Ordering by Flow near the Disorder–Order Transition of a Triblock Copolymer Styrene–Isoprene–Styrene

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ABSTRACT: An oriented morphology has been generated by cooling a triblock copolymer styrene-isoprenestyrene (SIS) below its order-disorder transition (ODT) temperature and annealing it there at constant quench depth ΔT while simultaneously shearing it. The polymer has an equilibrium microphase-separated morphology of hexagonally packed cylinders of polystyrene in a polyisoprene matrix. The evolving structure was investigated with rheology and small-angle X-ray scattering (SAXS). SAXS showed that mirophase separation occurred rapidly upon cooling below the ODT temperature while the growth of large-scale spatial order (~1- μ m scale) needed long annealing times as shown with low-frequency dynamic mechanical measurements. The slow part of the structuring process gave sufficient time for flow alignment of microphaseseparated domains during their growth phase. Near "single crystal" morphology was obtained through largeamplitude oscillatory shear at ~25 K below ODT. The low-frequency linear viscoelastic properties of the single crystal structure were found to be affected by the domain alignment in the flow direction. The quench depth ΔT is an important parameter: at a small quench depth of $\Delta T \simeq 10$ K, microphase separation was found to be suppressed by the oscillatory shear.

Introduction

Block copolymers at temperatures below the orderdisorder transition (ODT), T_{ODT} , form highly ordered morphologies with spatially periodic composition fluctuations (domains), while above T_{ODT} , the copolymer molecules are randomly mixed in a disordered state. Block copolymer phase transitions are weakly first order.¹ Roe et al.² and Hashimoto et al.³⁻⁸ were the first groups to use scattering techniques for observing structural changes in block copolymers near the T_{ODT} . Small-angle X-ray scattering (SAXS) data on their diblock copolymer revealed that secondary peaks, showing long-range order, disappeared as the T_{ODT} was approached. The first-order peak intensity dropped to a weak intensity level relevant to the broad scattering maximum from disordered melts which was difficult to detect at short counting times for the X-ray scattering. It has also been well-established that the order-disorder transition affects the mechanical properties.⁹⁻¹⁴ The long relaxation modes, as observed in the dynamic moduli at low frequencies, dropped significantly when heating through the ODT. Bates and coworkers^{15,16} reported an interesting evolution of lowfrequency dynamic mechanical properties above the $T_{\rm ODT}$ of a diblock copolymer. The ordered sample showed an extended power law relaxation region at low frequencies with $G' = G'' \sim \omega^{0.5}$. The dynamic mechanical behavior was in good agreement with consecutive small-angle neutron scattering measurements on the same diblocks.¹⁷

Han et al.¹⁸ studied SAXS and rheology of a triblock copolymer near ODT and found the corresponding T_{ODT} 's to be in agreement with each other. Similarly, Koberstein et al.¹⁹ studied the ODT of a triblock copolymer and

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suggested a temperature difference of ~45 K between $T_{\rm ODT}$ by SAXS and $T_{\rm ODT}$ by rheology. This might be attributed to composition fluctuation effects on the scattering measurements. Using SAXS and rheology, Stühn et al.²⁰ observed a single ODT for a low molecular weight diblock copolymer (nearly symmetric composition). The transition behavior was symmetric in heating and cooling.

This study is concerned with the ordering of a strongly microphase separating triblock copolymer which forms cylindrical domains of the minor component in a continuous matrix of the major component. The cylinders arrange in a highly regular hexagonal lattice. The local order is defined by the direction of the cylindrical domains and by the orientation of the lattice planes. In the as-cast sample, the order is uniform within grains of $\sim 1 \,\mu$ m, but the directors of domains and lattice planes vary randomly from grain to grain.

In the following, we will distinguish between (1) the single-phased or disordered structure, (2) the microphaseseparated structure (local concentration fluctuations; formation of hexagonal lattice; microdomain scale ~ 50 nm), (3) the grain network structure (grains of uniformly ordered structure, $\sim 1 \ \mu$ m, and random director change from grain to grain; continuity of PS domains across grain boundaries), and (4) the long-range order in which domain orientation and lattice orientation are uniform throughout the sample (~ 1 -mm scale). A sample with such long-range order has been termed "single crystal".²¹

Macroscopic orientation is achievable by flow. Keller et al.,²¹ Hadziioannou et al.,²² Pakula et al.,²³ Morrison et al.,^{24,25} and Almdal et al.^{26,27} demonstrated that shear can align the grain morphology and produce a "single crystal" structure. Long-range order can also be achieved by extensional flow.²⁸ In this study, we will use largeamplitude oscillatory shear (LAOS), which has been shown to generate a high degree of domain orientation.²² LAOS was chosen since it can be applied slowly over long periods of time and under good temperature control.

