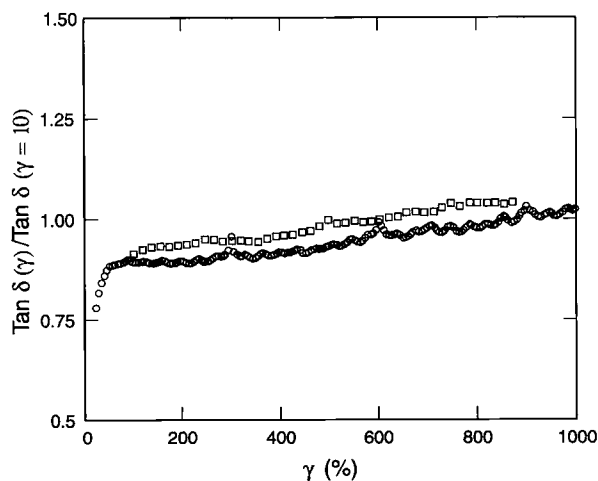


Figure 9 $\tan \delta$ of SB2 measured during shear (superposed flow). Probe frequency = 1.8 rad/s; $T = 210^\circ\text{C}$; shear rate: (○) 0.03 s^{-1} ; (□) 0.1 s^{-1} .

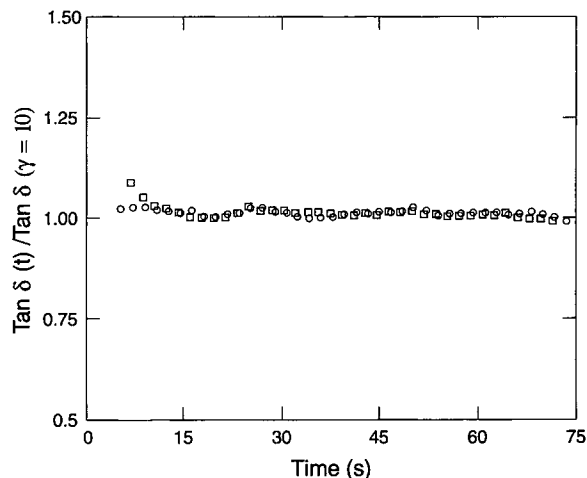


Figure 10 $\tan \delta$ of SB2 measured at cessation of steady shear. Probe frequency = 1.8 rad/s; $T = 210^\circ\text{C}$; shear rate: (○) 0.03 s^{-1} ; (□) 0.1 s^{-1} .

possible to obtain imaging of the morphology of the polymer for the case of the long-term structural changes. Conventional TEM analysis was made of sheared specimens of the lamellar polymer, SB2, to provide representative information about what the long-term test data were indicating about morphological changes. Micrographs of sheared samples presented here provide views in the 1–2 plane.

The morphology of SB2 in its initial, unsheared state is shown in Figure 1(b). The morphology is typical of that of lamellar block copolymers in that there are local regions that exhibit alignment, but there is no long length scale alignment to the polymer. From the micrographs, it does appear that SB2 in its initial state is largely nonoriented on a global length scale. However, without small-angle X-ray scattering (SAXS) data it is not possible to quantify this. Therefore, for micrographs of the initial state, and subsequent ones of sheared samples, only qualitative statements will be made of the degree of global alignment.

When SB2 is sheared to $\sim 7 \text{ SU}$, there is a large change in the morphology of the polymer. From Figure 11(a), it can be seen that there is very good alignment of the lamellae at this level of shear strain. Micrographs indicated alignment extended over a distance of $\sim 2 \text{ mm}$ and translation of the sample in the TEM indicated alignment over larger length scales. However, the morphology was not without defects. The defects are apparent in the top half of Figure 11(b) and are similar to those observed by Winey et al.⁷ when their sample was subjected to steady shear strain. Although these defects are present, they are few in number. At this level of

