Macromolecules **1993,** *26,* 2542–2549

Interdependence of Shear Deformations and Block Copolymer Morphology

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Received October 18, 1992; Revised Manuscript Received January 21, 1993

ABSTRACT: A lamellar poly(styrene-*b*-isoprene) diblock copolymer is well-aligned, as observed by TEM and SAXS, by continous, nonlinear oscillatory shearing, at a surprisingly low strain amplitude, specifically 5%, and a temperature 20 °C above the glass transition temperature of the PS block. This aligned state exhibits lamellae parallel to the sample plane, that is, with the normal of the lamellae parallel to the shear gradient. The onset of nonlinear viscoelastic effects occurs at small strains, ~1%. Oscillatory shear within the linear regime does not effectively align the block copolymer morphology. Steady shear disrupts well-aligned samples by introducing defects, namely wall and focal conic defects. We distinguish between intermediate and global length scales of alignment using TEM and SAXS, respectively. Although significant morphological differences exist between the various samples, the dynamic mechanical responses of these copolymer samples are indistinguishable over the frequency range examined. Our experimental results are inconsistent with the proposed grain rotation mechanism as the sole mechanism of alignment of block copolymer; a destruction/reformation mechanism is necessary to explain the transformation of the initial morphology to having global alignment.

1. Introduction

Block copolymers exhibit order or a specific arrangement over a variety of length scales. Along a single block copolymer chain, monomer units are arranged into long sequences of a particular monomer type, called blocks. When two or three blocks of different monomer types are covalently bonded together, diblock copolymers or triblock copolymers result, each of which has an intrinsic chemical length scale. At temperatures where the different blocks of the copolymer are incompatible, another length scale of order is introduced as the junctions between the blocks of the copolymer collectively segregate or self-assemble into an interfacial region. These interfaces or intermaterial dividing surfaces separate the block copolymer system into microdomains which are compositionally rich in one or the other monomer type. The shape uniformity of these microdomains and the extent of periodicity between neighboring microdomains indicate the extent of block copolymer order at longer length scales.

Throughout an idealized block copolymer system, the microdomains have a uniform size and shape (planar, cylindrical, etc.). These microdomains are also periodic relative to neighboring microdomains, so as to meet the space filling or constant density requirements of polymers. The microdomain size is determined primarily by the molecular weight of the copolymer, and the combination of microdomain shape and symmetry in the idealized strong segregation limit is primarily determined by the volume fractions of the copolymer.

Order over a range of length scales from microdomains to an intermediate length scale of ~1–10 μm is readily observed by transmission electron microscopy (TEM). Longer-range order can be attained using a variety of preparations and can be detected using small-angle X-ray scattering (SAXS), which samples ~0.1 mm^3 per scattering experiment. This longer or global length scale refers to the orientation of the microdomains relative to the macroscopic sample. The intermediate and global length scales of microdomain order, from ~10 nm to 1 μm and further to 1 mm, are the focus of this paper. Dynamic mechanical measurements are particularly advantageous in the study of block copolymers, because they probe time scales that are correlated with the various length scales we intend to study.

Early methods for aligning block copolymers on a macroscopic size scale used extrusion through an extended tube[1–3] and large amplitude backward and forward shearing at constant speed.[4] Considerable work has been done using steady shearing[5–8] and oscillatory shearing[5,7,9] to change the global alignment of block copolymers, and we shall use similar techniques here. A new method to obtain extended alignment, roll-casting, was recently introduced which combines the advantages of the high mobility of copolymer chains in solutions and mechanical deformation.[10,11] This roll-casting technique applies both elongation and shear to a solution as the solvent evaporates and produces large block copolymer samples (on the order of 50 × 100 × 3 mm) containing uniform, well-aligned microdomains.

We have studied a low molecular weight poly(styrene–isoprene) diblock copolymer which exhibits the lamellar morphology. After our experimental methods are presented, the rheological and morphological results of the initial condition are given which show nonlinear effects above a surprisingly low critical strain amplitude. Section 4 describes the influence of oscillatory shear on this initial condition, especially the ability to align the diblock copolymer using only 5% strain amplitude. Disruption of this aligned state using steady shearing is detailed in section 5, which includes identification of two defect types. In the Discussion, we distinguish block copolymer order at the intermediate and global length scales and support an alignment mechanism other than grain rotation.

2. Experimental Section

The lamellar poly(styrene-*b*-isoprene) diblock copolymer used in this study was synthesized by Watanabe using conventional anionic polymerization techniques.[12] The PS and PI block

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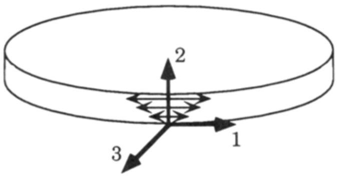

1: velocity, tangential
2: gradient, perpendicular to disk
3: neutral, radial

Figure 1. Schematic of the sample disk showing our conventions for the three principal directions.

molecular weights are 12 500 and 9500, respectively, and the copolymer will be identified here as SI 12/9. Using a Perkin-Elmer System 7 DSC at 20 °C/min, the glass transition temperature of the PS block was determined to be 78 °C. (Dielectric relaxation measurements on this diblock copolymer found a somewhat higher glass transition temperature, as expected for a dynamic method.[12])

Approximately 1 wt % of an antioxidant, Irganox 1010 from Ciba-Geigy, was added to a dilute solution of the diblock copolymer in toluene. In order to produce a more random orientation of the microphase-separated copolymer, the solution was stirred occasionally during the late stages of solvent evaporation at room temperature. The sample was then dried thoroughly under vacuum above room temperature, pressed into a 25-mm disk at room temperature, and annealed at $\sim$100 °C under vacuum.

