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# Viscoelastic Characterization of an Order−Order Transition in a Mixture of Di- and Triblock Copolymers

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ABSTRACT: The phase behavior and linear viscoelasticity of a mixture of a matched diblock and triblock copolymer of styrene and ethylene−butene-1 are reported. The mixture undergoes reversible thermotropic transitions from a cylindrically ordered state at low temperatures to a spherically ordered state at intermediate temperatures to a disordered state at high temperatures. The morphological assignments were based on TEM and SANS measurements, which also revealed a decrease in the domain size in the spherically ordered state as compared to the cylindrically ordered state. The kinetics of the order−order transition are extremely slow, with the sample exhibiting rheological characteristics similar to a disordered material immediately after heating from the cylindrical to the spherical state. The transition exhibits a long induction period wherein the sample continues to behave like a disordered material followed by a rapid increase in the storage modulus and a final plateau value. The kinetics and rheological characteristics of a material quenched from the disordered state to the spherical state are remarkably similar to those obtained after heating from the cylindrical to the spherical state, suggesting that the transition from cylindrically ordered to spherically ordered microdomains proceeds via a mesoscopically disordered state.

## Introduction

Block copolymers form microphase-separated structures as a result of chain connectivity and the inherent thermodynamic incompatibility between the constituents of the copolymer. Depending on the relative lengths of the constituents, block copolymers can microphase segregate into lamellae, cylinders, and spheres, with several novel microstructures intervening between these broad boundaries such as hexagonally perforated lamellae, hexagonally modulated lamellae, and gyroid being prominent.[1,2] The microphase separation of block copolymers results in many useful mechanical properties and also certain detrimental properties from a processing standpoint, i.e., high viscosities and strong memory effects even in the melt state.

Commercially the most prominently used block copolymers are termed *thermoplastic elastomers* and typically consist of a highly asymmetric microphase separated triblock copolymer with a *hard* segment such as polystyrene as the minority end blocks. Due to the asymmetry, these materials form spherical microdomains with the hard block forming the spherical microdomain and the soft block providing the continuous matrix. This results in a material that behaves at low temperatures like an elastomer and at elevated temperatures as a material that can be processed like a conventional thermoplastic. To render these materials with useful adhesive properties, triblocks are traditionally mixed with diblock copolymers, which also tend to lower the elasticity of the material in the melt, thereby making the material more processible. The diblocks used typically have the same composition and half the molecular weight of the triblock, and the mixture is conveniently produced by synthesizing a diblock copolymer that is then coupled with a relatively inefficient coupling agent.

In this study we focus attention on one such material—a commercial material—Kraton G 1657: a mixture of a styrene−ethylene-*co*-butene-1−styrene triblock (65 wt %) and a matched styrene−ethylene-*co*-butene-1 diblock (35 wt %), each containing 14 wt % styrene. This material exhibits a transition from cylindrically ordered microdomains (at temperatures below the order−order transition) to spherically ordered microdomains (at temperatures between the order−order and order−disorder transition) to a disordered state (at temperatures above the order−disorder transition). In this study we focus on the kinetics and the rheological signatures of the pathway for the transition from cylinders to spheres.

Block copolymers near the order−disorder transition (ODT) and with appropriate composition are expected on the basis of several theories[3−5] to exhibit order−order transitions (OOT). Recent studies by Koppi et al.,[6] Hamley et al.,[7] Hajduk et al.,[8] Sakurai et al.,[9−11] and Ryu et al.[12] have all experimentally confirmed the existence of such an OOT. Koppi et al.,[6] Sakurai et al.,[9−11] and Ryu et al.[12] in fact identify an OOT between hexagonally packed cylinders and body-centered-cubic array of spheres in three chemically distinct block copolymer systems. The transition, which might or might not be accompanied by a change in domain size, was shown to proceed epitaxially; i.e., the cylinder axis coincided with the [111] direction of the cubic lattice of spheres. For systems diluted with a neutral solvent, Sakurai et al.[10] found that the order−order transition is in fact a reversible transition.

The effects of blending of matched diblocks with triblocks on the phase behavior were studied by Gehlsen et al.[13] and Schulz et al.[14] The order−disorder transition temperature, $T_{ODT}$, was shown to vary monotonically with added diblock. Similar results were also obtained by Berglund and Mckay[15] and by Mckay et al.[16] These

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studies also examined the effect of blending on the viscoelasticity and found that the addition of the diblock diminished the complex shear modulus and elasticity of the triblock. The study by Ryu et al.[12] clearly suggests that the architecture of the block copolymer does not affect the existence of the OOT, although the specific temperature of the transition is altered upon going from diblock to triblock architecture.

While the epitaxial nature and thermodynamic underpinnings of the OOT along with the consequences of the OOT on bulk properties such as moduli have been studied,[8−11,17−19] the kinetics of the transition from cylinders to spheres has not been examined experimentally. Recently Qi and Wang[20] have examined the kinetics of the cylinder to sphere OOT using a time-dependent Ginzburg−Landau approach using both computer simulations and a simple analytical two-mode model. Their results suggest that the pathway for the OOT is nontrivial and could be extremely slow.

In this paper we investigate the phase behavior and viscoelastic behavior of a mixture of a diblock and its matched triblock copolymer. We characterize the viscoelasticity of the cylindrically ordered and spherically ordered microstructures using melt state rheology. Using small-angle neutron scattering (SANS) and transmission electron microscopy (TEM), we ascertain our assignment of the microstructure. Furthermore, we study the kinetics of the transition from cylinders to spheres using linear viscoelastic measurements and compare these kinetics with the growth of the spherical structure from an initially disordered state. These studies suggest that the pathway for the transition from cylinders to spheres occurs with an intermediate state that is poorly ordered (or even disordered) and in qualitative agreement with the theory of Qi and Wang.[20]

## Experimental Section

The sample examined in this study was a mixture of a triblock and a diblock copolymer of styrene and ethylene-*co*-butene-1, a commercial sample named Kraton G 1657 supplied by Shell Chemical Co. The sample contains 65 wt % S-EB-S triblock and 35 wt % S-EB diblock, with the triblock being exactly twice the molecular weight of the diblock (as a result of the coupling of the diblock to produce the triblock). The ethylene-*co*-butene-1 block was prepared by saturation of a 1,4−1,2-polybutadiene with 37.5 mol % butene-1 (equivalently saturated 1,2-polybutadiene) as per NMR measurements. The block copolymers contain styrene blocks of $M_w = 5500$ with the total styrene content in the copolymer being 14 wt %. (The $M_w$ of the EB block in the diblock is 35 000 and in the triblock 70 000.) DSC measurements, using a Perkin-Elmer Pyris I DSC, revealed a glass transition temperature of −63.6 °C and melting transition at ∼14 °C corresponding to the thermal transitions of the EB block, with no transitions being discerned for the PS block. The thermal transitions reported are consistent with those of a pure ethylene-*co*-butene-1 polymer containing 37.5 mol % butene-1.[21]

Dynamic oscillatory shear measurements were performed using a Rheometrics ARES rheometer equipped with 25 mm diameter parallel plates and a transducer with an operating range of 0.2−200 g cm. Samples of 2 mm thickness were vacuum molded at 180 °C for 30 min using a force of 1 ton in a Carver press. After loading between parallel plates, the sample was heated to 220 °C and held there for at least 20 min to erase all prior thermomechanical history, and then the temperature was lowered to the ordered state while ensuring that the normal force was always close to zero. Such a procedure was adopted to ensure a macroscopically isotropic reproducible ordered state. Due to the dependence of the viscoelastic properties on the exact thermal history, details of the thermal history in the ordered state are provided along with the results. Oscillatory shear of the form $\gamma(t) = \gamma_0 \sin(\omega t)$, where $\gamma_0$ is the strain amplitude and $\omega$ is the frequency, was imposed, and the measured oscillatory shear stress was broken down into the in-phase storage modulus $G'$ and the out-of-phase loss modulus $G''$. Measurements were carried out as a function of temperature over a frequency range of 0.001−100 rad/s, using small strain amplitudes. The viscoelastic data reported here were ascertained to be in the linear viscoelastic regime by applying higher and lower $\gamma_0$ (typically at twice and half of the $\gamma_0$ for which data are reported in this paper) at select frequencies and ensuring that the moduli were independent of $\gamma_0$. For temperatures greater than 140 °C, the rheometer was operated under an inert nitrogen environment, so as to ensure no thermal degradation. Samples were examined using GPC (at 25 °C in THF, Waters 150 C) after the long annealing studies, and the weight-average molecular weight and distribution were found to be unchanged.