The strains for flow-induced ordering should be fairly small. A large imposed strain tends to disrupt the structure.^{28,29} Large strains have been found to lower the shear viscosity in molten triblocks since they reduce the ratio of bridge to loop molecules; i.e., they reduce the probability of bridge molecules between separate domains and favor loop molecules which have both ends in the same domain.³⁰ These phenomena will be avoided here by choosing strains which do not exceed 4 shear units.

To date, techniques to produce long-range order have been mostly limited to applying deformation in the microphase-separated state. Shearing while cooling through ODT and below has been employed by Almdal et al.²⁷ for their study of ordering transitions in diblock copolymers.

Our approach is to thermally quench the sample from the single-phase state and anneal it at a constant quench depth ΔT just below ODT. Shearing is started immediately after the quench, and it is continued during annealing over a long time period. Shearing aligns the microphaseseparated domains while they are growing. This structuring technique exploits the microphase-separating ordering kinetics, which is slowed down by the relatively high molecular weight of the polymer. After shear modification, both the rheology and morphology were investigated.

Experimental Section

Materials and Sample Preparation. Poly(styrene-blockisoprene-block-styrene) (SIS) (designated as SIS56) was prepared by anionic polymerization in cyclohexane using sec-butyllithium as initiator and the antioxidant 2,6-di-*tert*-butyl-4-methylphenol. The 1,4-content is 95 mol % (90% cis, 5% trans) and 5 mol % are 3,4 units. The number average molecular weight, $M_n = 56$ 000, was determined by membrane osmometry and $M_w/M_n = 1.1$ by GPC. The weight percent composition is 24.3% polystyrene and 75.7% polyisoprene by C NMR, giving an equilibrium microphase-separated morphology of hexagonally packed cylinders of polystyrene (PS) in a polyisoprene (PI) matrix (evidenced by TEM and SAXS). The PI chains are much above and the PS chains are much below their entanglement molecular weight.

Films were cast from 10 wt % toluene solution at room temperature for 1 week. To further remove toluene and reduce stresses from solvent evaporation, the films were vacuum-dried at 120 °C or 24 h.

Small-Angle X-ray Scattering. SAXS experiments were performed with the apparatus described in detail elsewhere.^{7,31} The SAXS apparatus consists of a 12-kW rotating anode X-ray generator, a graphite crystal for incident beam monochromatization, a 1.5-m camera, and a one-dimensional position-sensitive proportional counter (PSPC). Line-focused Cu K α radiation (λ = 0.154 nm) was used. The SAXS profiles were corrected for absorption due to the sample, air scattering, background scattering arising from thermal diffuse scattering due to density fluctuations, and slit height and slit width smearings.³² The absolute scattered intensity was obtained by the nickel foil method.³³

The SAXS profiles were measured in situ as a function of temperature from 30 to 180 °C by incremental heating, using the temperature enclosure as described elsewhere.⁴ The solution-cast film prepared as described above was used as a starting sample. The profiles at each temperature were obtained in situ with about 0.8-1.5 h of exposure to the X-ray beam on samples preheated for 0.5 h, to ensure thermal equilibration.

Two-dimensional SAXS with imaging plates as 2D detector was used for studying the order in the sheared samples. The SAXS patterns were corrected for sample absorption and air scattering. A newly developed image enhancement technique recovers higher order maxima. This will be discussed in conjunction with the results. **Rheometry.** Dynamic mechanical properties were measured in a Rheometrics Dynamic spectrometer (RDS-7700) with parallel plate geometry using small-amplitude oscillatory shear ($\gamma = 0.03$). Three different types of dynamic mechanical measurements were chosen to characterize the ODT of SIS56: temperature sweeps at constant frequency ($\omega = 0.1 \text{ rad/s}$), isothermal frequency sweeps over four decades of frequency (0.01 rad/s < ω < 100 rad/s), and isothermal time sweeps at constant frequency ($\omega = 0.1 \text{ rad/s}$). Isothermal data were shifted both horizontally and vertically using the time-temperature superposition principle for the highfrequency end of the data. Shifting was performed with the interactive IRIS software.³⁴

Results

ODT Determination by SAXS. The relative SAXS intensity, I, vs the magnitude of the wave vector, \mathbf{q} , observed at various temperatures is shown in Figure 1a,b, where \mathbf{q} is defined as

$$\mathbf{q} = (4\pi/\lambda)\sin(\theta/2) \tag{1}$$

 λ and θ are the wavelength of the X-ray and the scattering angle, respectively.

