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Rheology of the Lower Critical Ordering Transition

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ABSTRACT: Linear viscoelastic dynamic rheological measurements were performed on symmetric diblock copolymers of deuterated polystyrene and poly(*n*-butyl methacrylate), denoted P(d-S-*b*-nBMA). Isothermal frequency sweep data were time–temperature superposed. A transition from a disordered to ordered morphology was found with increasing temperature as a function of molecular weight. P(d-S-*b*-nBMA) with molecular weights less than 6.8×10^4 were always disordered, as evidenced by the scaling of the storage and loss moduli with frequency at low frequencies, $G' \propto \omega^2$ and $G'' \propto \omega$. Copolymers with molecular weights above 9.9×10^4 were always ordered, exhibiting very long relaxation times and appearing almost solidlike in the low-frequency limit. Mixtures of the 6.8×10^4 and 9.9×10^4 copolymers, however, showed a transition from fluid to solidlike behavior as the temperature was increased. This rheological data is consistent with the existence of a lower critical ordering temperature, LCOT, where a transition from a disordered to ordered state occurs with increasing temperature.

Introduction

Up to now, diblock copolymers have been extensively studied in the microphase-separated or ordered state with spherical, cylindrical, and lamellar morphologies predominantly observed.[1-4] A transition from a microphase-separated morphology to a phase-mixed or disordered state is seen with increasing temperature. This occurs when the nonfavorable segmental interactions are weakened sufficiently such that the entropy gain on segmentally mixing the copolymer overcomes the enthalpic loss. The transition from the disordered state to the microphase-separated state during cooling has been characterized as a fluctuation-induced first-order phase transition by combined scattering and rheological studies on well-defined systems.[5-10] Theoretically and experimentally, significant concentration fluctuations in the disordered state as one approaches the ordering transition give rise to a pretransitional stretching of the copolymer chains.[10-15]

Recently, small-angle X-ray and neutron scattering studies on a symmetric diblock copolymer of perdeuterated polystyrene and poly(*n*-butyl methacrylate), denoted P(d-S-*b*-nBMA), have demonstrated the existence of a new phase transition in diblock copolymers.[16] Upon heating, P(d-S-*b*-nBMA) undergoes a transition from a disordered to a microphase-separated state. In analogy to the lower critical solution temperature, LCST, seen for some homopolymer mixtures, this transition in diblock copolymers is referred to as the lower critical ordering temperature, LCOT.[16] These results suggest that the classic treatment of the block copolymer phase diagram assuming an incompressible system characterized by a positive segmental interaction parameter, χ, is inappropriate for this case.[11,17] As a result of these findings several theoretical treatments have emerged[18,19] wherein, as with homopolymer mixtures,[20,21] equation of state effects on the interaction parameter are introduced. Although quantitative comparisons with experiment are needed, these theoretical arguments do predict, qualitatively, the observed behavior.

Determining the precise location of the microphase separation transition temperature by scattering methods is complicated by concentration fluctuations in the disordered state, which dominate the scattering near the transition to the ordered state. Rheological measurements, on the other hand, have provided a more sensitive means of evaluating the upper critical ordering transition temperature.[5-8,22] As long as the copolymer remains either phase mixed or microphase separated, data taken over a range of frequencies at different temperatures can be time–temperature superposed. If, on the other hand, the copolymer undergoes a transition from the disordered to ordered state, the dynamic mechanical data cannot be made to overlap by shifts along the frequency axis.

Here, dynamic rheological measurements on pure P(d-S-*b*-nBMA) symmetric diblock copolymers and mixtures of P(d-S-*b*-nBMA) copolymers having different molecular weights are presented. Results from these studies provide strong supporting evidence of the LCOT and demonstrate the molecular weight dependence of the transition temperature.