Small-angle neutron scattering (SANS) measurements were performed at the cold neutron research facility at the National Institute of Standards and Technology in Gaithersburg, MD, using the NG3 beamline (30 m SANS).[22] Neutrons with wavelength $\lambda = 6$ Å ($\Delta\lambda/\lambda = 0.15$) were used with a sample-to-detector distance of 6.55 m. Samples were sandwiched between aluminum shear cell plates, and the data obtained are reported as is without any corrections applied. Bulk rheology samples were cryomicrotomed at −130 °C to obtain ultrathin sections (<100 nm thick) for transmission electron microscopy (TEM). These sections were stained using $RuO_4$ and examined using a 160 keV Phillips EM 300 TEM.[23]

## Results

**Thermotropic Transitions.** The linear viscoelastic response of all ordered block copolymers is sensitive to the thermomechanical history of the sample. In addition, due to a slow thermal transition associated with the system studied here (as will be elaborated below), the thermal history was carefully controlled and detailed here. In Figure 1, the linear viscoelastic response as measured by the storage modulus $G'$ and loss modulus $G''$ for a sample first disordered by heating to 220 °C (a temperature that will be later shown to be well above any thermal transitions associated with the system) and equilibrating for 30 min followed by quenching to 120 °C and allowing the sample to equilibrate for several hours. Subsequently, data were obtained in 10 °C (and in some cases 5 °C) intervals, with the sample not allowed to remain at any temperature for more than 45 min. Longer holding times resulted in irreproducible rheological data, which we will later attribute to an order−order transition.

In Figure 1 it is observed that for $T < 140$ °C both $G'$ and $G''$ are adequately represented by $\omega^{\alpha}$, where $\alpha \sim 0.2-0.3$. This power-law behavior is consistent with the viscoelastic response of a hexagonally closely packed (hcp) cylindrically ordered block copolymer.[2,24] For temperatures greater than 140 °C, the low-frequency response of $G'$ and $G''$ is characteristic of a disordered block copolymer,[2,24] i.e., $G' \propto \omega^{>1}$ and $G'' \propto \omega^{1}$. We thus infer that the polymer undergoes a microphase transition in the range of 135 and 150 °C (and denoted temporarily as $(T_{ODT})_{app}$). This is further verified from the results shown as isochronal plots in Figure 2. A gradual drop in the magnitude of $G'$ at low frequencies, corresponding to long times, is observed between 135 and 150 °C.[25]

Figure 3 shows the temporal evolution of the viscoelastic response at $\omega = 0.03$ rad/s and $T = 150$ °C following a temperature jump from 120 °C. The sample had previously been disordered by heating to 220 °C and

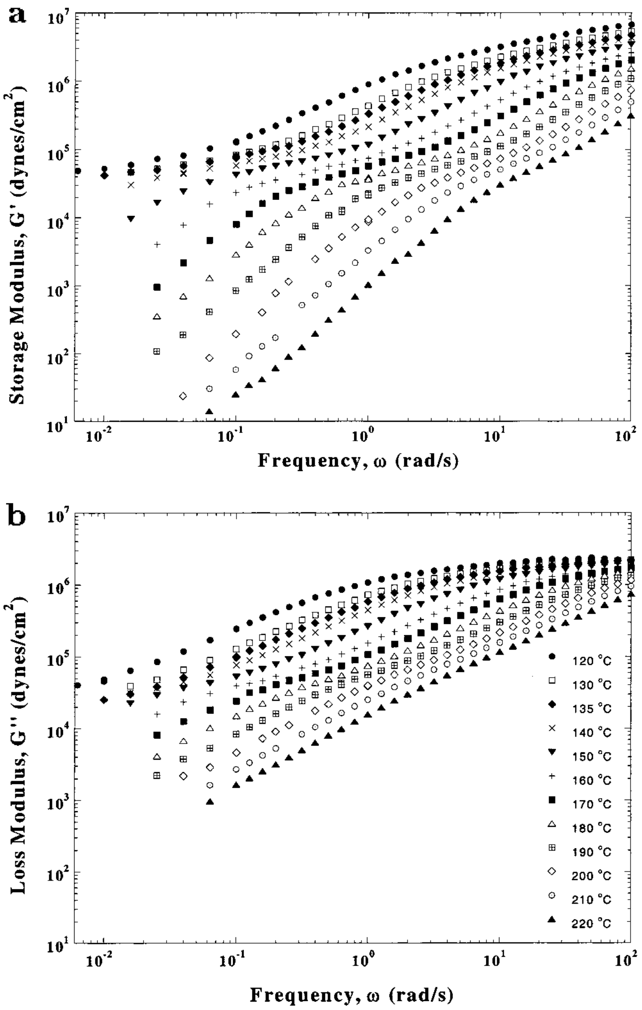

**Figure 1.** Frequency ($\omega$) dependence of the storage (a) and loss (b) moduli, $G'$ and $G''$, respectively, for a sample first heated to 220 °C followed by a rapid quench to 120 °C and subsequent heating in 10 °C steps. The sample was kept at most at any given temperature for no more than 45 min. The linear viscoelastic response was measured by constant strain−amplitude frequency scan isotherms as described in the Experimental Section. The temperatures are noted in the legend of (b).

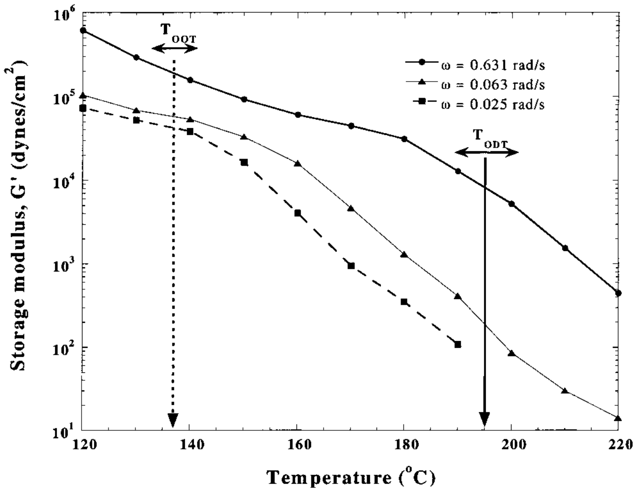

**Figure 2.** Isochronal plots of $G'$ vs temperature for three distinct frequencies for the sample whose thermal history is described in Figure 1. Only a small change in magnitude is observed at the lowest frequency in the region corresponding to the OOT, while no sudden precipitous change is observed near the ODT.