Samples were prepared for TEM by microtoming thin sections at approximately −100 °C and selectively staining the PI microdomains with the vapors of an aqueous OsO_4 solution. Different planes of the bulk sample were assessed by mounting small pieces of the sample disk in the three principal directions relative to the knife edge. Due to availability three different electron microscopies were used in this study: JEOL 100CX, JEOL 2000FX, and Phillips 400T.

The X-rays were generated by a Rigaku CN2203E1 sealed tube source typically operated at 35 kV and 10 mA. The copper radiation was not monochromated, resulting in two predominant wavelengths, Cu Kα at 1.542 Å and Cu Kβ at 1.392 Å. This results in spreading the scattered beam along the scattering vector. The incident radiation was collimated using two slits and a pinhole and the scattered radiation was detected using Kodak DEF 5 film at a distance of 200 mm. Scattering experiments were performed in the three principal directions relative to the sample disk by cutting and mounting small pieces of the original sample. The path length through the sample, $\sim$2 mm, and the exposure conditions were held constant, so that the SAXS intensities can be directly compared.

A Rheometrics System IV was used to measure the dynamic mechanical properties of the diblock copolymer in both oscillatory and steady shear. The parallel plate sample geometry was used with a diameter of 25 mm and a gap of $\sim$0.8 mm. The majority of the experiments were performed at 98 °C which is 20 °C above the glass transition of the PS block of the copolymer. χN for SI 12/9 ($N = 260$) at 98 °C $\sim$16.1, using the mean-field temperature dependence of χ.[13] The order–disorder transition for SI 12/9 is 152 °C,[14] which corresponds to $\chi N = 12.7$.

Figure 1 shows the sample disk along with our conventions for identifying the directions in the sample. Prior to applying shear, we refer to the directions as the tangential, through, and radial directions, while after shearing, we refer to the directions as the 1 (velocity), 2 (gradient), and 3 (neutral) directions. Because these three directions are mutually orthogonal, their reciprocal space directions are parallel to the real space directions. We have indicated the reciprocal directions in the SAXS patterns with an asterisk (*).

3. Initial Condition

The initial condition refers to SI 12/9 after the treatment of nonquiescent casting with stirring, molding, and annealing. Figure 2 shows the through-tangential plane of the initial sample, which is indistinguishable from the through-radial plane. Distinct microdomains of PS and PI are evident, indicating that the initial condition of the diblock copolymer is in the microphase-separated state, as expected for a sample prepared below the order–disorder transition temperature, $\sim$152 °C.[14] These microdomains of PS and PI are of a nearly uniform size, which is characteristic of the molecular weight of the diblock copolymer; however, the microdomains are not uniform in shape. The majority of the sample appears "pebbly", and only a small fraction of the sample has clearly defined lamellae exhibiting planar interfaces. The lamellar microdomains show some periodicity with neighboring lamellar microdomains within groups which range from approximately 10 lamellae repeats to as small as 2 lamellae.

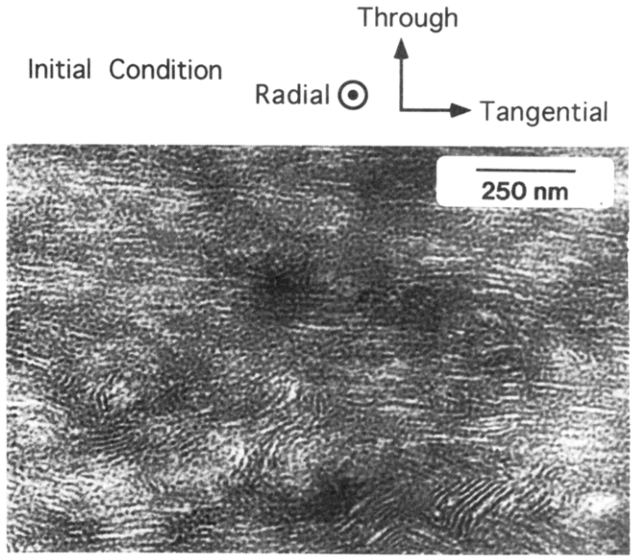

Figure 2. Transmission electron micrographs of the initial morphology of SI 12/9 prepared by solvent casting with periodic disruptions, drying, molding, and annealing. Throughout this paper the polyisoprene microdomains are stained dark via OsO_4.

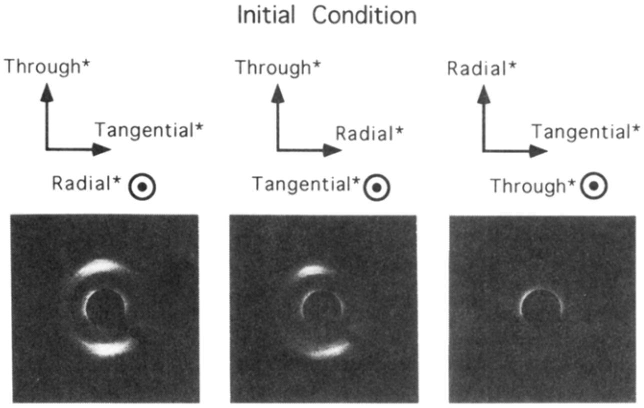

Figure 3. Small-angle X-ray scattering pattern of the initial morphology taken with the beam oriented in three orthogonal directions with respect to the molded disk. Reflection corresponds to a 17-nm lamellae thickness.