The initial morphology after solution casting consists of hexagonally packed cylinders of PS in a PI matrix. The cylinders align with a common director within grains. The director varies randomly from grain to grain herewith, producing a macroscopically isotropic structure. From the SAXS profile shown in Figure 1a (top curve), the peak positions can be estimated to be as follows: $\theta = 21.8, 39.1$, 45.8, 59.8, and 68.4 min which have a relation of 1, $\sqrt{3}, \sqrt{4}, \sqrt{7}, \text{ and } \sqrt{9}$. This is typical for *d*-spacings of a hexagonally close packed array of cylinders with sufficiently long-range order. The intercylinder distance (lattice parameter) was calculated to be 28.1 nm. A cylinder diameter of 14.5 nm can be calculated from the lattice parameter and the volume fraction of PS, assuming a complete segregation of the constituent copolymer chains in their respective domains.

As the temperature was increased (Figure 1a,b), the higher order intensity maxima gradually disappeared and for $T \ge 140$ °C only the first-order maximum could be observed. However, it would be premature to regard these profiles at $T \ge 140$ °C as those in the disordered state. The higher order maxima attributed to the regularity in the microdomain structures are known to become very weak in the vicinity of the ODT.

For SAXS measurements, earlier findings^{8,35} suggest that the ODT can be characterized in two ways, the first one based on the Landau-type mean field theory developed by Leibler in the context of the random-phase approximation,³⁶⁻⁴⁰ and the second one based on the Ornstein– Zernike theory.⁴¹

(i) From Figure 1, a characteristic size D can be estimated both for the spatial segmental density fluctuations in the ordered state and for the thermal segmental density fluctuations in the disordered state,

$$D = 2\pi/q_{\rm m} \tag{2}$$

where q_m is **q** at the scattering angle θ_m of the first-order maximum. In the disordered state, this D or q_m is independent of temperature except for minor changes due to the temperature dependence of the radius of gyration (R_g) of polymer coils, i.e.,

$$D \sim T^0$$
 (disordered) (3)

While in the ordered state, D or q_m depends on temperature⁸

$$D \sim T^{1/3}$$
 (ordered) (4)

The transition from T^0 to $T^{1/3}$ behavior characterizes the ODT.



Figure 1. SAXS intensity profiles for heating (a) from 30 to 130 °C and (b), from 130 to 180 °C. Curves: (1) 30, (2) 80, (3) 100, (4) 110, (5) 120, (6) 130, (7) 140, (8) 150, (9) 160, (10) 170, and (11) 180 °C.

(ii) An alternative way to characterize the ODT involves the intensity measurements at any given \mathbf{q} near q_m as a function of temperature. The intensity depends on χN , and if χ is written as found in most experimental results,

$$\chi = A + B/T \tag{5}$$

where A and B are constant values, then Leibler's Landautype mean field theory predicts that, in the disordered state, $I^{-1}(\mathbf{q})$ linearly decreases with increasing T^{-1} ,

$$I^{-1}(\mathbf{q}) \sim T^{-1}$$
 (disordered) (6)

The deviations from eqs 3 and 6 are attributed to a consequence of an onset of the microphase separation and the microdomain formation. It was suggested that these two types of deviation should be simultaneously utilized to determine ODT.⁴²



Figure 2. Inverse SAXS intensity (O) and characteristic size, $D(\Delta)$, vs inverse temperature plotted to determine the ODT, where $q^* = 0.278 \text{ nm}^{-1}$.