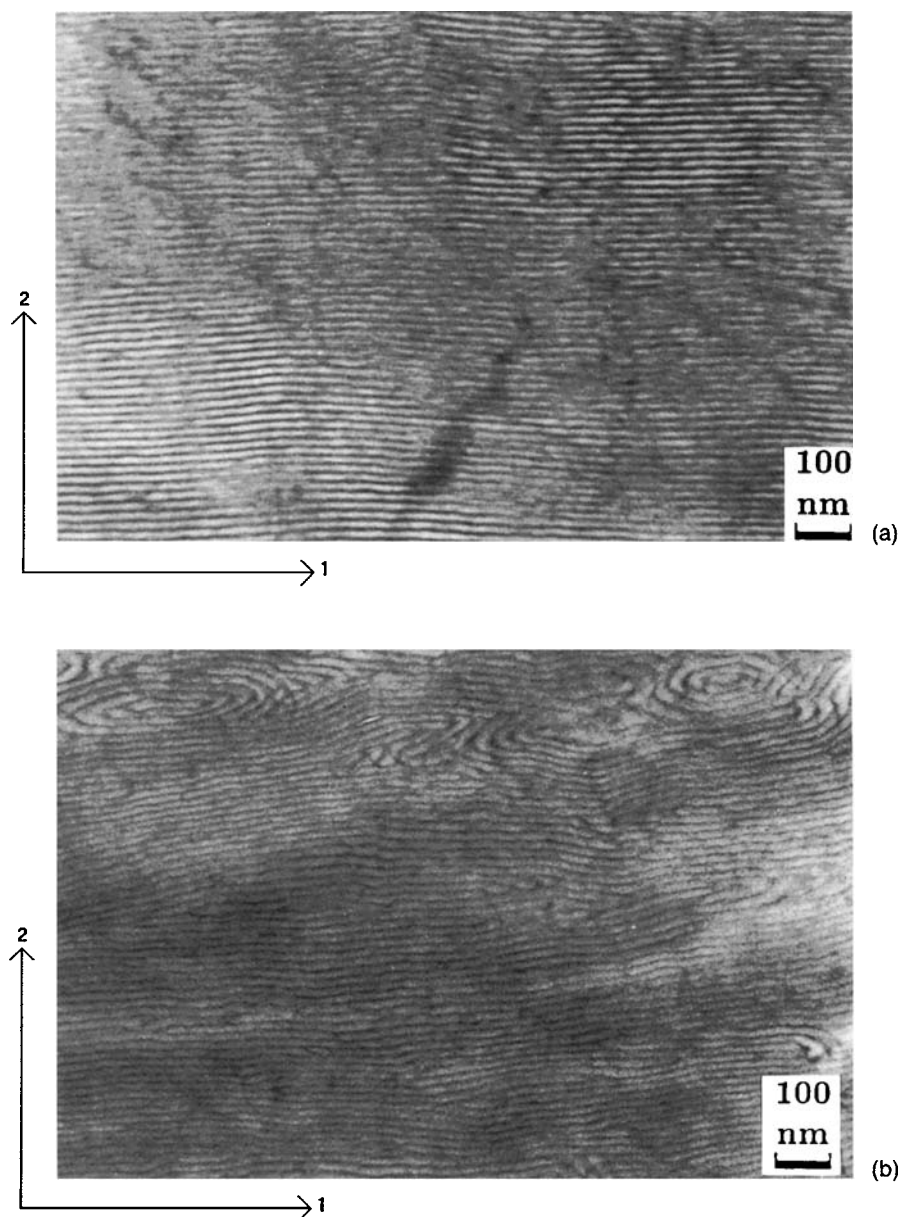


Figure 11 TEM micrograph of SB2 sheared to 7 SU at 0.03 s^{-1} and $T = 210^\circ\text{C}$: (a) well-aligned lamellae; (b) defects.

strain, it appears that well-oriented lamellae dominate.

It might have been possible to obtain better alignment of the sample through nonlinear, low amplitude oscillatory shear as reported by Winey et al.⁷ However, the purpose of this work was to investigate what information rheological measurements might provide regarding structural changes, and rheological changes with deformation were only significant at high strains. By examining Figure 8 again, it would be anticipated that at 7 SU there would be a significant increase in $\tan \delta$.

This combined with the large change in alignment of SB2 [Fig. 11(a)] would seem to indicate that the rheological measurement was reflecting morphological change. However, it is interesting to note that although there is good alignment of the sample at this strain level there is still a significant amount of increase in $\tan \delta$ to be expected by applying increasing amounts of shear strain to SB2. Therefore, if the change in $\tan \delta$ in shearing the sample 7 SU reflects a relatively well-aligned morphology, then it is of interest to determine what further changes in morphology are reflected

by $\tan \delta$'s increase in magnitude with greater applied shear.