Experimental Section

Symmetric diblock copolymers of P(d-S-*b*-nBMA) were synthesized anionically. The characteristics of the copolymers are given in Table 1. Samples were melt pressed at 160 °C into disks ~1 cm in diameter with a thickness of 1 mm. In some cases, mixtures of copolymers with molecular weights of 6.8×10^4 (68K) and 9.9×10^4 (99K) were investigated. Here, the appropriate fractions of the copolymers were dissolved in toluene, making a 2% w/v solution. The solution was then dropwise added to a large excess of methanol to coprecipitate the mixed copolymers. The precipitate was allowed to settle overnight, filtered, and then dried under vacuum at room temperature to remove the excess methanol. The powdered

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Table 1. Specifications of Copolymers and Mixtures

copolymer	$M_{w,S}$[a]	$M_{w,c}$[b]		$M_{w,c}/M_{n,c}$[c]	f_S[d]
26K	16000	26000		1.04	0.60
68K	34500	68000		1.02	0.50
72K			mixture		
76K			mixture		
83K			mixture		
87K			mixture		
93K			mixture		
99K	47000	99000		1.04	0.45
170K	93100	170000		1.05	0.53

[a] $M_{w,S}$ is the weight-average molecular weight of the styrene block. [b] $M_{w,c}$ is the weight-average molecular weight of the copolymer. [c] $M_{n,c}$ is the number-average molecular weight of the copolymer. [d] f_S is the volume fraction of styrene in the copolymer.

mixture was melt pressed at 160 °C. In the microphase-separated state, the glass transition temperature, T_g, of the d-PS is 105 °C, as measured using differential scanning calorimetry, whereas the T_g of the P(nBMA) microphase is 34 °C. The lowest temperature at which rheological measurements were carried out was near the T_g of the d-PS.

Rheological measurements were performed using a Carrimed CSL 500 stress rheometer equipped with a high-temperature oven. The cone-and-plate fixture was 1 cm in diameter with a 1° angle. The strain was set at 0.5%, which is within the range of linear viscoelastic response for these materials.[23] Samples were loaded by preheating the fixtures to 150 °C and closing the fixtures slowly to avoid shearing the sample prior to measurements. A nitrogen purge was continuously running throughout the tests to inhibit the oxidative degradation of the copolymer. The dynamic viscoelastic data were obtained isothermally between 50 and 300 °C at 25 °C intervals. At each temperature, measurements were made at a number of discrete oscillation frequencies between 0.0075 and 250 rad/s. The lowest frequency for which data for each temperature are reported was determined by the shear modulus of the sample. Data collected when the shear modulus was too low contained excessive noise and were discarded. After the fixtures had reached the set temperature, an additional minute was allowed for sample equilibration. Size exclusion chromatography was performed on selected samples before and after the rheological measurements to verify the absence of thermal decomposition. The rheological data were reproducible after thermal cycling as long as the sample was not held at or above 275 °C for an extended period of time.

The rheological properties of the P(d-S-*b*-nBMA) diblock copolymers were investigated for each of the molecular weights specified in Table 1. Mixtures of P(d-S-*b*-nBMA) were also studied to adjust the molecular weight such that the LCOT was within the experimentally accessible range of temperature and frequency. Table 1 lists the average molecular weights of the copolymer mixtures, defined as $\bar{M}_w = \sum w_i M_{w,i}$ where w_i is the weight fraction of P(d-S-*b*-nBMA) with a weight average molecular weight $M_{w,i}$.