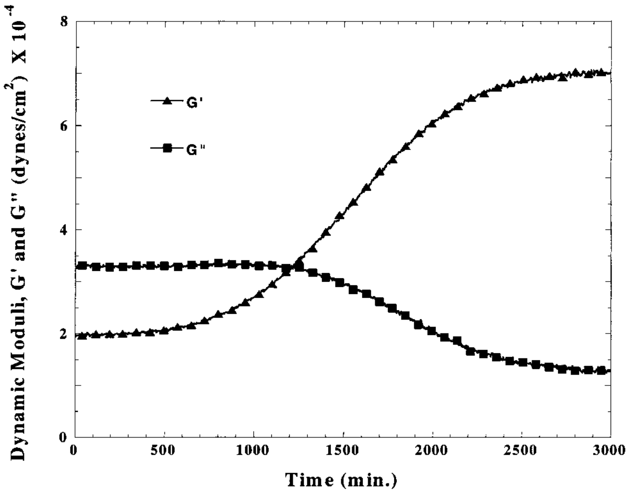

**Figure 3.** Temporal evolution of $G'$ and $G''$ at a frequency $\omega$ = 0.03 rad/s using a constant strain−amplitude $\gamma_0$ = 1.5% at $T$ = 150 °C after annealing at 120 °C for ~24 h. The sample was initially disordered by heating to 220 °C and then rapidly quenched to 120 °C where it was annealed for 24 h before increasing the temperature to 150 °C. Typically the sample temperature equilibrated within 5 min after raising it from 120 to 150 °C.

then quenched to 120 °C, where it was allowed to equilibrate for ~24 h. The conditions of frequency, $\omega$, and strain amplitude, $\gamma_0$, were chosen so as to ensure a linear viscoelastic response with little or no attendant changes in the microstructure as a result of the rheological testing, a torque signal that was larger than the instrumental resolution, and a sampling time that was practically short enough but not at the cost of compromising the sensitivity of the kinetic data. After an initial incubation period of ~650 min, $G'$ abruptly increases and $G''$ abruptly decreases, followed by a saturation after ~ 2000 min at a much higher value of $G'$ and a correspondingly much lower value of $G''$. It is precisely because of this slow transformation kinetics that we adopted a measurement schedule described in Figure 1. Holding times of much longer than 45 min at temperatures greater than 150 °C typically led to irreproducible data. The frequency dependence of $G'$ at 150 °C before (i.e., during the initial incubation period; similar to that shown in Figure 1) and after the thermal annealing is shown in Figure 4. While $G'$ before annealing exhibits homopolymer-like behavior in the terminal regime, the data for $G'$ after annealing exhibit a near frequency independence ($G' \propto \omega^{\alpha}$, $\alpha < 0.1$), suggesting a spherical ordered microdomain structure.[2,24] Interestingly, for a sample quenched from the disordered state (220 °C) to 150 °C, the frequency dependence of the moduli obtained immediately after thermal equilibration is almost identical to the one obtained in the incubation period after a temperature jump from 120 to 150 °C.

We surmise that the sample, in fact, undergoes an order−order transition (OOT) and not an order−disorder transition between 135 and 150 °C. Specifically, because of the observed frequency dependence of $G'$ in the well-equilibrated states at 135 and 150 °C (Figures 1 and 4, respectively), we suggest that at $T$ = 150 °C the sample forms a spherical microdomain structure while at $T$ = 135 °C it forms hcp cylinders.[2,24] Thus, we reassign the thermal transition to be an order−order transition ($T_{OOT}$) and not the previously assigned order−

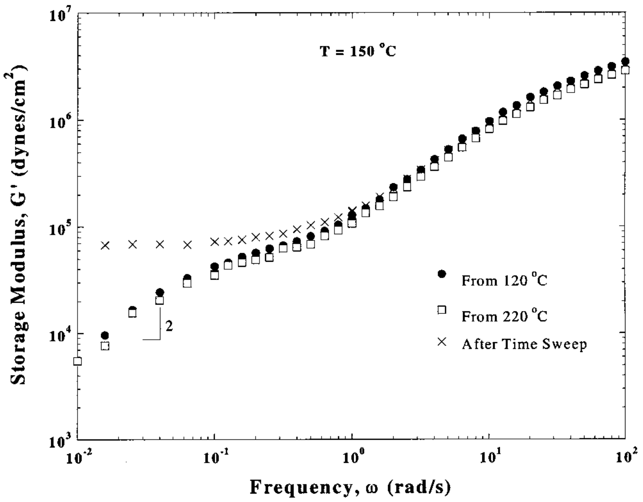

**Figure 4.** Plot of the frequency dependence of $G'$ at $T = 150$ °C before and after the temporal evolution described in Figure 3. Note the distinct change in the frequency dependence of $G'$: going from $\omega^2$ to $\omega^{0.1}$ before and after the temporal evolution. Also shown are the data obtained at $T = 150$ °C after a temperature jump from 220 °C. Note the remarkable similarity in the data obtained after temperature jumps from 120 and 220 to 150 °C.

disorder transition ($(T_{\mathrm{ODT}})_{\mathrm{app}}$). Further, on the basis of ordering studies carried out using the rheological techniques at 135, 140, and 150 °C, and confirming the microstructure at each temperature using TEM (not shown here), we assign this $T_{\mathrm{OOT}}$ to be 138 ± 3 °C. These results will be presented in a separate publication.[27]

The linear viscoelastic properties of this sample after prolonged annealing at 150 °C were obtained by frequency sweeps conducted in 10 °C increments from 120 to 220 °C as shown in Figure 5. Although the cylinder-to-sphere transition is reversible, the kinetics of the sphere-to-cylinder transition (to be published in ref 27) are much slower than that of the cylinder-to-sphere transition and thus does not affect the data presented here. At low frequencies, a dramatic change in slope is observed in the isotherms when going from 190 to 200 °C, indicating a $T_{\mathrm{ODT}}$ of 195 ± 5 °C. Similar behavior is noticed at low frequencies in the isochronal plot as shown in Figure 6. On comparing Figures 1 and 5 at low frequencies for $T < 180$ °C, the frequency dependencies of $G'$ are distinctly different. For $T \geq 200$ °C, the viscoelastic response is identical to that obtained in Figure 1 and is characteristic of a disordered system. The data in Figure 1 for $T > 140$ °C (i.e., for temperatures greater than $T_{\mathrm{OOT}}$) exhibit disordered block copolymer-like behavior. Further, a comparison of the low-frequency behavior at low temperature (i.e., 120 and 130 °C) in Figures 1 and 5 clearly indicates a significant difference; i.e., in Figure 1 $G' \propto \omega^{0.3}$, while in Figure 5 $G' \propto \omega^{0-0.1}$. Another important observation as noted in Figure 5 is that $G'$ at low frequencies remains independent of $\omega$ as the temperature is increased through 150 °C, indicating the spherically ordered structure persists once it is formed, contrary to that seen in Figure 1 regarding the cylindrical microdomain structure. On the basis of the frequency dependence of $G'$ at low frequencies,[2,24] we assign the data in Figure 1 to the hcp cylinder state ($T < 140$ °C), metastable disordered state (140 °C $< T <$ 190 °C), and the disordered state ($T > 200$ °C). On the other hand, the data in Figure 5 represent a spherical state for $T < 190$ °C and that of a disordered polymer for $T > 200$ °C.