The results of D and $I^{-1}(\mathbf{q})$ as a function of T^{-1} are shown in Figure 2 for $\mathbf{q} = q_{\rm m} = 0.278$ nm⁻¹, the wavenumber for the scattering maximum in the profile at 180 °C. Notice that there is a regime where D is independent of T while $I^{-1}(\mathbf{q})$ linearly decreases with increasing T^{-1} . Deviations from the relations expressed by eqs 3 and 6 were observed at 130 °C $\leq T \leq 140$ °C. This crossover temperature corresponds to the order-disorder temperature ($T_{\rm ODT}$). In comparison, higher order maxima had been observed in the profile at 130 °C in Figure 1, which means SIS56 at 130 °C is still in the ordered state. Thus, from both Figures 1 and 2 the $T_{\rm ODT}$ was evaluated to be in between 130 °C $\leq T \leq 140$ °C.

It should be noted that a small curvature or a weak deviation from the linearity of I^{-1} with respect to T^{-1} is seen in the plot of I^{-1} vs T^{-1} at T > 130 °C (broken curve in Figure 2). This confirms findings of Bates et al.^{43,44} and Almdal et al.²⁷ on other block copolymers. The curvature or the deviation from the linearity is attributed to the finite size effect proposed by Fredrickson and Helfand.¹ However, it is emphasized that this effect is small compared to the deviation from linearity at $T \leq 130$ °C, i.e., below ODT.

ODT Determination by Rheology. We observed the occurrence of the ODT by two types of dynamic mechanical experiments. A convenient first test was to heat the microphase-separated sample gradually (2 K/min) in the rheometer while G' and G'' were measured at a low constant frequency ($\omega = 0.1$ rad/s) in the linear viscoelastic region, as shown in Figure 3. The elastic moduli were found to drop significantly during heating from 130 to 140 °C, indicating the nascence of the ODT. As the temperature increased above 135 °C, G' dropped by several orders of magnitude as the disordered phase was developing. By use of this technique, it was a good assessment that the ODT occurred near 135 °C.

Figure 4 shows reduced master curves of the elastic moduli over several decades of frequency determined from isothermal frequency sweeps shifted to a reference temperature of 160 °C. We assume that the high-frequency G' and G'' were unaffected by the order-disorder transition



Figure 3. First heating curve (2 K/min) at $\omega = 0.1$ rad/s.



Figure 4. Master curves for heating with $T_{ref} = 160$ °C. Slopes of 2 and 1 are indicated as a reference in the low-frequency region. and that they could be used to determine the horizontal and vertical shift factors a_T and b_T as plotted in Figure 5. The vertical shift was very small ($b_{\rm T} \approx 1$). Lowfrequency moduli, for instance at $\omega = 0.1$ rad/s as used in Figure 3, changed by about 2–3 orders of magnitude. From Figure 4, it is obvious that there is a material characteristic frequency ($\sim 100 \text{ rad/s}$ for SIS56 at 160 °C) below which a typical drop of G' and G'' due to the ODT can clearly be seen. Therefore, most emphasis was placed here on the low-frequency G' and G'' data. The microphaseseparated sample (top curve in each of the graphs of Figure 4) has relaxation modes over a wide frequency range, much beyond the experimentally accessible range. The disordered sample (bottom curve in each of the graphs of Figure 4) has a characteristic relaxation time which is fairly short $(\sim 10^{-4} \text{ s})$. Its terminal zone dominates nearly half the accessible frequency window. The entanglement plateau, which is typical for melts of high molecular weight, begins to show at the highest frequencies in Figure 4.



Figure 5. Shift factors, a_T and b_T vs inverse temperature, $T_{ref} = 160$ °C.



Figure 6. Cooling curve (-2 K/min) at $\omega = 0.1$ rad/s.



Figure 7. Isothermal time sweep at T = 125 °C and $\omega = 0.1$ rad/s after heating above ODT. Isothermal frequency sweeps were taken after 70 min, 160 min, and 11 h as marked by 1, 2, and 3, respectively.

Ordering Processes Encountered by Quenching from Disordered State to Ordered State (No Flow). (a) Rheological Observation. A sample was heated to 160 °C and then cooled through the T_{ODT} at a rate of -2K/min. The low-frequency G' and G" were measured as a function of temperature (Figure 6). The cooling curve significantly differs from the heating curve as one sees by comparing Figures 6 and 3. The ordering process as observed by low-frequency G' and G" does not appear to be instantaneously reversible but is orders of magnitude slower than the disordering process.

In a separate annealing experiment, samples were rapidly cooled through ODT and then held isothermally at 125 °C. G' and G" at $\omega = 0.1$ rad/s were monitored (Figure 7) for 11 h until they finally returned to their initial values of the as-cast samples. In the same experiment, three frequency sweeps were performed at selected times, as indicated by the arrows on Figure 7: after 70 min, 160 min, and 11 h. The corresponding data in Figures



Figure 8. Frequency sweep at T = 125 °C after annealing for 70 min.