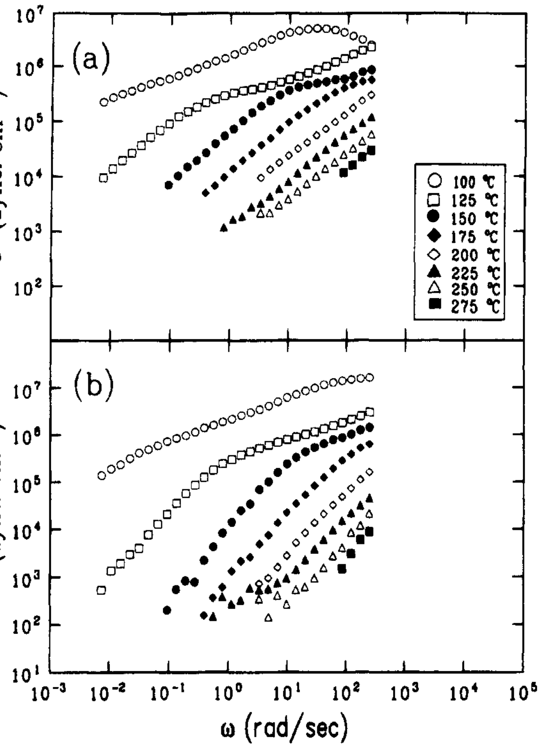

Figure 1. (a) Loss modulus, G'', and (b) storage modulus, G', as a function of the oscillation frequency, ω, for the 68K molecular weight P(d-S-*b*-nBMA) copolymer at the temperatures indicated in the legend.

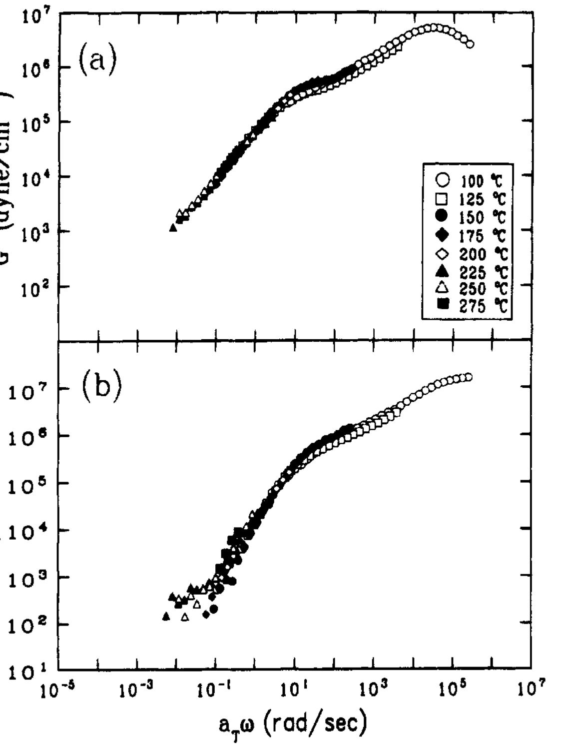

Figure 2. (a) Loss and (b) storage moduli as a function of reduced frequency, $a_T\omega$, for the 68K molecular weight copolymer at a reference temperature of 150 °C.

Results and Discussion

Shown in Figure 1 are, the loss (G'') and storage (G') moduli of the 68K P(d-S-*b*-nBMA) as a function of oscillation frequency, ω, at different temperatures. Neutron and X-ray scattering measurements indicate that this diblock copolymer is phase mixed over the entire temperature range though the scattering increases with increasing temperature. The increase in scattering can be explained by concentration fluctuations in the disordered state that increase with the approach to a microphase separation transition.[17,19] Both G' and G'' are typical for a phase-mixed diblock copolymer where, at high temperatures, G' follows a limiting low-frequency power law behavior close to ω^2 and G'' follows an ω^1 behavior. Using 150 °C as a reference temperature, G' and G'' were shifted along the frequency axis to superpose the data. The shift factors, a_T, will be discussed separately; the data were shifted along the frequency axis to obtain maximum overlap of the data measured at successive temperatures. The shifted data for the 68K copolymer are shown in Figure 2. These master plots, extending over ~8 decades in reduced frequency, show that the superpositioning