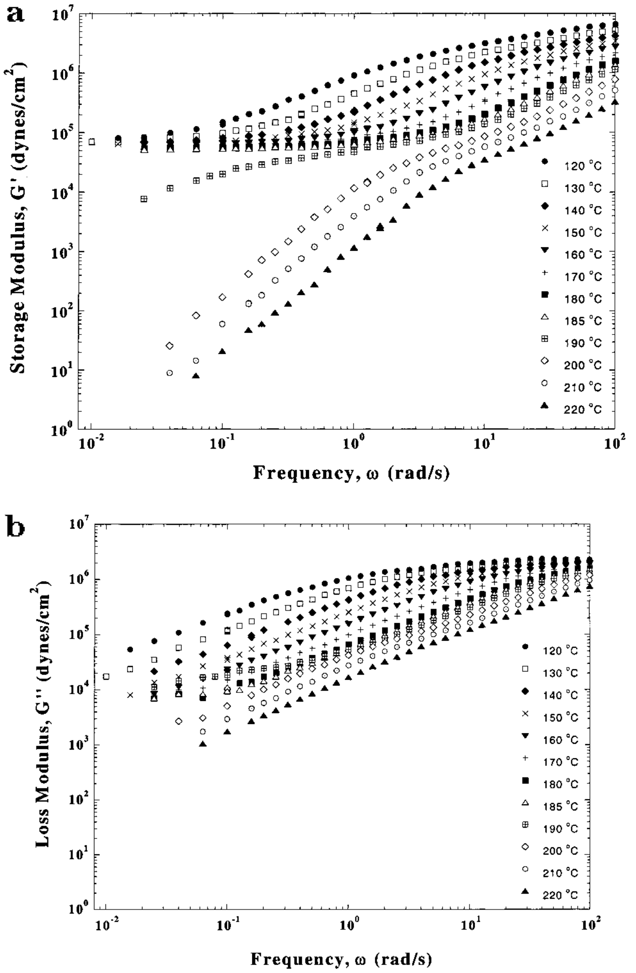

**Figure 5.** Frequency ($\omega$) dependence of the $G'$ (a) and $G''$ (b), for a sample annealed at 150 °C as described in Figure 3. The temperatures are noted in the legend of the figures. The low-frequency behavior for $T < 180$ °C is consistent with the presence of spherical microdomains. The transition of spheres to cylinders is extremely slow and does not affect the data presented here.

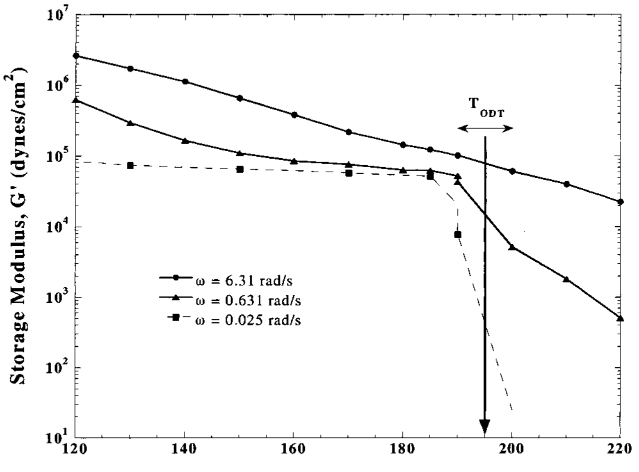

**Figure 6.** Isochronal plot of $G'$ for the sample in Figure 5. Note the abrupt slope change between 190 and 200 °C, indicating a $T_{\mathrm{ODT}}$ while $G'$ is nearly independent of $\omega$ for $T <$ 190 °C.

Support for these structural assignments is provided by TEM micrographs and SANS measurements. The micrographs for samples annealed at 120 and 150 °C (in the absence of external shear) are shown in Figure

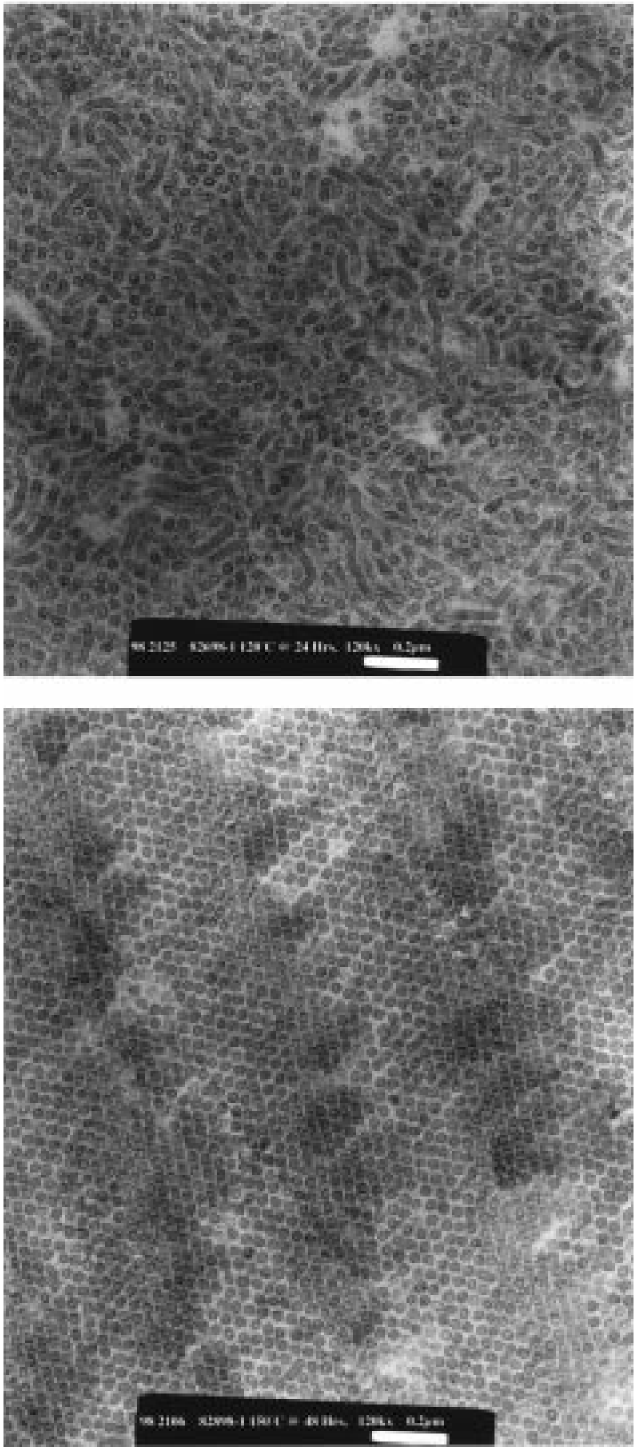

**Figure 7.** Transmission electron micrographs of samples annealed at (top) 120 and (bottom) 150 °C. The samples were stained with $RuO_4$, which is preferentially absorbed by polystyrene. The dark regions correspond to the styrene-rich domains. The sample annealed at 120 °C shows a cylindrically ordered microdomain with an approximate size of 270 Å, and the sample annealed at 150 °C shows a spherically ordered microdomain with an approximate size of 230 Å.

7. The micrographs clearly show the existence of cylindrical microdomains at 120 °C with cylinders of PS with diameters of ~270 Å (shown in dark because of the $RuO_4$ staining), while at 150 °C it exhibits a spherical microdomain with PS spheres of ~230 Å diameter. The cylindrical state micrograph (Figure 7a) exhibits wormlike cylindrical structures and not the classical hexagonally closed packed cylindrical microstructure. These structures can be improved dramatically to exhibit almost single-crystal-like morphology with the application of large-amplitude oscillatory shear.[27] The results of the SANS measurements are shown in Figure 8. For the sample annealed at 130 °C, higher-order peaks at $\sqrt{3}$ are observed, while for the sample annealed at 150 °C higher-order peaks can be discerned at $\sqrt{2}$ and $\sqrt{3}$, consistent with the assignment of cylindrical and spherical microstructures, respectively, at those two temperatures.[6,26] In addition, the primary peak position $q^*$ shifts quite dramatically between the two temperatures ($q^* = 0.023$ Å$^{-1}$ at 130 °C and $q^* = 0.026$ Å$^{-1}$ at 150 °C) and cannot be accounted for by simple thermal expansion. The kinetics of the cylinder-to-sphere transformation is currently being studied by SANS and the subject of a separate paper[27] and will not be discussed further here.