Figure 9. Frequency sweep at T = 125 °C after annealing for 160 min.



Figure 10. Frequency sweep at T = 125 °C after annealing for 11 h.

8–10 clearly show the slow recovery of the low-frequency moduli over time.

(b) SAXS Observation. SAXS measurements started out with preheating an as-cast film to 125 °C for 30 min. Subsequently, the sample was heated to 160 °C and annealed for 30 min, where the SAXS profile was measured for 1 h. Then, the sample was quenched to 125 °C, by quickly transferring the cell to another temperature enclosure at 125 °C. Temperature equilibrium was attained in less than 1 min. The SAXS profiles were measured during the ordering process at 125 °C as a function of time; see Figure 11.

Figure 11 shows the profiles measured from 0 to 20 min (curve 2), from 13 to 14 h (curve 3) after quenching, together with the profile measured in situ at 125 °C after heat-treating the as-cast film at 125 °C for a long time so as to achieve equilibrium (curve 1), and that at 160 °C (curve 4). Although not shown here, the profiles obtained from 40 to 60 min and from 2 to 3 h after quenching were identical to that shown by curve 2. The time changes of



Figure 11. SAXS profiles at T = 125 °C as a function of time after quenching from 160 °C.



Figure 12. Time changes of the intensity maxima (O) and the half-width at half-maximum (hwhm, in units of minutes in θ) (Δ) for 1-h SAXS scattering profile shown in Figure 11. Two horizontal reference lines show the intensity maxima and hwhm for SAXS profiles measured at 125 °C during the heating cycle of the as-cast specimens.

the peak intensity and the half-width at half-maximum (hwhm) for the scattering maximum after the quenching from 160 to 125 °C are given in Figure 12, where the solid lines show the corresponding quantities after heat-treating the as-cast film at 125 °C. The results shown in Figures 11 and 12 clearly indicate that the microdomain formation and the lattice ordering as observed by SAXS are quite rapid, occurring within the first time frame of 20 min. The directions of the fluctuations and the lattice planes are random. A slight broadening of the scattering profiles and a decrease of the peak intensity occurred very gradually after 3 h. The origin of this gradual change of the scattering profiles is not understood at present, but it might be related to a long-range reorganization into the grain structure which was probed by rheology. The sample morphology does not seem to return to the as-cast (+ annealed) state. at least not during the short experimental time.

Shearing at Constant Quench Depth ΔT . The ascast material was mounted in the RDS-7700 and heated to 160 °C for 20 min in order to establish the disordered state. The sample was then cooled (at ~-5 K/min) to a temperature below the T_{ODT} and held there while largeamplitude oscillatory shear at a low frequency, $\omega = 0.01$ rad/s, and a shear strain amplitude, $\gamma = 4$, was applied. The required shearing time varied depending on the temperature. The four quench temperatures used were



Figure 13. SAXS patterns after LAOS at 110 °C. Patterns a-c were obtained with the incident X-ray beam parallel to the 1-, 2-, and 3-axes of the shear flow, respectively.

125 °C for 10 h, 110 °C for 10 h, 100 °C for 4 h, and 80 °C for 2 h. The shear-induced domain orientation was investigated with birefringence, electron microscopy (TEM), and SAXS, all done on room-temperature-cooled samples. Figure 13 shows the SAXS pictures of the 110 °C sample.

On the basis of the quiescent structuring observations, we first chose 125 °C as the annealing temperature for LAOS. However, no macroscopic orientation was seen, and even more importantly, there was no long-range order in the TEM image. The shearing process seemed to have disturbed the delicate microphase separation process. As the temperature for shearing was lowered, the driving force for phase separation increased and domain orientation was seen at an annealing temperature as low as 80 °C. An optimum temperature for the LAOS structuring seems to be ~110 °C. It provides sufficient molecular mobility and sufficient thermodynamic driving force for microphase separation.