Figure 3 shows the small-angle X-ray scattering patterns taken along the radial, tangential, and through directions of the sample. The characteristic spacing in these SAXS patterns, as in all the subsequent SAXS patterns, is 17 nm. If grains of ordered lamellae were randomly distributed in space, the three SAXS patterns would each exhibit a weak, uniform ring of intensity. The broad maximum in the through direction, indicates slight global alignment such that the lamellae are in the plane of the sample disk. This extent of global alignment is introduced during the molding process. The TEM and SAXS results combine

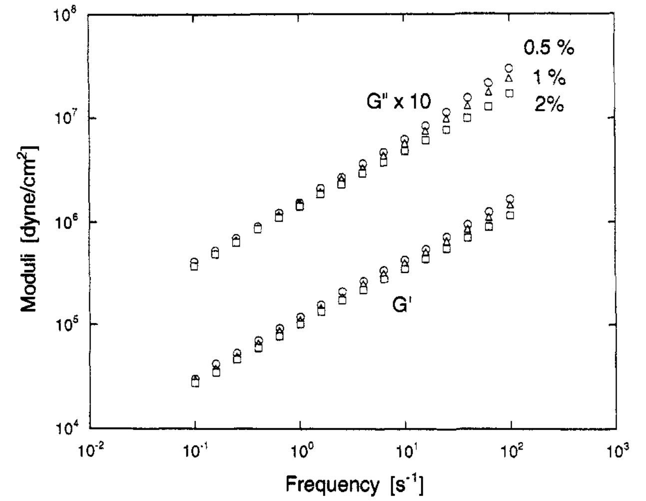

Figure 4. Frequency dependence of the storage, G', and storage, G'', shear moduli for SI 12/9 in the initial morphology measured at $T = T_g + 20$ °C = 98 °C and three strain amplitudes: 0.5, 1, and 2% strain.

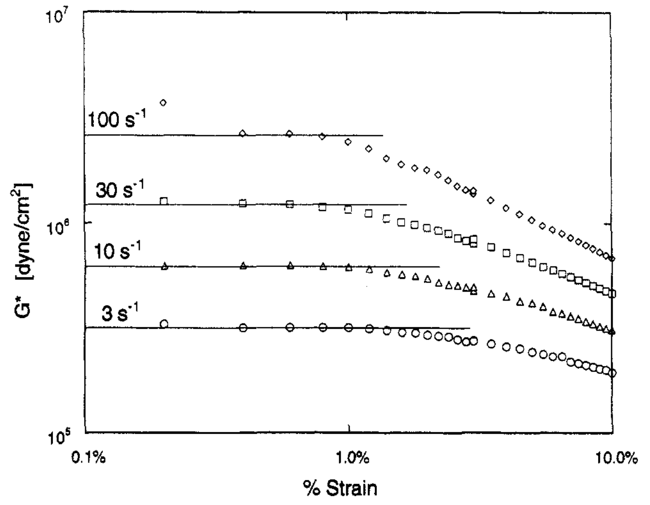

Figure 5. Strain dependence of the magnitude of the complex shear modulus, $G^* = (G'^2 + G''^2)^{1/2}$, for SI 12/9 in the initial condition measured at 98 °C and various frequencies: 3, 10, 30, and 100 rad/s.

to define the initial morphology in the ordered state as having very limited intermediate order and slight global order.

The frequency dependence of the storage, G', and loss, G'', moduli for SI 12/9 in the initial condition depends on the strain amplitude, Figure 4. This strain amplitude dependence is more pronounced at higher frequencies. Figure 5 shows the magnitude of the complex modulus, $G^* = (G'^2 + G''^2)^{1/2}$, as a function of strain amplitude, and clearly indicates a critical strain amplitude of ~1%. The critical strain amplitude increases slightly with decreasing frequency. At the temperature of these experiments, 98 °C, the linear regime, that is, the strain values over which the moduli are independent of strain, is quite small.

If individual frequency sweeps are taken within the limited linear regime, time–temperature superposition is obeyed for SI 12/9, Figure 6. The shift factors used to superpose these data span 5 orders of magnitude between 85 and 110 °C and fit the Arrhenius relationship; that is, a plot of $\log(a_T)$ versus $1/T$ (K) is linear. The WLF equation did not fit the shift factors. Both the storage and loss reduced moduli exhibit approximate power law dependencies over 4 decades of reduced frequency: $G' \sim \omega^{0.54}$ and $G'' \sim \omega^{0.63}$. The power laws cannot be exact since the Kramers–Kronig relationship requires G' and G'' to have the same power law exponent. The observed frequency dependence is attributed to the locally ordered nature of the diblock copolymer. Terminal behavior is not observed in this microphase-separated diblock copolymer even though the molecular weights of the blocks, M_{block}(PS) = 12 500 and M_{block}(PI) = 9500, do not significantly exceed the entanglement molecular weights, M_e(PS) ≅ 18 000 and M_e(PI) ≅ 6000.[15]

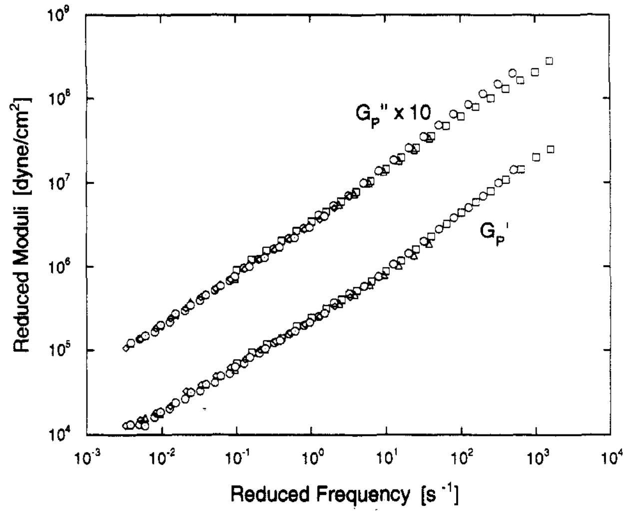

Figure 6. Master curve for SI 12/9 having a reference temperature of 90 °C. Symbols indicate temperature: squares 80 °C ($a_T = 20$), circles 90 °C ($a_T = 1$), triangles 100 °C ($a_T = 0.075$), diamonds 105 °C ($a_T = 0.0065$), and circles with center spot 110 °C ($a_T = 0.0030$).