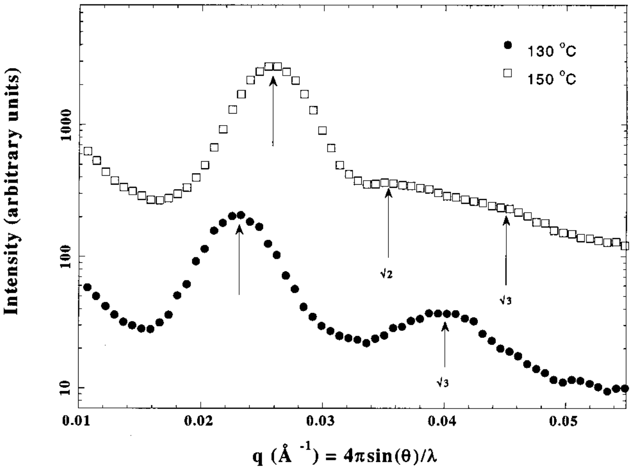

**Figure 8.** Small-angle neutron scattering (SANS) measurements of the sample at 130 and 150 °C. The intensities are in arbitrary units and have not been converted to absolute values. For the sample at 130 °C, reflections are observed with $q$ ratios of $1{:}\sqrt{3}$, while at 150 °C reflections are observed with $q$ ratios of $1{:}\sqrt{2}{:}\sqrt{3}$. Also, the $q$ position of the primary peak is shifted from 0.023 to 0.026 Å$^{-1}$ when the temperature is raised from 130 to 150 °C. This change in domain spacing is consistent with the observations from TEM described in Figure 7.

**Time−Temperature Superposition.** Time−temperature superposition (TTS) was applied to the viscoelastic data in Figures 1 and 5 to generate rheological master curves. Frequency and modulus shift factors, $a_T$ and $b_T$, respectively, were applied with respect to a reference temperature ($T_0$) so as to obtain simultaneous agreement in all viscoelastic functions. Superposition of the linear viscoelastic data was imposed at high frequencies, where the viscoelastic response is expected to be dominated by molecular relaxations and independent of any mesoscopic structure.[28,29] Figure 9 shows the master curves obtained by shifting the data in Figure 1. In Figure 9 and all other master curves discussed hereafter a common reference temperature $T_0$ of 180 °C is chosen. This set of master curves (Figure 9) corresponds to the cylindrically ordered−metastable disordered−disordered states for the block copolymer material. Good agreement is obtained at high frequencies for all the viscoelastic functions. However, significant divergence of the data is observed at low frequencies, particularly for $T > 140$ °C, beyond which the sample is in the metastable-disordered or disordered states. This lack of low $\omega$ superposition could be attributed to the large composition fluctuations that would be expected to be present in the metastable-disordered and

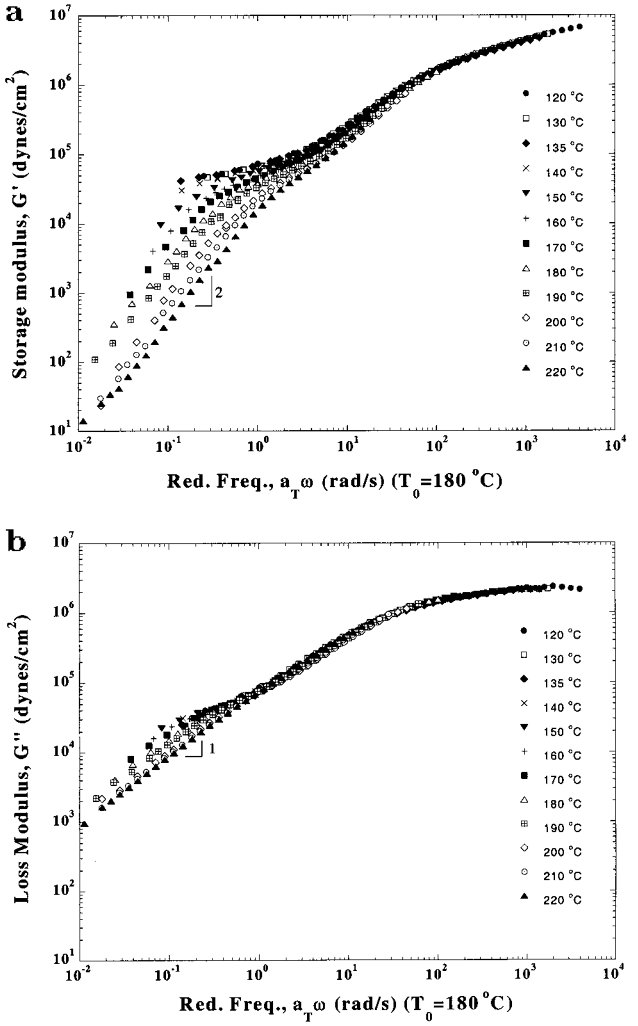

**Figure 9.** Master curve of $G'$ (a) and $G''$ (b) for the sample forming hcp cylindrical ordered microdomain. The data correspond to the set presented in Figure 1 with the basis for superposition being in agreement of all viscoelastic functions at the highest frequencies. The reference temperature $T_0$ is 180 °C, and the horizontal shift factors employed are tabulated in Table 1. Excellent agreement is observed at high frequencies at all temperatures. At low frequencies and for $T < T_{\mathrm{OOT}}$, all the viscoelastic data collapse on to a single master curve. For $T > T_{\mathrm{OOT}}$, no set of shift factors led to superposition of all viscoelastic data over the entire frequency range, and the failure is attributed to the large composition fluctuations associated with the metastable disordered and disordered states.

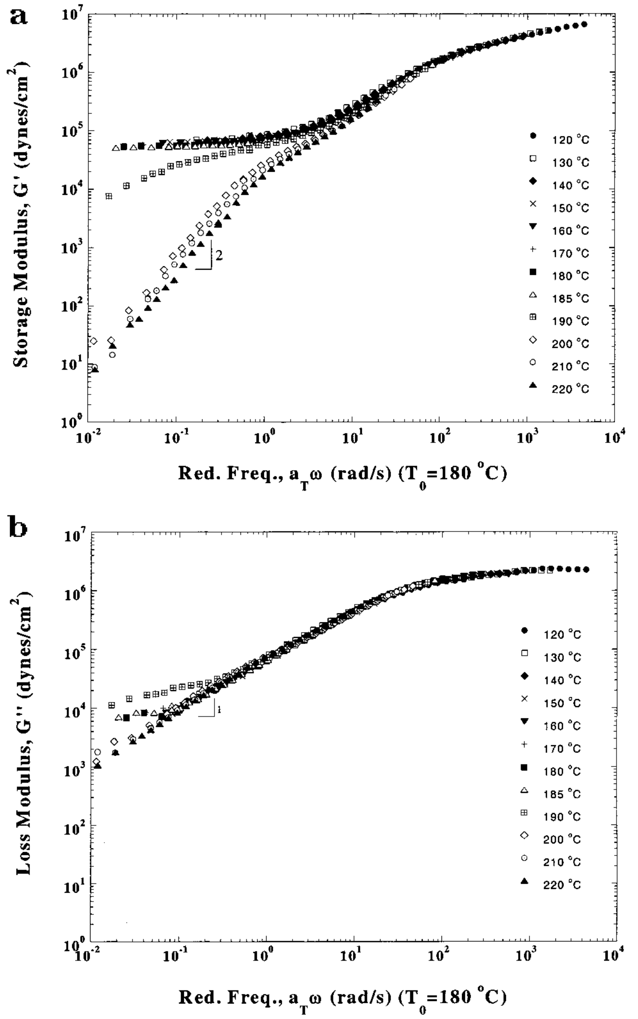

**Figure 10.** Master curve of $G'$ (a) and $G''$ (b) for the sample forming spherically ordered microdomain. The data correspond to the set presented in Figure 5, and the thermal history is detailed in the text. The shifting was performed to achieve superposition of all viscoelastic functions at the highest frequencies with a reference temperature $T_0$ = 180 °C, and the horizontal shift factors employed are listed in Table 1. The data for $T < 180$ °C show remarkable superposability over the entire frequency range. For higher temperatures the data in the low-frequency region diverge presumably due to the large concentration fluctuations present in these systems near the order−disorder transition.

disordered states in the proximity of the ODT[2,24,30−32] or to the continuously evolving microstructure in the metastable-disordered state. Interestingly for temperatures below the $T_{\mathrm{OOT}}$, the viscoelastic data superposed well over the entire frequency range.