To determine the morphology corresponding to the maximum measured value of $\tan \delta$, a sample was sheared to ~ 90 SU. The micrograph of this sample [Fig. 12(b)] indicates that there is still alignment of the lamellae at this strain level. However, there are distinct differences between this sample and that strained to 7 SU. First, although the lamellae appear aligned, the continuity of the lamellae is less than at 7 SU. There appears to be disruptions along the

length of a given lamella that occur on relatively short length scales. The other difference is that although some of the lamellae are of similar dimensions as that of SB2 sheared to 7 SU, for the sample sheared 90 SU, there appears to be a mixture of dimensions of lamellar thickness and interlamellar distances. This can be seen more clearly when comparing the sample sheared 7 SU with that sheared 90 SU at the same magnification [Fig. 12(a) and (b), respectively]. It is unclear what is causing this phenomenon; however, it might be possible that

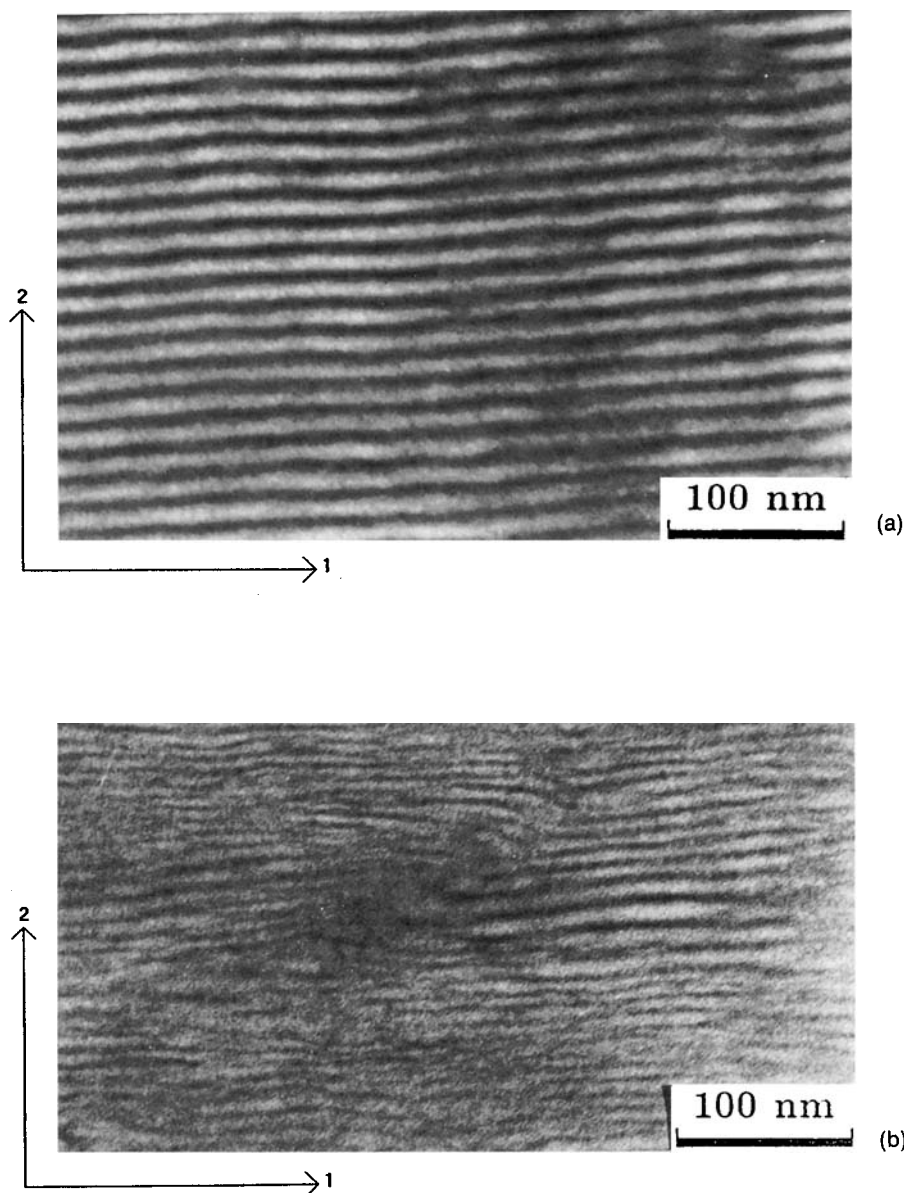


Figure 12 TEM micrograph of SB2 sheared at 0.03 s^{-1} and $T = 210^\circ\text{C}$ to strains of (a) 7 SU and (b) 90 SU.

some degree of homogenization is occurring at this high level of strain. Also, there may be a compositional influence due to the complex assemblage of multiblock copolymers in this system. Observation has been made of different domain sizes for a cylindrical morphology styrene-butadiene triblock copolymer by Morrison et al.¹² and Jackson et al.¹³ In their work, extensive discussion is provided as to the observation of domains of different dimensions and of the possible explanations of this phenomenon in terms of a martensitic transformation. Whatever the explanation, it appears that the rheological measurement is reflecting these changes in going from the initial state, to the aligned state at 7 SU, to the morphology exhibited at 90 SU.

The observation by Winey et al.⁷ that good alignment can occur at low strains and with no change in linear viscoelastic properties (within the measurable frequency range), coupled with our observation of relatively good alignment with moderate levels of strain (7 SU) and only moderate changes in rheological properties, questions the idea that rheological properties reflect morphological alignment changes alone. Also, Scott et al.⁴ found for a styrene-butadiene triblock copolymer that moderate levels of applied strain (12 SU) provided the best alignment (as determined by SAXS) of the cylindrical morphology. Higher levels of strain led to deterioration of the alignment. Therefore, it seems, depending on the polymer system and mode of shearing, that it is possible to generate a well-aligned morphology with low to moderate strain levels. In the work of Winey et al.