Figure 13 contains the SAXS patterns taken along all three principal directions of the sample after LAOS at 110 °C. The pattern in Figure 13a is the diffraction intensity distribution in the plane passing through the origin of reciprocal space and parallel to the axes 3 and 2. Likewise, the pattern in Figure 13b belongs to the axes 1 and 3 and the pattern in Figure 13c to the axes 1 and 2. More rigorously, the pattern in Figure 13c presumably belongs to the plane parallel to axis 1 and line c. With the beam parallel to the flow direction, the 1-axis, Figure 13a, shows a very sharp six-point pattern from (100) planes, indicating that the cylinders are aligned in the flow direction and packed with hexagonal symmetry in the plane perpendicular to the flow direction. Higher order diffractions from (110), (200), (210), and (300) were made visible by the following enhancement procedure:45

1. We divide the pattern into several concentric circles as is demonstrated in Figure 14, so that each of the concentric circles contains diffractions from equivalent planes.

2. The maximum intensity within each circle is normalized to 1. Then parts of the pattern with intensity levels between 0.5 and 1 are shown by white color and the



Figure 14. Schematic of the diffraction pattern in Figure 13a. The relative intensities of (100), (110), (200), (210), and (300) diffractions are approximately 1000:20:3:2:1.

rest of the pattern is printed black (binarization). This allows comparison of intensity levels within each circle, but excluded comparisons of intensity levels between different circles.

The shape and intensity of the spots shown in Figure 13a are not perfectly symmetric. This effect is also seen in the patterns of Figure 13b,c. The slight asymmetry of the pattern is due to the slightly imperfect alignment of the specimen. The pattern was found to be very sensitive to how the specimens were cut from the sheared sheet and how they were mounted into the X-ray beam.

This same enhancement technique was also applied with the beam in normal and radial directions, the 2-axis and 3-axis views, respectively. Parts b and c of Figure 13 show only equatorial scattering normal to the flow axis 1, confirming that the cylinders are well aligned in the flow direction.

The equatorial distribution in the pattern in Figure 13b corresponds to the intensity distribution along line b in Figure 13a. While (100) diffractions can be seen in the pattern in Figure 13b, the corresponding diffraction cannot be seen along line b. However, this does not mean that there is no (100) diffraction along line b. In fact, the (100) diffraction intensity on line b is stronger than that of (110), though it is weaker than the (100) diffraction spots in off-equatorial positions. The fact that the (100) diffraction



Figure 15. TEM of room-temperature sample after shearing at 110 °C; same sample as for Figure 13.

appears in Figure 13b and that its intensity is stronger than the (110) diffraction intensity is due to the orientational distribution of the hexagonal lattice around axis \mathbf{a}_3 . Along line c, the (100) diffraction is about 50 times stronger than the (110) diffraction. Therefore, even a small fraction of cylinders with their primitive lattice vector \mathbf{a}_1 aligned parallel to the 2-axis may give rise to (100) diffractions, even if the major fraction of the lattice planes have an orientation as shown in Figure 13d.

The equatorial intensity distribution in the pattern in Figure 13c corresponds to the intensity distribution along line c in Figure 13a. Peak positions of the (100) diffractions are not symmetric, and this asymmetry is also seen along line c in pattern (13a). We attribute this asymmetry, and also the fact that (110) and (210) diffractions are found in addition to the (100) and (300) diffractions, to the imperfect alignment of the sample against the X-ray beam.

The periodic structure can also be seen in TEM; see Figure 15. The cylindrical domains show a slight undulation.

Linear Viscoelastic Properties of the Single Crystal. Linear viscoelastic measurements were made before and after LAOS. Frequency sweeps for the single crystal structure and isotropic structure (microphase well-separated) are shown in Figures 16 and 17, at 120 and 130 °C, respectively. The high-frequency values of G' and G'' are



Figure 16. Frequency sweep at 120 °C after LAOS at 110 °C, unfilled symbols. The as-cast sample is represented by the filled symbols.



Figure 17. Frequency sweep at 130 °C after LAOS at 110 °C, unfilled symbols. The as-cast sample is represented by the filled symbols.

not affected by the ordering process; i.e., these values are about the same for the single crystal structure and the as-cast morphology. At intermediate frequencies, the alignment somewhat reduces G' and increases G'' when sheared in the direction of the cylindrical domains. However, the differences are quite small. The largest differences are seen at the lowest frequencies since the crossover to the terminal zone was shifted (shortening of the longest relaxation time of the plateau regime). The terminal zone itself is outside the experimental window so that it cannot be analyzed here.