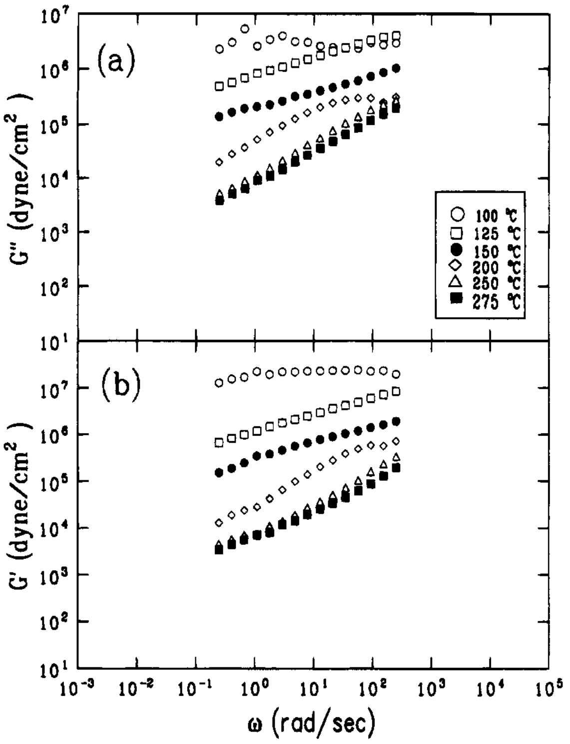

Figure 3. (a) Loss and (b) storage moduli as a function of the oscillation frequency, ω, for the 170K molecular weight P(d-S-*d*-nBMA) copolymer at the temperatures indicated in the legend.

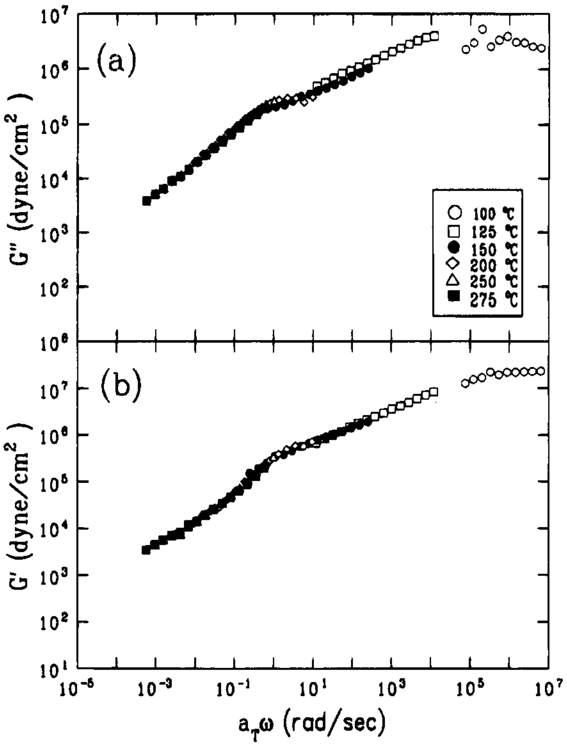

Figure 4. (a) Loss and (b) storage moduli as a function of reduced frequency, $a_T\omega$, for the 170K molecular weight copolymer at a reference temperature of 150 °C.

works well for this copolymer in the phase-mixed state. In addition to the asymptotic behavior observed at low reduced frequencies, there are clear indications of relaxations occurring at reduced frequencies, $a_T\omega$, of $\sim$20 r and $\sim$2 × 10^4 rad/s. The higher frequency relaxation can be attributed to the approach of the glass transition temperature. The origin of the intermediate relaxation is unknown at present. The 26K copolymer shows rheological properties essentially identical to those of the 68K copolymer with the exception that the shoulder in G' and G'' occurring at intermediate reduced frequencies is found at $a_T\omega$ of $\sim$3 × 10^2 rad/s. For both the 26K and 68K copolymers, no evidence of ordering at high or low temperatures is evident. It should be noted that the scatter in the G' data at low frequencies is due to noise in the data since the measurements were done near the lower limit of the torque specification of the rheometer. This scatter in the data does not affect the interpretation of the results.

In Figure 3 G'' and G' for the 170K P(d-S-*b*-nBMA) are shown as a function of the oscillation frequency at the temperatures indicated. Both X-ray and neutron scattering studies have shown that this copolymer is microphase separated over the entire temperature range. G' and G'' for this copolymer exhibit markedly different behavior from the 68K and 26K copolymers. At higher temperatures both G' and G'' follow a limiting power law behavior at low frequencies, varying as $\sim\omega^{1/2}$. This is in keeping with previous studies on microphase-separated diblock copolymers where both components are above their T_g.[6,7] As with the 68K data, G' and G'' were time-temperature superposed by shifting the data along the frequency axis to a reference temperature of 150 °C, as shown in Figure 4. Again, the data were shifted along the frequency axis to obtain a maximum overlap of the data measured at successive temperatures. The shift factors, as will be discussed later, were found to be close to those used for the 68K copolymer. While the behavior for the 170K copolymer is no different from that for other microphase-separated copolymers where both components are above their T_g, again, an intermediate relaxation of the copolymer is observed. This relaxation, characterized by the shoulder in the G' and G'' data, occurs near $a_T\omega \sim 1$ rad/s.