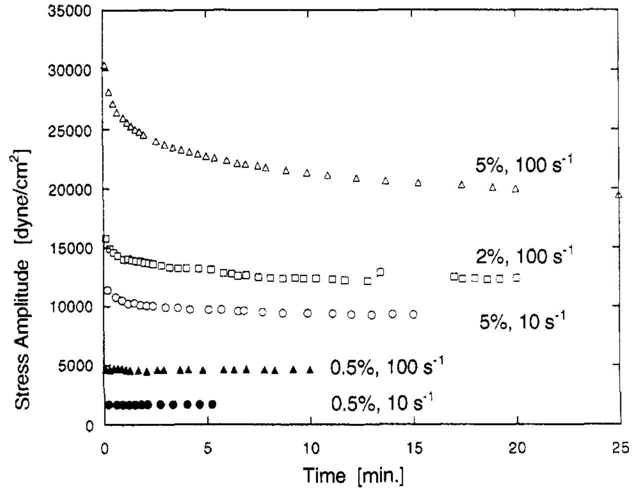

Figure 7. Shear stress amplitude as a function of time as oscillatory shear is continuously applied to the sample at 98 °C. Solid and open symbols indicate shearing conditions (amplitude and frequency) within the linear and nonlinear regimes, respectively.

4. Oscillatory Shear Applied to the Initial Condition

Continuous oscillatory shear was applied to the SI 12/9 diblock copolymer in the initial condition described above and, during this, the stress amplitude was monitored. Figure 7 shows the stress amplitude as a function of time for shearing conditions in the linear and the nonlinear regime. Within the linear regime, 0.5% strain at 10 or 100 rad/s, the stress amplitude is invariant with time. In contrast, within the nonlinear regime, 2% strain at 100 rad/s and 5% strain at 10 or 100 rad/s, the stress amplitude decays with time. The magnitude of the stress decay

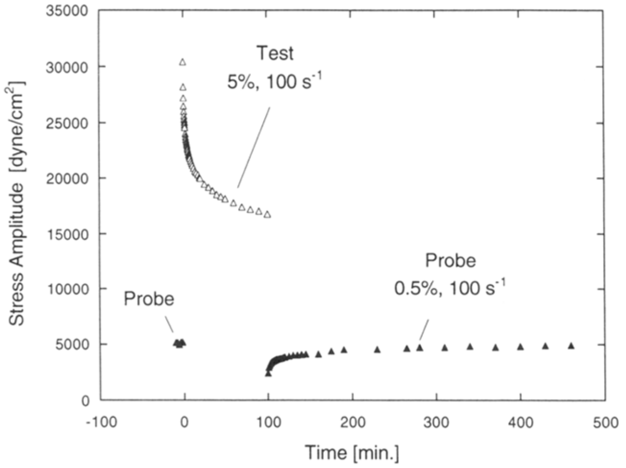

Figure 8. Shear stress amplitude decay and recovery as a function of time. Solid symbols indicate individual single tests in the linear regime, 0.5% and 100 rad/s. Open symbols indicate continuous shearing in the nonlinear regime, 5% and 100 rad/s.

increases with the strain amplitude and the frequency of the applied continuous oscillations; see Figure 7.

The observed decay in shear–stress amplitude is fully recoverable and repeatable. We illustrate this point by selecting a set of conditions in the linear regime, 0.5% strain at 100 rad/s, to probe the sample and a second set of conditions in the nonlinear regime, 5% strain at 100 rad/s, to induce the stress amplitude decay. The initial rheological response was established by performing single tests at the probing conditions, Figure 8. Then, beginning at time zero, the nonlinear or test conditions were applied continuously to induce a stress amplitude decay. Though the stress amplitude drops more quickly initially, it is still decreasing after 100 min for a total reduction of approximately 50%. This contrasts with the results of Morrison et al., wherein a few cycles of large amplitude oscillatory shear reduce G' and G'' to a limited lower value in a SBS triblock copolymer.[5] After stopping the continuous nonlinear oscillatory shear, single tests using the probe conditions were performed to follow the recovery of the stress amplitude. The stress amplitude is shown to recover to the original level, ~5000 dyne/cm^2, in approximately 400 min (see Figure 8). Increasing the magnitude of the stress decay, by increasing the strain amplitude, frequency, or duration of the continuous oscillatory shear, increases the time required to recover the initial rheological response. In all cases for SI 12/9 at 98 °C, the initial rheological response was recovered and the observed stress amplitude decay could be repeated. (The strain-dependent moduli shown in Figure 5 are measured quickly enough that they are not affected significantly by the time dependence described here.)

The apparent softening of the diblock copolymer with time is currently open to interpretation. One interpretation attributes the observed stress amplitude decay to a temporary, local destruction of the PS and PI microdomains induced by the continual nonlinear oscillatory shear. Such a destruction of microdomains requires mixing of the PS and PI blocks. This explanation seems energetically unfavorable, because the energy put into the system by shearing is ~10^2 smaller than the free energy for mixing.[16] The flow or shear energy is the product of the product of the moduli and strain. The free energy of mixing was estimated with the lattice model for homopolymer blends, substituting in the interaction parameter[13] and the volume fractions and degrees of polymerization of the PS and PI blocks. This estimate does not account for the connection between the copolymer blocks or the possibility of nonuniform strain within the sample due to varying extents of alignment. An alternative interpretation attributes this behavior to slip between the tools and the "solidlike" sample. The sample might be considered solidlike because the frequency dependence is not that of a liquid and the moduli at the higher frequencies, 10 or 100 rad/s, are in the range 4×10^5–3×10^6 dyne/cm^2. Gouinlock and Porter briefly refer to slippage in the nonlinear strain region for a SBS triblock copolymer.[17] To investigate this explanation further, a low molecular weight homopolystyrene (M = 10 000) was studied at 120 °C. The homopolymer exhibits a time-dependent stress amplitude decay and recovery qualitatively similar to that of SI 12/9, though compared with SI 12/9, the initial stress amplitude is larger by as much as 1 order of magnitude using similar shearing conditions, and the overall time dependence of the decay/recovery is slower. While these results suggest slip is occurring for both SI 12/9 and this homopolystyrene near their glass transition temperatures, the torque signals from both the diblock copolymer and the homopolymer exhibit sinusoidal waveforms. This is in contrast to recent observations of Hatzikiriakos and Dealy on high-density polyethylene, in which the measured torque signal deviated significantly from a sinusoidal output during slip.[18]