The master curves obtained by imposing agreement at high frequencies for the spherical microdomain and disordered (based on Figure 5) states are shown in Figure 10. For temperatures well below the ODT ($T <$ 180 °C), the data superpose well over the entire range of frequencies. On the other hand, the data near and above the order−disorder transition do not superpose well at low frequencies. For $T > 190$ °C we note that $G' \propto \omega^2$ and $G'' \propto \omega^1$, consistent with the behavior of a disordered material.[2,24] The deviation from TTS observed in the disordered state is most likely due to the presence of large composition fluctuations associated with the materials in close proximity to the order−disorder transition. The bimodal molecular weight distribution is not expected to play a significant role in the superposability of the data at times significantly longer than the terminal relaxation time (i.e., frequency much lower than the crossover frequency) of both chemically identical components.[2,24]

The frequency shift factors for the master curves shown in Figures 9 and 10 are tabulated in Table 1. Values for the two sets of data are similar. They vary linearly with $1/T$ and obey the Arrhenius equation with an activation energy of 21.7 ± 1.1 kcal/mol, comparable to the value for an ethylene-*co*-butene-1 polymer with 37.5 mol % butene-1.[21] In addition, the vertical or modulus shift factors $b_{\mathrm{T}}$ were in all cases close to unity, with the value always in the range $0.98 \le b_{\mathrm{T}} \le 1.02$.

## Discussion

On the basis of the viscoelastic data presented in Figures 1−6 and the supporting structural information

**Table 1. Summary of Shift Factors**

| temp (°C) | $a_T$<br>bcc spherical microdomains | <br>hcp cylindrical microdomains |
|---|---|---|
| 120 | 44 | 40 |
| 130 | 17 | 17.5 |
| 135 | | 14 |
| 140 | 9 | 9 |
| 150 | 5.3 | 5.25 |
| 160 | 2.8 | 2.7 |
| 170 | 1.65 | 1.5 |
| 180 | 1 | 1 |
| 185 | 0.82 | |
| 190 | 0.68 | 0.61 |
| 200 | 0.46 | 0.45 |
| 210 | 0.3 | 0.28 |
| 220 | 0.19 | 0.18 |

from TEM and SANS presented in Figures 7 and 8, respectively, the following aspects have been established: there exists an order–order transition temperature ($T_{OOT}$) at 138 ± 3 °C from cylindrical to spherical microdomain structures[25] and an order–disorder temperature $T_{ODT}$ (spherical microdomain to disorder) at 195 ± 5 °C. The order–order transition from cylinders to spheres appears to be mediated, based on the rheological signature, by the disordered state. The kinetics, as measured by rheology, of the cylinder-to-sphere transition appear to be extremely slow. Furthermore, this order–order transition is thermally reversible, although the kinetics of the sphere-to-cylinder transition are considerably slower than that of the cylinder-to-sphere transition.[27] These results are summarized schematically in Figure 11. The apex denotes the disordered state ($T \geq 200$ °C), the two branches represent the two separately attainable ordered microdomains (hcp cylinders and bcc spheres), and the hash in the middle indicates a thermally reversible transformation between the two ordered states due to a slow ordering process.

Estimates of the ODT based on the thermodynamic interaction parameters ($\chi$), the known molecular weights of the constituent blocks, and the mean field phase diagram are consistent with our assignment. We calculate a $\chi$ of 0.095 (based on a reference volume of $\sqrt{v_1 v_2}$, where $v_1$ and $v_2$ are the molar volumes of styrene and ethylene-*co*-butene-1, respectively) for styrene and ethylene-*co*-butene-1 at 195 ± 5 °C. The values of $\chi$ in the literature[26,33] are in the range 0.08–0.11 and accompanied by a rather weak temperature dependence.

Previously order–order transitions have been observed in both the melt and neutral solvent diluted block copolymers. Hajduk and co-workers[8] examined a reversible thermotropic transition in a S-EB-S triblock copolymer from lamellar to cylindrical microstructures using SAXS and TEM. Their results suggested the transition from lamellar to cylindrical microdomains progressed in two steps: initially the fluctuations at the interface between the minority and majority components drive the lamellae to break into a partially disordered array of cylinders followed by annealing of the cylinders of the cylinders into a hexagonally packed geometry. Interestingly, the reverse transformation appears to proceed without any intermediate states.

Hamley et al.[7] have studied the morphological transition from lamellar to cylindrical microdomains in a weakly segregated poly(ethylenepropylene)–poly(ethylethylene) (PEP–PEE) diblock copolymer. They identified two new equilibrium structures, hexagonally modified lamellae and hexagonally perforated lamellae, which intervene the thermotropic transition from lamellae to cylinders.

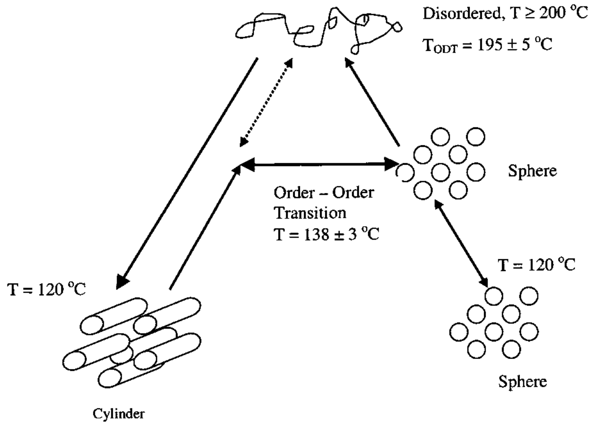

**Figure 11.** Schematic representation of thermal transitions observed in the sample. The transition from cylinders to spheres is reversible. The spherically ordered state is the equilibrium structure for $T \geq 138 \pm 3$ °C, and due to the extremely slow ordering kinetics of the spherical structure (from the disordered and cylindrical structures), we assign a metastable disordered state to intervene between the cylindrical and truly disordered state.

Koppi et al.[6] have studied two asymmetric diblock copolymers of PEP–PEE and examined the nature of the hexagonally closed packed cylinders to body-centered-cubic spheres to the disordered state using rheology and SANS measurements. They find that the transformation occurs epitaxially with no sudden discontinuous change in the value of the primary SANS peak, $q^*$.

Sakurai et al.[9] reported the presence of a thermoreversible morphological transition (MT) between ordered morphologies in polystyrene–polyisoprene (S–I) diblock copolymers in the presence of a neutral solvent. In a later discussion,[10] they demonstrated that the value of $T_{OOT}$ increased with increasing polymer concentration. Furthermore, they also found the thermoreversibility of the cylinder–sphere transition occurred in the solutions with lower polymer concentrations.

In contrast, in our study we employ a diblock–triblock mixture and examine the cylinder-to-sphere transformation in the bulk. Studies by Hajduk et al.[8] and Sakurai et al.[9–11] on AB diblocks and ABBA triblocks of styrene and ethylene-*co*-butene-1 suggest that the order–order transition from lamellae to cylinders is in fact independent of the architecture. However, in the present study it is unclear whether the observed cylindrical-to-spherical microdomain transformation is in fact a result of the blending of the di- and triblocks or a result that is independent of architecture and is solely a result of the composition of the block copolymer.