For the 99K P(d-S-*b*-nBMA) X-ray scattering measurements indicate that at $\sim$80 °C the copolymer undergoes a transition from an ordered state to a disordered state (UCOT) and, with further heating, a transition from a disordered state to an ordered state (LCOT) occurs near $\sim$125 °C. G'' and G' for the 99K copolymer are shown in Figure 5 as a function of the oscillation frequency for the different temperatures measured. At higher temperatures, the data for the 99K copolymer are quite different from the data for the other molecular weights. At low $a_T\omega$, neither G'' nor G' exhibits a clear limiting power law behavior as a function of frequency. If anything, the power law is much lower than that for the 170K copolymer. An attempt was made to time–temperature superpose the data for the 99K copolymer. However, the 125 °C data could not be made to superpose on the 150 °C data by shifting along the frequency axis. Shown in Figure 6 are the curves obtained by shifting the data along the frequency axis to obtain maximum overlap between the data at successive temperatures. At high temperatures, the data could be superposed well with shift factors essentially identical to those used for the other copolymers. However, near $a_T\omega \sim 8$ rad/s, G'' and G' exhibit a complex dependence on the oscillation frequency. Extrapolation of the data from the other copolymers suggests that this frequency corresponds to that of the relaxation occurring at intermediate frequencies. One possible reason that the data do not superpose well is that the copolymer is undergoing an ordering transition. However, these data could not be considered as conclusive evidence of an LCOT in this copolymer. Also, the

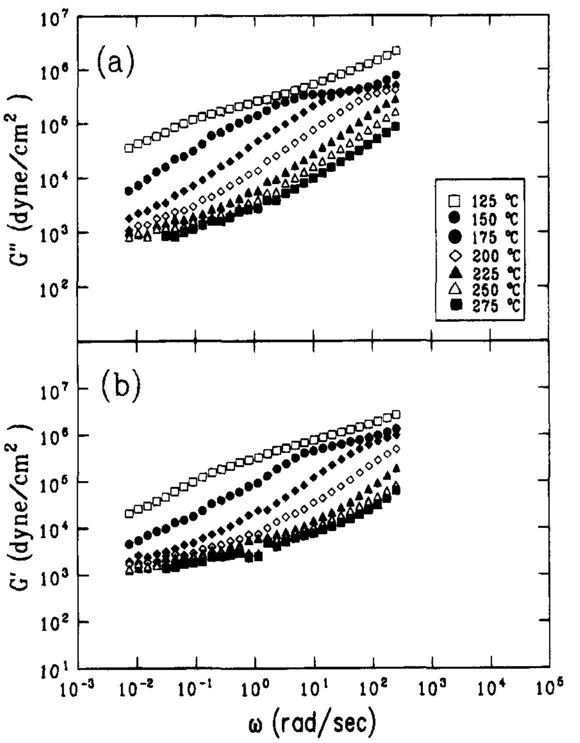

Figure 5. (a) Loss and (b) storage moduli as a function of the oscillation frequency, ω, for the 99K molecular weight P(d-S-*b*-nBMA) copolymer at the temperatures indicated in the legend.