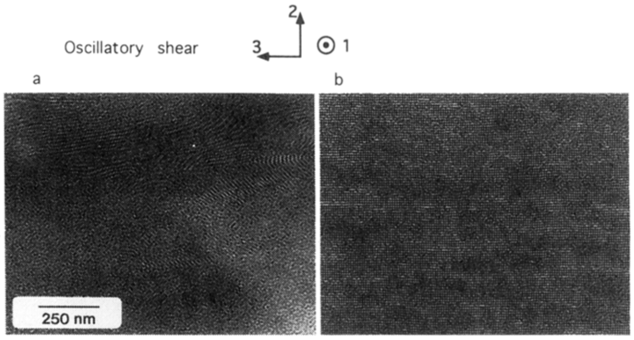

Figure 9. Transmission electron micrographs showing the 2–3 plane of SI 12/9 subjected to (a) continuous shearing in the linear regime (0.5%, 10 rad/s, 100 min) and (b) continuous shearing in the nonlinear regime (5%, 10 rad/s, 40 min and 5%, 100 rad/s, 100 min).

Regardless of our interpretation of the observed stress amplitude decay, samples sheared in the linear and nonlinear regimes exhibit dramatically different morphologies. Figure 9 shows representative electron micrographs of the 2–3 plane, that is looking along the flow direction, for two sets of shearing conditions. For these conditions, similar images were obtained for the 1–2 plane (not shown) and the 2–3 plane. The morphology of the sample sheared using strain amplitudes below 1% is comparable to the morphology of the initial condition, although with a somewhat better developed lamellar morphology. Oscillatory shear in the linear regime is only slightly effective in aligning the sample at temperatures near the glass transition. The sample sheared using 5% strain amplitudes, however, exhibits very well developed lamellae which extend across the entire field of view. Translating our sample in the TEM indicates that this sample has highly regular lamellae with grains exceeding 10 μm across. Oscillatory shear in the nonlinear regime, even with a strain as small as 5% is extremely effective at temperatures near the glass transition temperature in aligning the lamellar diblock copolymer from the initial condition. This is in contrast to previous reports of aligning block copolymers with strain amplitudes on the order of 100% and low frequencies.[4,5,7,9]

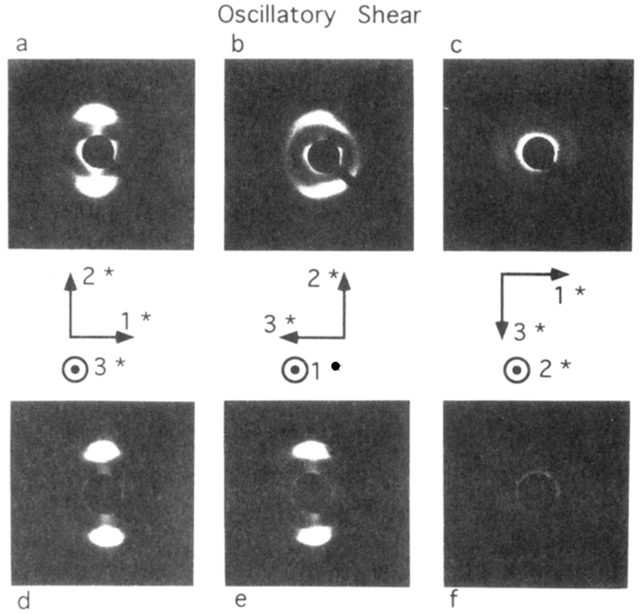

Figure 10. SAXS patterns of the resultant morphology induced by continuous (a–c) linear deformation and (d–f) nonlinear deformations, as detailed in Figure 9.

SAXS patterns of samples subjected to linear and nonlinear oscillatory shear are given in Figure 10. Continuous oscillations in the linear regime of strain enhance the global alignment of the lamellae diblock copolymer relative to the initial condition, as evidenced by the increase in scattered intensity along the 2* direction, although there is considerable spreading of this reflection in the 2*–3* plane. As expected, the spread in the 1*–2* plane is significantly less, indicating that lamellae with the normal along the velocity direction, 1*, are least favorable. When the SI 12/9 diblock copolymer is sheared in the nonlinear regime, the global alignment nears perfection, as evidenced by negligible scattering in the 1* and 3* directions and very strong, sharp peaks along the 2* direction. A second-order peak is evident along the 2* direction on the original negatives. This global orientation corresponds to lamellae lying in the plane of the sample disk.

In an effort to monitor the progress of alignment during oscillatory shearing, a single sample disk was intermittently removed from and returned to the rheometer in order to obtain SAXS patterns. The incident X-ray beam was oriented along the 2 direction of the sample. A variety of conditions were found to improve the extent of alignment: 1% strain at 0.1 rad/s, 5% strain at 0.1 rad/s, 5% strain at 10 rad/s, and 5% strain at 100 rad/s. Strain amplitudes of this magnitude, 1–5%, progressively align the diblock copolymer with continuous oscillatory shearing over a range of frequencies. Progressive alignment was also recently reported by Scott et al. for a triblock copolymer subjected to limited steady shear.[8] In our experiments with oscillatory shear, a much larger strain amplitude of 200% disrupts the alignment as the sample is expelled from the gap. The mechanism for this expulsion is unknown but may be related to a secondary flow or flow instability. Such instabilities occur in ordinary homopolymer solutions and melts, apparently as a result of large normal stress differences in these fluids.[19,20]

Figure 11 shows that the frequency dependence of the storage and loss moduli are indistinguishable for the two extreme examples of morphology, namely the initial condition and the sample aligned with nonlinear oscillatory deformation. We were surprised to find that over the range of frequencies probed, the dynamic mechanical properties of the sample were not affected by the degree of shear-induced alignment. (Recently, the SI 12/9 sample was quenched in the rheometer from the disordered state, thus producing a globally unaligned morphology. In comparison with the initial morphology or the well-aligned morphology of this study, the globally unaligned sample exhibits moduli which are ~5 times higher and have the same frequency dependence.[14]) Within the current study, the rheological results in Figures 4–8 are representative of SI 12/9 and independent of the shearing history of the sample.