⁷ and in the current work, these relatively well-aligned samples exhibited negligible to moderate changes in rheological properties. Therefore, there are indications that our observed changes in $\tan \delta$ with increasing strain may reflect more than just lamellar alignment. It is possible that the switch from the initial state to the well-aligned state may occur with only small changes in the rheological properties and that the changes in rheological properties at higher levels of applied strain may be due to other sources of morphological and molecular rearrangements. To separate out the effects on rheological properties of morphological and molecular rearrangements, additional methods will be required. Possibly the technique of dynamic infrared dichroism referred to by Kornfield and Kannan⁸ could help resolve this issue.

CONCLUSIONS

Three rheological tests were investigated to determine what information they might provide

regarding shear-induced structural changes in styrene-butadiene multiblock copolymers. One of the tests, which was based on established methods, probed long-term structural changes in the polymer. Two new tests were introduced which probed transient structural changes. The first was based on parallel superposition techniques and it probed structural changes that occurred during steady shearing. The second probed structure recovery that occurs at the cessation of steady shear flow.

The transient tests provided useful information that could not otherwise be obtained from the long-term test alone. The data indicated differences between SB1, which had cylindrical morphology, and SB2, which had lamellar morphology. In the case of SB1, there were indications from the transient tests that there were structural changes occurring during steady shear that were recovered upon the cessation of flow. The recovery took place on time scales that could be significant in polymer processing. However, lacking transient imaging techniques, it was not possible to determine if the structural changes occurring during shear corresponded to some specific microphase change or if they were due to more local molecular rearrangements. It would be useful in future work to determine if any microphase changes are associated with this transient flow.

The long-term structure change test also indicated significant differences between SB1 and SB2 and how they responded to different levels of applied strain. In both cases, there were large increases in $\tan \delta$ with strain up to some saturation level. In the case of SB2, TEM analysis was provided to determine how rheological changes related to morphological changes. It was found that there were significant changes in morphology in going from the unsheared, initial state to the saturation level of strain. However, it appeared that the switch from the initial morphology to the well-aligned microphase morphology occurred at moderately low strains with only moderate changes in the rheological properties. Larger changes in the rheological properties with increasing levels of strain seem to relate to some other morphological or molecular rearrangement.

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