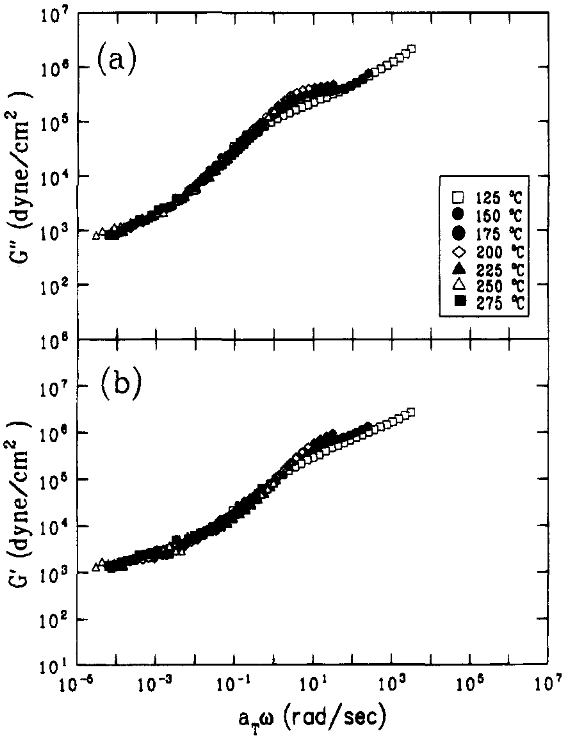

Figure 6. (a) Loss and (b) storage moduli as a function of reduced frequency, $a_T\omega$, for the 99K molecular weight copolymer at a reference of 150 °C.

proximity of the LCOT and UCOT to one another for this copolymer, where there is only a narrow range of temperatures where the copolymer is disordered, could introduce other ambiguities in the interpretation of the rheological data.

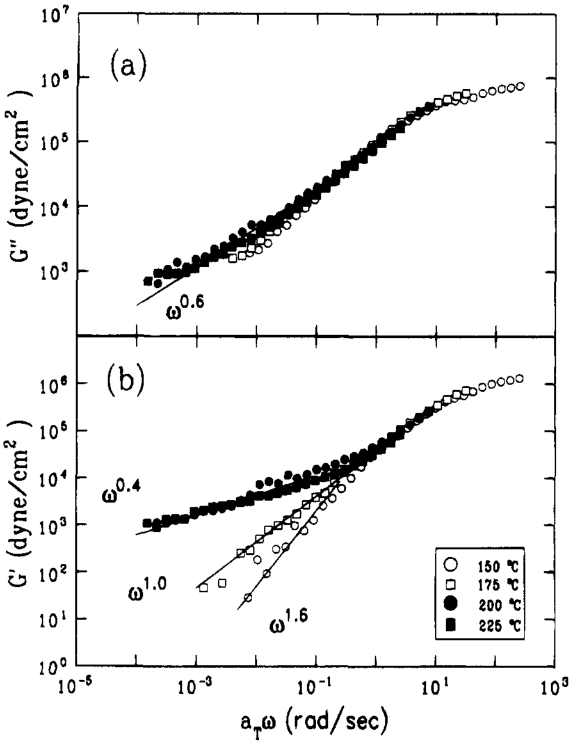

Figure 7. (a) Loss and (b) storage moduli as a function of reduced frequency, $a_T\omega$, for a mixture of the 68K and 99K molecular weight copolymers, with an average molecular weight of 76K, measured at the temperatures indicated in the legend with a reference temperature of 150 °C.

Comparison of the data in Figures 1 and 2 with the data in Figures 3 and 4 shows that the rheological responses of the 68K and 170K copolymers are markedly different. Together with the scattering data, the results are consistent with the copolymer undergoing a transition from a disordered state to an ordered state with increasing molecular weight. In order to obtain a large gap between the LCOT and UCOT and to increase the temperature where the LCOT occurs, mixtures of these copolymers were investigated in a manner proposed initially by Bates and co-workers.[7] Typical results for the mixtures are exemplified by the data shown in Figure 7 for the 76K copolymer mixture. Here, G' is shown as a function of the reduced frequency, $a_T\omega$, where the data were shifted along the frequency axis relative to the data at 150 °C to obtain the maximum overlap in the high-frequency range. For all the mixtures, time–temperature superpositioning was not possible. Between 150 and 225 °C the low-frequency G'' varies as $\omega^{0.6}$. At 150 °C the low-frequency G' varies as $\omega^{1.6}$. However, with increasing temperature the limiting low-frequency power law dependence of G' on ω became 0.4, which is close to the 0.5 power law response characteristic of an ordered morphology. The inability to superpose the data is the signature of a material undergoing a phase transition. Since the increase in the low-frequency G' for the 76K copolymer is not accompanied by a corresponding increase in G'', the microphase separation affects the rheological properties through the formation of an equilibrium modulus rather than by the contribution of very long time scale relaxation modes. Critical fluctuations, on the other hand, are transient in nature but exist in a dynamic steady state so they would tend to contribute a relaxation mode rather than an equilibrium modulus. Studies of creep and recovery are necessary to clarify these issues. In Figure 7a distinct change in the rheological response of the copolymer is observed between 175 and 200 °C. Thus, from the rheological measurements, the