Discussion

ODT Determination during Heating. The ODT gave rise to gross changes in the elastic modulus near the T_{ODT} . During the transition, the time-resolved low-frequency rheological properties changed so rapidly that even "point" measurements were affected. The magnitude of this experimental problem can be estimated with the mutation number⁴⁶

$$N_{\rm mu} = \Delta t \frac{1}{g} \frac{\partial g}{\partial t} \tag{7}$$

g stands for the quantity to be measured in the transitory experiment and $\partial g/\partial t$ is the rate of change of this quantity (here, g stands for either G' or G''). $\Delta t \simeq 2\pi/\omega$ is the experimental time for obtaining a single data point. For an acceptable measurement, the mutation number should be 0.1 or smaller for both G' and G'', which is not the case during the temperature-induced transition. This is the origin of the large scatter in both the G' and G'' transition data (Figure 3). At high temperatures, beyond the T_{ODT} , the rate of change was small and the G'' data became acceptable again while G' was orders of magnitude smaller than G'' so that it could not be resolved any more. The

Macromolecules, Vol. 26, No. 26, 1993

scatter in the G' data (not the G'' data) expresses this limited resolution of the experiment.

Figure 4 shows the linear viscoelastic behavior both above and below the T_{ODT} . G' has a plateau region at intermediate frequencies as long as the polymer is microphase-separated. This plateau is not due to molecular entanglements (which would remain when heating above ODT), but it is indicative of a "grain network structure" formed by continuity of the cylindrical microdomains through the grain boundary region. Above the ODT, the low-frequency properties are characteristic of a liquidlike behavior. Both the grain network and the domains are dissolved into a disordered melt above the T_{ODT} .

In the disordered state (bottom curve in each of the graphs of Figure 4), the entanglement behavior of the PI midblock seems to be drastically altered by the polystyrene end blocks. The polyisoprene midblock of SIS56, with an average molecular weight of \sim 42 000, has an entanglement behavior which differs substantially from that of pure PI chains of the same length. A difference in plateau modulus is not noticeable (not enough high-frequency data on SIS56 to confirm), but the molecular relaxation dynamics is somehow changed so that the entanglement region is shifted to much higher frequencies or shorter times. A pure chain of PI with the same molecular weight would have a characteristic relaxation time \sim 100 times larger than that of SIS56.

The second special feature of the disordered SIS56 melt is the broadening of the spectrum between about $10^2 < \omega$ $< 10^4 \text{ s}^{-1}$. The spectrum of a nearly monodisperse homopolymer melt, such as the disordered SIS56, would be cut off at the beginning of the entanglement plateau,⁴⁷ while the disordered SIS56 has been observed to have additional slow modes. The characteristics of these slow modes will be explored further in the near future.

The disordering process as observed by SAXS was also found to be rapid, and the dissolution of the microdomains was found to occur within minutes after a temperature jump from an ordered state to a disorderd state for other block copolymer systems.^{3,6,7,47} The SAXS results are in good agreement with the rheological ODT determination as long as the ODT is determined by heating.

Ordering Process during Cooling (No Flow). After quenching below the T_{ODt} , sufficient annealing must be performed to establish the fully developed grain network structure. The required annealing time is shortest at an intermediate annealing temperature, since the molecular mobility is decreased with decreasing temperature while the thermodynamic driving force for microphase separation increases with decreasing temperature, and vice versa. 125 °C was found to be a suitable intermediate temperature for our sample when annealing at rest. The dynamic moduli grew in a sigmoidal curve (Figure 7) which resembles a nucleation and growth process, similar to crystallization kinetics, which has been theoretically developed to describe the ordering process as a homogeneous nucleation and growth process for symmetric diblocks.⁴⁹ Rosedale and Bates¹⁶ also observed such rheological behavior using a diblock copolymer.

The ordering process seems to have two different time constants, a short characteristic time for the structure which is probed by SAXS and a long characteristic time for the structure which is probed by rheology. The ordering as observed by SAXS is completed within the first 20 min after quenching while the ordering as observed by rheology requires ~ 11 h. The apparent difference reflects different length scales at which the two methods tend to detect space-time organization of block copolymers in the microphase separation process. The SAXS data are more sensitive to the microdomain formation (local concentration fluctuations), i.e. time evolution of the order parameter in the length of the lattice parameter. On the other hand, the rheology is more sensitive to the grain network formation and annihilation of defects in the grain boundaries. The two data sets combined give a picture in which the microdomain formation occurs rapidly on the domain scale, but the long-range structure reorganization resulting in the grain network formation requires a much longer time scale.