A recent study by Ryu et al.[12] has examined the influence of the architecture (i.e., AB diblock vs ABBA triblock) on the order–order and order–disorder transitions using rheology, SAXS, and TEM. They examined an asymmetric polystyrene–polyisoprene based diblock and triblock copolymers and clearly demonstrated that the cylinder-to-sphere transitions does occur in both materials. However, the order–order and order–disorder transitions for the triblock are somewhat higher than those for the diblock copolymer. In addition, their SAXS data indicated that the $q^*$ value decreased by about 10% upon transforming the cylinders to spheres, similar to the results described in this work. These results tend to support the notion that the observed effects in this paper are a result of the block copolymer composition and not a result of the blending of the diblock with the triblock. We are currently studying the influence of blending on the order–order and order–disorder transition as well as the kinetics of this transition, and these will be discussed in a future publication.[27]

The nature of the transition from cylinders to spheres as measured by linear viscoelasticity is intriguing. The measurements at 150 °C during the initial incubation period and after complete annealing, shown in Figure 4, suggest that the system first disorders, at least on a mesoscopic scale, before reordering. Further support for this hypothesis is provided by the remarkable similarity of the linear viscoelastic moduli obtained for a sample quenched from the disordered state to 150 °C and that obtained immediately after a temperature jump from the cylindrically ordered state to 150 °C (Figure 4). While the molecular origins of the diminished power-law dependence of the terminal stage viscoelastic properties are an unresolved issue, several different notions have been put forth. It has been suggested that the presence of a mesoscopic structure (i.e., grains) with defects is responsible for the observed frequency dependence.[34,35] Further, it has also been suggested that the tethering of chains to microdomains could also lead to a diminished terminal zone power-law dependence.[35,36] Even though these issues cannot be addressed as a result of this work, the evolution of the terminal zone viscoelastic behavior is significant. The frequency dependence of $G'$ in the terminal zone increases dramatically upon heating the sample from 120 to 150 °C, but with prolonged annealing a near frequency-independent behavior is recovered. This suggests that a poorly defined structure or a disordered state intervenes the structural transformation from cylinders to spheres.

In this light we present in Figure 12 a comparison of the temporal evolution of $G'$ and $G''$ upon cooling from 220 (disordered) to 150 °C and heating from 120 (cylindrical microdomains) to 150 °C. Two observations are to be noted: the values of both $G'$ and $G''$ during the initial incubation period are comparable, and the temporal evolution to the final spherical microdomain structure is remarkably similar.

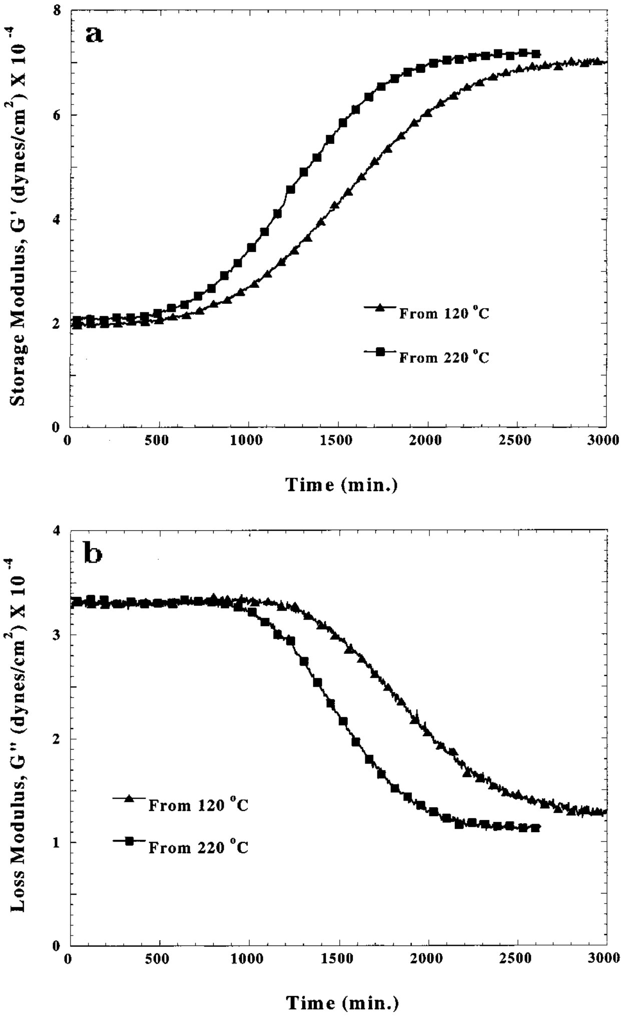

**Figure 12.** Temporal evolution of $G'$ (a) and $G''$ (b) for the sample from two separate equilibrated states: cylindrically ordered ($T$ = 120 °C) and the disordered state ($T$ = 220 °C). Note the remarkable similarity in the initial modulus, the induction period, and growth phase of the development of the spherical structure.

We thus suggest that the transformation of the sample from cylinders to spheres goes through a state wherein the large-scale mesostructure is destroyed either by a disordering process, by dramatically increased fluctuations, or by a dramatic and sudden increase in defect density and shrinking of grains. Structural studies using SANS, SAXS, and TEM are currently underway to probe the precise microscopic evolution of the transformation and the reason for the "disorder"-like bulk viscoelastic behavior exhibited by the sample upon heating from a cylindrical state.[27] This hypothesis and the data presented in this paper are supported by recent theoretical work of Qi and Wang,[20] where they have investigated the kinetics of cylindrical-to-spherical microdomains in a diblock copolymer in the weak segregation limit using a time-dependent Ginzburg–Landau method. They study the kinetics of this transition by monitoring the amplitude of the hexagonal and bcc waves. Upon performing a temperature jump from the hexagonal structure to the bcc sphere phase, the hexagonal waves diminish rapidly, and the spherical waves become appreciable only after considerable time. In the intervening time, i.e., after the relatively short time to erase the hexagonal waves and prior to the long time to develop the bcc waves, the system would be expected to exhibit disordered state-like behavior. This would suggest that, irrespective of the exact molecular origins of the linear viscoelasticity of the hexagonally and spherically ordered microdomains, the system during the incubation period should not be reflective of either a hexagonally ordered or a spherically ordered system and in fact be reflective of a disordered state.

Previous studies[8–11,17–19] of order–order transitions from cylinders to spheres have seldom discussed the kinetics of the transition. In fact, based on the rheological signatures presented in some of those studies, the transition does in fact occur quite rapidly. These studies were typically performed on diblock systems, with one case even using a neutral solvent.[10] The study by Ryu et al.[12] was performed on reasonably high molecular weight styrene–isoprene–styrene triblock copolymers, and even there it appears that the transition does occur quite rapidly. In this light the kinetics reported here are surprisingly slow. It is worthwhile to note that, in both our study and that by Ryu et al.,[12] the $T_{OOT}$ is sufficiently higher than the styrene $T_g$ and unlikely to be the source of difference. On the basis of the linear viscoelastic data presented, in both cases the chains have terminal relaxation times of the order at most of a second (for the polymer studied here at 150 °C the relaxation time is estimated to be <0.1 s), and hence the viscoelastic parameters such as differences in the number of entanglements are unlikely to play a role in determining the observed slowness of the kinetics. The blending of the di- and triblock could be a factor in determining the kinetics of the OOT and is in fact being currently investigated. It is possible that the OOT is different for the diblock and the triblock, a hypothesis that is consistent with the findings of Ryu et al.,[12] and blending causes the OOT to be shifted from that of either pure component. Alternatively, it is possible that the mechanism of the OOT is altered as a result of blending, thereby leading to significantly longer transition times for the blends as opposed to either pure component. These issues will presumably be resolved by a study of the order−order transition kinetics as a function of blend composition and probably more importantly by systematic scattering studies of the transition.

## Concluding Remarks

We have reported the thermal behavior as examined by linear viscoelastic measurements for a mixture of a styrene ethylene-*co*-butene-1 based triblock copolymer with its matched diblock copolymer. The blend undergoes a reversible order−order transition followed by an order−disorder transition at higher temperatures. On the basis of TEM and SANS measurements of the two ordered states, we ascertain that the lower temperature ordered state corresponds to a cylindrical structure, while the higher temperature ordered state corresponds to a spherical microdomain state. Additionally, a sharp decrease in domain size is observed going from the cylindrical to spherical microdomain structure.