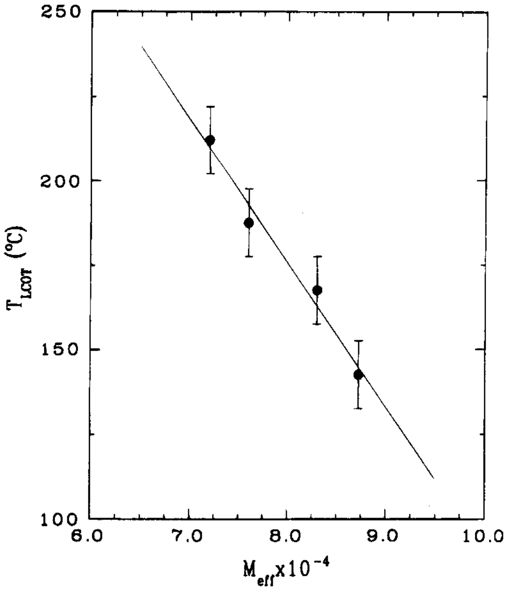

Figure 8. Variation in the LCOT temperature as a function of the weight-average molecular weight for mixtures of the 68K and 99K molecular weight P(d-S-*b*-nBMA) copolymers.

LCOT can be identified as 187 ± 12 °C. In contrast to other copolymers discussed in the literature to date, the P(d-S-*b*-nBMA) copolymer undergoes an ordering transition with increasing temperature. Aside from the inverted temperature response, however, the characteristics of the LCOT seem to be quite similar to those of the UCOT, more commonly called the ODT or MST. Without question, however, the rheological data from mixtures of the 68K and 99K P(d-S-*b*-nBMA) show clear evidence for an LCOT.

It should be noted that the temperature range over which the LCOT occurs in these copolymer mixtures is rather broad, i.e., ~25 °C. None of the pure copolymers studied exhibited a clear transition from the disordered to ordered state. However, by analogy with the poly(ethylenepropylene)−poly(ethylethylene) (PEP−PEE) copolymers, the transition for pure copolymers is expected to be sharp, within a few degrees, whereas the transition for mixtures is broadened. Bates and coworkers[7] speculated that the broadening for the mixtures was due to a solidus−liquidus type of phase behavior where ordered and disordered states coexist within a limited temperature range. While the transition behavior for the P(d-S-*b*-nBMA) mixtures is broad, small-angle neutron scattering studies on these same mixtures[24] yielded no support for a coexistence region, which should exhibit two characteristic length scales associated with the high and low molecular weight rich phases.

From the variation in the viscoelastic properties as a function of temperature, a distinct pattern of changes is observed accompanying the LCOT. Figure 8 shows the temperature at which the LCOT occurs rheologically as a function of the molecular weight, M_w, of the mixture. The transition temperature is seen to decrease linearly with increasing M_w. This behavior can be understood qualitatively by comparison to the UCOT at which the copolymer microphase separates when $(\chi N)_c$ equals a constant, where χ is the Flory−Huggins segmental interaction parameter and N is the number of segments in the copolymer. Since $\chi \propto T^{-1}$, then $T_c \propto N$ as observed. Recent theoretical arguments dealing with the LCOT behavior provide a more quantitative description of the molecular weight dependence of the transition temperature[18,19] and are currently being applied to the systems under investigation here.