Independently, and in parallel to this study, Schuster and Stühn⁵⁰ also observed two time scales for the structuring, however, for a low molecular weight diblock. This suggests that the observed phenomenon is of a more general significance.

Shear-Induced Orientation. LAOS is uniquely suited for slowly orienting the growing domains during microphase structure formation. The stress and strain vary sinusoidally, applying only high stress and strain for part of the cycle. As the cylindrical domains start to form and grow, the flow field supplies enough energy to influence the direction of domain formation. The cylindrical domains formed in the direction of flow give rise to smaller stresses than the domains perpendicular to flow, as we saw on separate measurements with a SBS triblock copolymer (not reported here). This lets us believe that the structuring is due to the merging of domains which are aligned with the flow direction and that these aligned domains remain unaltered by the flow. Newly formed small domains of different orientation can gradually reorient with the shear flow. The growth of large perpendicular domains, which would have to be broken up before aligning in flow direction,²⁸ are believed to be suppressed by the shear.

The cylindrical domains order into a hexagonal lattice structure. As was seen on SBS,²⁸ LAOS on SIS has a strong tendency for aligning the (100) hexagonal lattice planes normal to the 2-axis of the shear flow; see Figure 13. The cylindrical domains in these lattice planes are part of the shear surfaces of the imposed shear flow. The favoring of this lattice alignment lets us conclude that it requires the lowest energy during shearing. A surface-induced ordering cannot be excluded, but it is highly unlikely for a sample thickness of 1 mm.

The flow-induced order is quite high, as can be seen by the narrow arcs of the diffraction patterns in Figure 13. If it were perfect as shown in Figure 13d, (100) diffractions should not be seen in Figure 13b since the (100) planes do not satisfy the diffraction conditions. However, we found (100) and (210) diffractions in addition to the (110) diffractions. This is attributed to slight imperfections in the order and to difficultiies in speciment alignment with the X-ray beam.

It was quite unexpected that a shearing temperature near T_{ODT} (~10 K below) did not give sufficient structuring while a lower temperature produced the desired structuring effect. It seems that the development of the microphaseseparated structure was suppressed or kept at extremely small scale by the LAOS and the room-temperature quenched samples showed no noticeable order in TEM and SAXS. However, even in the event that shear disturbed the microphase separation at 125 °C, the microphase separation should have developed a microdomain morphology after cessation of shear flow and during cooling of the specimen. Such microdomain morphology did not show under TEM. This compares to an earlier observation in which application of strong mechanical disturbances to a similar system at T > 120°C, such as constant shear stress to large strains ($\gamma > 20$). permanently altered the degree of microphase separation.²⁵

Conclusions

SAXS and rheology probe the morpholgy at very different length scales. SAXS measurements provide detailed structural information on a 10-nm scale. Lowfrequency dynamic mechanical measurements are mostly affected by the $1-\mu$ m-scale grain morphology. Rheology locates the transition somewhere between 130 and 140 °C, in good agreement with the SAXS results. The ODT can best be measured in a heating scan since the disordering occurs rapidly on all length scales. On the other hand, the ordering transition depends on the size of the structure and it will appear delayed depending on the scale of observation. During the quiescent ordering process (no flow) at 125 °C, SAXS measurements detected wellseparated microphase domains within 20 min (first frame) while G' and G'' show that formation of equilibrium grain morphology takes many hours.

The rapid microphase separation and the slow development of extended domains provide suitable conditions for shear alignment of the developing morphology. Shear flow prescribes the direction in which the cylindrical domains prefer to grow and hexagon planes prefer to align. The director is uniform for the growing grain morphology; i.e., grain boundaries are avoided. The flow-induced ordering is optimum at an intermediate temperature. The temperature must be sufficiently far below T_{ODT} so that induced microphase separation is strong, but the temperature must also be high enough to maintain sufficient molecular mobility. The suppression of microphase separation by shearing at small quench depth is an unexpected result which was not the objective of this study. It is a most interesting phenomenon which will require further study.

The drop of low-frequency G' and G'' values at ODT is much larger for SIS56 than for diblock copolymers as investigated in other laboratories. Otherwise, the ODT has a very similar effect on relaxation dynamics and the involved time scales. This is rather surprising since the underlying morphologies for SIS56 and for diblocks are very different.

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