The viscoelastic measurements also suggest that the transformation from the cylindrical microdomain structure to the spherical structure is extremely slow—with a long incubation period followed by a rapid increase in the modulus. Further, in the incubation period following heating from a cylindrically ordered state to the spherical state, the viscoelastic signatures associated with the sample are characteristic of a disordered (or metastable disordered) material. Remarkably, the frequency dependencies of the linear viscoelastic storage and loss moduli are identical for a sample quenched from the disordered state or heated from a cylindrically ordered state. Additionally, the temporal evolution of the spherical structure from the disordered state and the cylindrically ordered state are also remarkably similar.

We thus suggest that the pathway from cylindrically ordered to spherically ordered microdomains is mediated by the disordered state or a state wherein the mesoscopic order is poor. Theoretical work by Qi and Wang[20] suggests that in fact the pathway in diblock copolymer from cylindrically ordered to spherically ordered structure is mediated by a relatively long-lived poorly ordered state. Several issues need to be addressed: the nanoscopic pathway associated with the transition and the molecular origins of the slow kinetics in light of much faster kinetics reported for high molecular weight pure diblock and pure triblock copolymers being the most prominent. We are currently investigating the effect of blending on the location of the order−order transition and the kinetics of the order−order transition as well as studying the kinetics of the transition using SAXS and SANS.

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## References and Notes

(1) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990,** *41*, 525.
(2) Fredrickson, G. H.; Bates, F. S. *Annu. Rev. Mater. Sci.* **1996,** *26*, 501.
(3) Leibler, L. *Macromolecules* **1980,** *13*, 1602.
(4) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987,** *87*, 697.
(5) Matsen, M. W.; Bates, F. S. *Macromolecules* **1996,** *29*, 1091.
(6) Koppi, K. A.; Tirrell, M.; Bates, F. S.; Almdal, K.; Mortensen, K. *J. Rheol.* **1994,** *38*, 999.
(7) Hamley, I. W.; Gehlsen, M. D.; Khandpur, A. K.; Koppi, K. A.; Rosedale, J. H.; Schulz, M. F.; Bates, F. S.; Almdal, K.; Mortensen, K. *J. Phys. II (Paris)* **1994,** *4*, 2161.
(8) Hajduk, D. A.; Gruner, S. M.; Rangarajan, P.; Register, R. A.; Fetters, L. J.; Honeker, C.; Albalak, R. J.; Thomas, E. L. *Macromolecules* **1994,** *27*, 490.
(9) Sakurai, S.; Hashimoto, T.; Fetters, L. J. *J. Polym. Prepr., Jpn., Soc. Polym. Sci., Jpn.* **1991,** *40*, 770.
(10) Sakurai, S.; Hashimoto, T. *Macromolecules* **1996,** *29*, 740.
(11) Sakurai, S.; Umeda, H.; Taie, K.; Nomura, S. *J. Chem. Phys.* **1996,** *105*, 8902.
(12) Ryu, C. Y.; Lee, M. S.; Hajduk, D. A.; Lodge, T. P. *J. Polym. Sci., Part B: Polym. Phys.* **1997,** *35*, 2811.
(13) Gehlsen, M. D.; Almdal, K.; Bates, F. S. *Macromolecules* **1992,** *25*, 939.
(14) Schulz, M. F.; Bates, F. S.; Almdal, K.; Mortensen, K. *Phys. Rev. Lett.* **1994,** *73*, 86.
(15) Berglund, C. A.; McKay, K. W. *Polym. Eng. Sci.* **1993,** *33*, 1195.
(16) McKay, K. W.; Gros, W. A.; Diehl, C. F. *J. Appl. Polym. Sci.* **1995,** *56*, 947.
(17) Almdal, K.; Koppi, K. A.; Bates, F. S.; Mortensen, K. *Macromolecules* **1992,** *25*, 1743.
(18) Förster, S.; Khandpur, A. K.; Zhao, J.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W. *Macromolecules* **1994,** *27*, 6922.
(19) Sakurai, S.; Kawada, H.; Hashimoto, T.; Fetters, L. J. *Macromolecules* **1993,** *26*, 5796.
(20) Qi, S.; Wang, Z.-G. *Phys. Rev. Lett.* **1996,** *76*, 1679. Qi, S.; Wang, Z.-G. *Phys. Rev. E* **1997,** *55*, 1682.
(21) Carella, J. M.; Graessley, W. W.; Fetters, L. J. *Macromolecules* **1984,** *17*, 2775.
(22) Hammouda, B.; Krueger, S.; Glinka, C. J. *J. Res. NIST* **1993,** *98*, 31.
(23) Tse, M. F.; Wang, H.-C.; Shaffer, T. D.; McElrath, K. O.; Modi, M. A.; Krishnamoorti, R. *Polym. Eng. Sci.*, submitted for publication.
(24) Adams, L. J.; Graessley, W. W.; Register, R. A. *Macromolecules* **1994,** *27*, 6026.
(25) Although the largest changes in the rheology are observed between 140 and 150 °C, we assign the apparent ODT (later to be assigned as an order−order transition) to 138 ± 3 °C. This assignment was made on the basis of temperature jump annealing experiments carried out from 120 to 140, 220 to 140, and 220 to 135 °C, which revealed that the thermotropic transition was lower than 140 °C and higher than 135 °C. Details of these annealing studies will be reported in a manuscript that is currently under preparation.
(26) Adams, J. L.; Quiram, D. J.; Graessley, W. W.; Register, R. A.; Marchand, G. A. *Macromolecules* **1996,** *29*, 2929.
(27) Modi, M. A.; Krishnamoorti, R.; Tse, M. F.; Wang, H.-C. Manuscript in preparation.
(28) Graessley, W. W. *Adv. Polym. Sci.* **1974,** *16*, 1.
(29) Billmeyer, F. W., Jr. *Textbook of Polymer Science;* John Wiley & Sons: New York, 1984.
(30) Rosedale, J. H.; Bates, F. S. *Macromolecules* **1990,** *23*, 2329.

(31) Bates, F. S.; Rosedale, J. H.; Fredrickson, G. H. *J. Chem. Phys.* **1990,** *92*, 6255.
(32) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1988,** *89*, 5890.
(33) Koberstein, J. T.; Russell, T. P.; Walsh, D. J.; Pottick, L. *Macromolecules* **1990,** *23*, 877.
(34) Koppi, K. A.; Tirrell, M.; Bates, F. S.; Almdal, K.; Colby, R. H. *J. Phys. II (Paris)* **1993,** *2*, 1941. Kawasaki, K.; Onuki, A. *Phys. Rev. A* **1990,** *42*, 3664. Rubinstein, M.; Obukhov, S. P. *Macromolecules* **1993,** *26*, 1740. Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31. Larson, R. G.; Winey, K. I.; Patel, S. S.; Watanabe, H.; Bruinsma, R. *Rheol. Acta* **1993**, *32*, 245. Patel, S. S.; Larson, R. G.; Winey, K. I.; Watanabe, H. *Macromolecules* **1995**, *28*, 4313.
(35) Colby, R. H. *Curr. Opin. Colloids* **1996**, *1*, 454. Krishnamoorti, R.; Giannelis, E. P. *Macromolecules* **1997,** *30*, 4097. Colby, R. H.; Ober, C. K.; Gillmor, J. R.; Connely, R. W.; Duong, T.; Galli, G.; Laus, M. *Rheol. Acta* **1997**, *36*, 495.
(36) Witten, T. A.; Leibler, L.; Pincus, P. *Macromolecules* **1990,** *23*, 824.

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