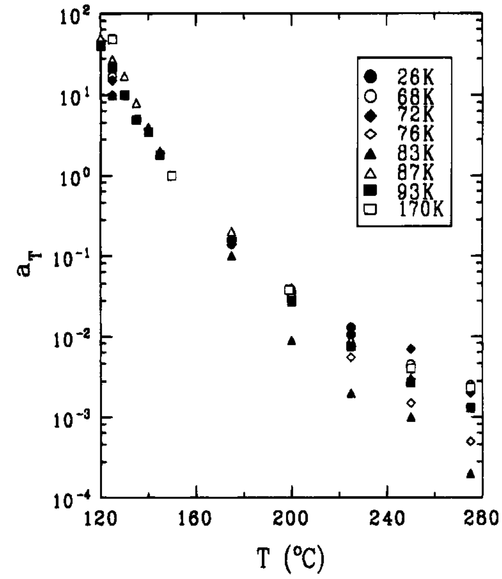

Figure 9. Shift factor, a_T, as a function of temperature for the copolymers and their mixtures, using a reference temperature of 150 °C.

As observed for PEP−PEE block copolymers,[5,6] the shift factor was nearly identical for all systems studied, whether they were pure copolymers or mixtures of copolymers having different molecular weights. Shown in Figure 9 are the shift factors for the pure copolymers and mixtures studied as a function of temperature. With the exception of the 83K mixture data, the shift factors fall on a single curve to within errors associated with superpositioning and decrease monotonically with increasing temperature. From the shift factors alone, no indications of UCOT or LCOT behavior are apparent. This is clearly shown by the data for the 76K P(d-S-*b*-nBMA) mixture where T_{LCOT} = 187 °C, 37 °C above the reference temperature. Since the shift factor is given by

$$\log a_T = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \tag{1}$$

then

$$\frac{T - T_0}{\log a_T} = \frac{-C_2}{C_1} - \frac{1}{C_1}(T - T_0) \tag{2}$$

Consequently a plot of $(T - T_0)/\log a_T$ should vary linearly with $T = T_0$. As shown in Figure 10 for the 76K copolymer mixture, to within experimental error this is found to be the case, even though the copolymer undergoes an ordering transition upon heating. This behavior was similarly reported near the UCOT of the PEP−PEE system.[6]

In conclusion, the rheological data presented are consistent with the existence of a lower critical ordering transition in diblock copolymers of P(d-S-*b*-nBMA) wherein the copolymer undergoes a transition from the disordered to ordered state with increasing temperature. The variation in the viscoelastic properties with frequency and temperature was used to determine the temperature at which the LCOT occurred, and this temperature was found to decrease linearly with increasing molecular weight. From a rheological view-

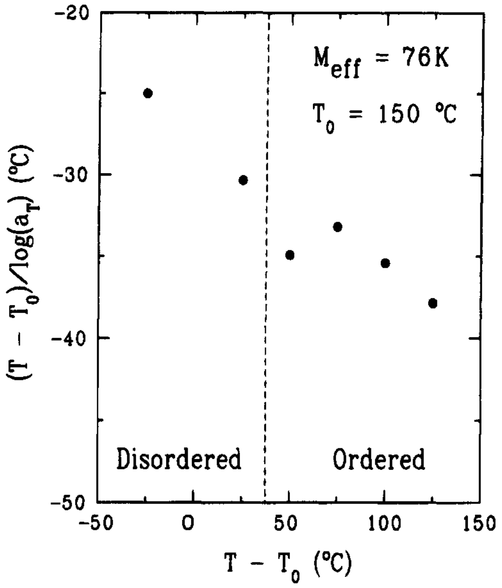

Figure 10. $(T - T_0)/\log a_T$ as a function of $T - T_0$ for 76 K P(d-S-*b*-nBMA) mixture where the reference temperature, T_0, is 150 °C. Temperature regions where the copolymer is ordered and disordered are separated by the dashed line.

point, the LCOT is analogous to the classical UCOT or ODT observed in other diblock copolymer systems.

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