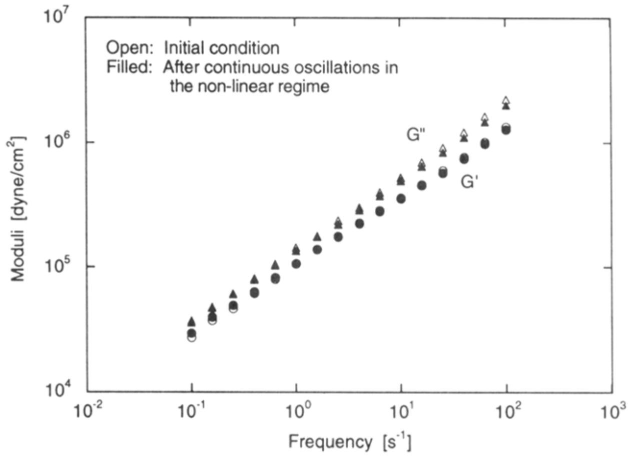

Figure 11. Frequency-dependent moduli for SI 12/9 at 98 °C and 1% strain in the initial condition (open symbols) and after being subjected to long periods of continuous oscillatory shearing under nonlinear conditions (solid symbols): 5%, 10 rad/s, 40 min and 5%, 100 rad/s, 100 min.

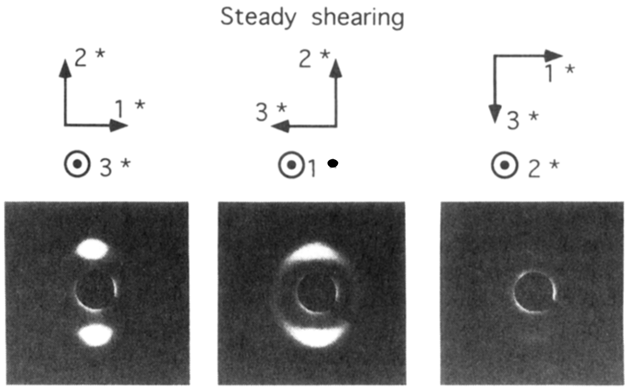

Figure 12. SAXS patterns of an aligned SI 12/9 sample after applying ~14 strain units at 0.003 s^{-1}.

5. Steady Shear Applied to the Aligned Diblock Copolymer

The rheological response of the well-aligned diblock copolymer was further investigated using steady shear at rates of 0.001–0.005 s^{-1}. The plateau stresses from start-up experiments are not linear with the shear rate, indicating that even at these lower rates, the aligned block copolymer does not exhibit the Newtonian behavior. The application of steady shearing to the aligned sample did, however, alter the morphology, and this will be the focus of the remainder of this section.

Figure 12 shows the three SAXS patterns for a sample of SI 12/9 which was first subjected to nonlinear oscillatory shear at 98 °C to globally align the lamellae in the sample plane and then subjected to ~14 strain units of steady shear at 0.003 s^{-1} also at 98 °C. The scattering patterns still have maxima along the 2* direction, but as in the sample sheared in the linear regime, this reflection is

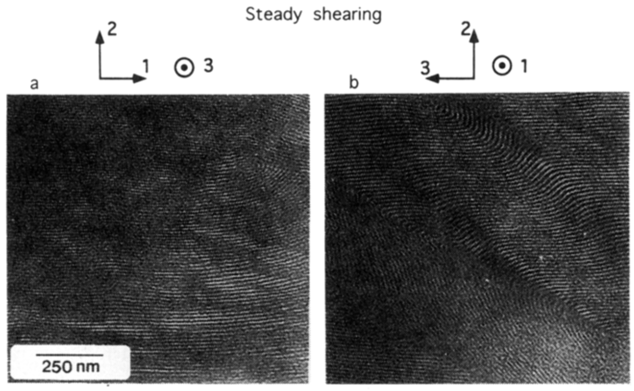

Figure 13. Transmission electron micrographs showing (a) the 1–2 plane and (b) the 2–3 plane of an aligned SI 9/12 sample subjected to steady shear, as detailed in Figure 12.

smeared in the 2*–3* plane. A separate sample was sheared using a higher rate to a total of 800 strain units, and the scattering patterns are similar. Evidently, steady shearing is capable of misaligning a well-aligned lamellar diblock copolymer sample in a specific manner but is not capable of fully realigning or rotating an aligned sample from a parallel to an upright orientation. Through a novel combination of extensional flow, sample construction, and steady shearing, Scott et al. recently demonstrated the realignment of cylindrical microdomains of a triblock copolymer from perpendicular to parallel, with respect to the shear direction, and the subsequent randomization of the microdomains with additional strain.[8]

The electron micrographs from the sample corresponding to Figure 12 show a marked difference in the 1–2 and 2–3 planes, Figure 13. In both cases the lamellae are moderately well developed on an intermediate length scale, unlike the initial condition, Figure 2, or the sample sheared in the linear regime, Figure 9a. While overall lamellar orientation is maintained, defects are evident and are more prevalent in the 2–3 plane than the 1–2 plane. Viewed in the 2–3 plane, lamellae commonly change orientation by bending within a narrow boundary, while maintaining registry with one another; these defects are called wall or tilt defects.[21,22] The vast majority of lamellae are continuous across the wall defects, thus avoiding the additional energy of free lamellar ends. The wall defects in SI 12/9 are frequently observed in groups, so that after a series of these, the orientation of the lamellae returns to the original orientation.

In addition to wall or planar defects, defects having lamellae curve around a focal point are observed in both the 1–2 and the 2–3 plane. Figure 14a shows typical examples of such defects in the 1–2 plane each having ∼15 lamellae bend around a focal point while maintaining an approximately constant lamellar spacing. This micrograph is consistent with focal conic defects, which include both Dupin cyclides having a conjugated hyperbola through an ellipse as the associated singularities and tori where the focal conic has degenerated into a line through a circle.[22] These idealized focal conic defects in cross-section exhibit two adjacent sets of concentric layers where the center points of the bending lamellae correspond to points on the elliptical singularity of the defect. The focal conic defects in SI 12/9 and other smectic systems[22] are somewhat different in that the layers are not concentric, but rather only the internal portion of the defect is formed and the external portion is eliminated so that the layers are coincident with the overall smectic planes. Figure 14b schematically shows focal conic defects within the 1–2 plane of SI 12/9 by illustrating the singularities. In addition, the focal conic defects in the 1–2 plane of SI 12/9 are found in rows along the 1 direction, as shown in Figure 14a, while in the 2–3 plane the focal conic defects are along the 3 direction. The apparent overlap of lamellae near the axes of the defects is attributed to the projection of the morphology through a microtomed section of finite thickness.

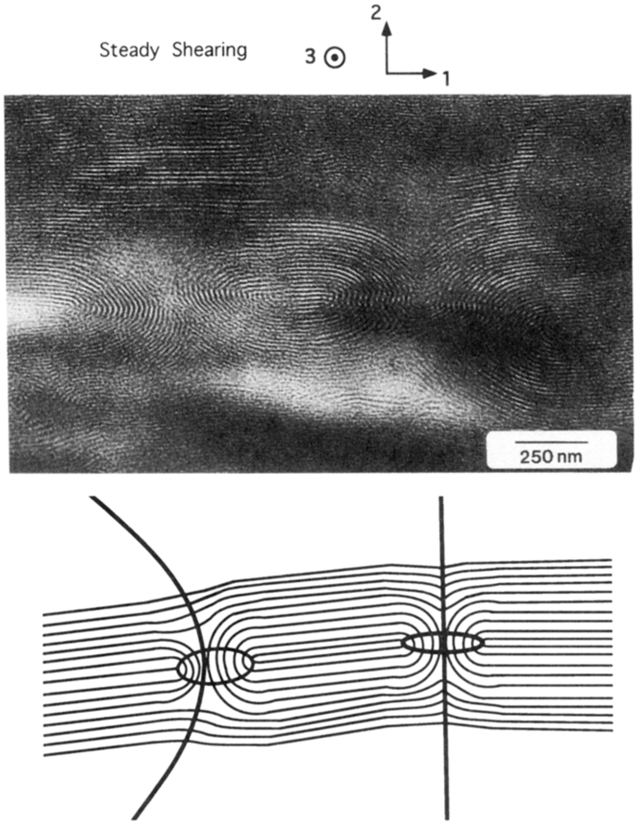

Figure 14. (a, Top) transmission electron micrograph of the sample described in Figure 12 showing a typical defect within the 1–2 plane. (b, Bottom) schematic of proposed focal conic defects showing the singularities which are an ellipse and a conjugated hyperbola.

As in the case of oscillatory shearing, altering the extent of alignment of the diblock copolymer by introducing defects did not alter the dynamic mechanical properties, over the range of frequencies presented here. In particular, an aligned sample was sheared for 15.5 strain units and SAXS indicated that the lamellar alignment was disrupted in the manner described above. This disrupted sample was then returned to the rheometer for dynamic mechanical testing. At 98 °C, the moduli measured between 0.01 and 100 rad/s at 0.5% strain are indistinguishable from the moduli of the initial condition. Applying continuous, nonlinear oscillatory shear restores the well-aligned morphology of the lamellae.

6. Discussion

Our morphological results illustrate the need to distinguish the local, intermediate, and global length scales of alignment. In the disordered state, at temperatures well above the order–disorder transition (ODT) temperature, block copolymers are random with respect to one another at all length scales. Below the ODT temperature, the junctions of the block copolymer segregate to interfaces producing alignment on a local or intermolecular scale. It is the orientation of these interfaces that determines the extent of alignment. The intermediate length scale is associated with the extent to which a lamellar microdomain

Table I. Summary of Alignment for Various Preparations

preparation	intermediate	global
initial condition	unaligned	slightly aligned
linear oscillations	unaligned	moderately aligned
nonlinear oscillations	well aligned	well aligned
steady shear	moderately aligned	moderately aligned

is correlated to the neighboring lamellar microdomains. The extent of alignment on the global length scale refers to the fraction of the sample which has lamellar microdomains oriented in a particular direction. The extents of intermediate and global alignment were determined primarily via TEM and SAXS, respectively, as summarized in Table I. Note that all the samples prepared in this study are organized on the local scale, because 98 °C is below the ODT temperature. The extent of local order is associated with the $\Delta(\chi N)$ from the order–disorder transition, which is ~ 3.5 in this study.

Though intermediate and global alignment are discussed here in terms of the lamellar morphology, the description could be applied to any block copolymer morphology. By distinguishing between intermediate and global length scales of alignment, insightful observations are possible. Samples exhibiting moderate alignment on the global length scale can exhibit no alignment (linear oscillations) or moderate alignment (steady shear) on the intermediate length scale. Only the samples subjected to continuous nonlinear oscillations have extensive alignment at *both* the intermediate and global length scales.

The wall and focal conic defects identified in section 5 for block copolymers are evident at the intermediate length scale. Our findings confirm that defects in block copolymer lamellar systems which contain free ends inducing splay are rare, while defects which maintain a constant lamellar spacing by bending the planar microdomains are common. The wall and focal conic defects are also typical of small molecule smectic systems.[21,22]

Previous investigators have proposed generally two types of mechanisms by which global alignment can be perfected, namely grain rotation[5,6] and microdomain destruction/reformation,[6–8] which may act either separately or together. The rotation of grains requires the initial sample to consist fully of grains exhibiting intermediate alignment which are not aligned with respect to one another, that is globally unaligned. The grain rotation mechanism proposes that the grains remain intact during the alignment procedure and rotate like hard bodies into the position of preferred alignment via motion at the grain boundaries. This mechanism is apparently not applicable to our molded samples of SI 12/9, because the initial morphology does not consist of well-developed grains exhibiting intermediate alignment.

The destruction/reformation mechanism produces global alignment piece by piece by partial dissolution of microdomains and by diffusion of either individual molecules or aggregates of molecules. In this way, microdomains that are aligned with respect to the preferred direction might grow at the expense of those that are misaligned with respect to the shear field. The energetic consideration presented earlier in the paper, section 4, which compare the free energy of mixing and the shearing energy, assume well-developed PS and PI microdomains. The transmission electron micrographs of the initial condition give evidence to the contrary. Consequently, the shearing energy applied to the initial condition may be sufficient to destroy microdomains, which do not have order on the intermediate length scale, in favor of well-developed planar microdomains. Therefore, we conclude that the alignment of a molded sample of SI 12/9 using nonlinear oscillatory shearing involves primarily a mechanism of destruction/reformation. The isolated lamellae oberved in the initial condition of SI 12/9 are likely sites of growth for the globally aligned lamellae.

We also observe that oscillatory shear can relign SI 12/9 after the alignment is disrupted by steady shearing. This implies that oscillatory shear can eliminate the wall and focal conic defects introduced by steady shearing. The wall defects effectively define grains, such that the mechanism of grain rotation is possible in this case due to the moderate alignment on the intermediate length scale. However, the focal conic defects can only be eliminated by locally rupturing or dissolving lamellae. Thus, a sample exhibiting moderate alignment on an intermediate length scale aligns via a mechanism of destruction/reformation, possibly combined with grain rotation.

Throughout our study, the linear viscoelastic properties of the lamellar diblock copolymer at the frequencies accessed here were unaltered by the extent or length scale of alignment or by the density of defects in SI 12/9. Lower frequencies were not experimentally accessible, because the limited linear regime prohibited increasing the strain amplitude to enhance the torque signal. Previous investigators report a change in moduli with block copolymer alignment or orientation at frequencies below the rubbery plateau.[5–7,9] We anticipate that if lower frequencies could have been probed, an influence of the morphology would have been observed.

In the case of block copolymer lamellae that are very well aligned, Witten et al. predict terminal behavior for oscillatory shearing, in which the layers slide past one another, and they predict a fractional power-law dependence of the terminal time on molecular weight.[23] Their predictions are based on a model of interpenetration and entanglements between the layers. From this model, we would expect very short relaxation times for the low molecular weight diblock copolymer, SI 12/9, used in this study. However, we find no terminal relaxation time for this lamellar diblock copolymer aligned at both the intermediate and global length scales, and our results establish that the terminal time, if it exists, must be longer than $\sim 10^3$ s at 98 °C. Consequently, remarkably long relaxation times exist in a polymeric sample which is barely entangled; these long relaxation times are evidently due to the presence of microdomains.

As a final note, further studies of SI 12/9 have recently shown that applying an oscillatory shear of a higher amplitude (100%) at a higher temperature (144 °C) produces upright lamellae, that is, with the normal to the lamellae in the 3 direction.[14,24,25] Of particular interest in this new work is the observation that SI 12/9 *does* exhibit different moduli for different types of morphological alignment. As stated above, the absence of a rheological change due to alignment in the present study is due to the limited amount of change in the global alignment and the inability to probe the sample at lower frequencies. Koppi et al. have also reported the transition from lamellae lying in the plane of the sample to upright lamellae with shearing at increased temperature.[9]

7. Summary

In order to facilitate the discussion of block copolymer alignment, an intermediate length scale is introduced which is evaluated using primarily electron microscopy. This study shows that a molded SI diblock copolymer can be well aligned on both the intermediate and global length scales by using relatively small amplitude oscillatory shear, 5%, frequencies of 0.1–100 rad/s, and a temperature 20 °C above the glass transition of the PS block. This aligned state exhibits lamellae parallel to the sample plane, that is with the normal of the lamellae parallel to the shear gradient. The results from the initial molded sample discount grain rotation as the sole mechanism for alignment but would be consistent with a destruction/reformation mechanism. Steady shear disrupts both the intermediate and global alignment of initially well-aligned samples by introducing focal conic and wall defects. Subsequent realignment of the sample involves the mechanism of destruction/reformation, possibly combined with grain rotation.

The various extents and length scales of lamellar alignment are not manifested in the rheological properties, within the measured frequency range. Our results should strongly discourage researchers from assuming that relatively mild oscillatory shear, such as 5% or 10%, does not produce significant changes in block copolymer alignment. Thus, while rheological tests are simple probes of shear-induced morphological changes, they can be misleading, and direct morphological studies are required to determine whether morphological changes have occurred.

Acknowledgment. The authors wish to thank D. D. Davis and M. E. Galvin for their experimental assistance. We have benefited from discussions with E. Helfand. K.I.W. also acknowledges the National Science Foundation, MRL Program, under Grant No. DMR91-20668, at the University of Pennsylvania where some of the electron microscopy was performed.

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