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Rheological Evidence of Composition Fluctuations in an Unentangled Diblock Copolymer Melt near the Order–Disorder Transition

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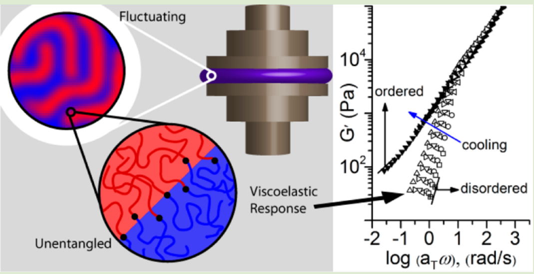
Ⓢ *Supporting Information*

ABSTRACT: Rheological and small-angle X-ray scattering (SAXS) measurements were conducted on a symmetric, low molar mass (M_n = 17.6 kg/mol), poly(*tert*-butylstyrene-*block*-methyl methacrylate) (PtBS-PMMA) diblock copolymer near the order–disorder transition temperature (T_{ODT} = 193 ± 1 °C). Evidence of composition fluctuations is apparent in the low frequency elastic (G′) and loss (G″) moduli and in the temperature dependence of the peak scattering intensity, $I(q^*)$, up to 50 °C above the T_{ODT}. These findings demonstrate that chain entanglements are not responsible for the well-documented fluctuation mode in the terminal viscoelastic regime of block copolymer melts.



The thermodynamics and dynamics of block polymers have been studied extensively, both theoretically and experimentally, over the last several decades.[1−10] Along with addressing certain fundamental scientific issues related to phase transitions in soft materials, understanding these fascinating compounds in the vicinity of the symmetry-breaking transition between a homogeneous disordered fluid and various ordered periodic solids is paramount for practical development of processing strategies and material properties.[11−13] Phase behavior in diblock copolymers, the simplest member of a countless number of possible molecular architectures,[14] is controlled by the degree of polymerization of each block (N_A and N_B), the composition ($f_A = N_A/N$, where $N = N_A + N_B$), and the strength of incompatibility between dissimilar segments, traditionally captured by the Flory–Huggins parameter, χ_{AB}. Here we focus on symmetric diblock copolymers ($f_A \approx f_B \approx 1/2$) where the ordering transition produces a lamellar (striped) phase. In the limit of infinite molar mass ($N \rightarrow \infty$) this order–disorder transition (ODT) is expected to be second-order.[15] Following a seminal paper by Brazovskii,[16] Fredrickson and Helfand[17] introduced fluctuation corrections to the classical mean-field treatment by Leibler,[15] demonstrating that at finite N the transition between disorder and lamellae becomes weakly first-order. Numerous reports have documented the existence and dynamics of the fluctuating disordered state at practical molar masses ($10^4 < N < 10^2$) using small-angle X-ray scattering (SAXS),[18−24] small-angle neutron scattering (SANS),[25−27] dynamic light scattering (DLS),[28−31] rheology,[32−34] dielectric spectroscopy,[35] and tracer diffusion.[36−38] A recent experimental study shows that the weak first-order character persists to surprisingly low values of N (≈ 50).[39]

This letter addresses an important and unresolved issue regarding block copolymer dynamics in the disordered state near the ODT, which have been clearly documented in the low-frequency ($\omega \ll \tau^{-1}$, where τ is the single chain relaxation time) linear dynamic elastic modulus, G′, in entangled systems.[32,33] (Increasing temperature weakens this effect, and this rheological feature disappears at $T_{ODT} + \Delta T$, where $\Delta T \approx$ 50 °C for various well-entangled diblocks.)[46] Several reports dealing with the viscoelastic behavior of relatively low molar mass (i.e., unentangled to marginally entangled) diblock copolymers have failed to show this rheological signature,[34,40−45] leading to speculation that the manifestation of fluctuation dynamics in G′ ($\omega \ll \tau^{-1}$) is predicated on block entanglements.[3,34] We have designed a new diblock copolymer system, poly(4-*tert*-butylstyrene-*block*-methyl methacrylate) (PtBS-PMMA), that is perfectly suited for the investigation of fluctuation effects in the limit of low N where the polymer blocks are *not* entangled. A recent publication details the synthesis and characterization of a relatively monodisperse and nearly symmetric series of PtBS-PMMA diblocks, including the identification of T_{ODT} = 193 ± 1 °C for a sample with f_{PtBS} = 0.53 and total molar mass M_n = 17.6 kg/mol (M_w/M_n = 1.18), referred to here as PtBS-PMMA-236 (N = 236 with a reference volume of 118 Å^3).[47] Neither block in PtBS-PMMA-236 ($M_{n,PtBS}$ = 8.4 kg/mol, $M_{n,PMMA}$ = 9.3 kg/mol) is entangled in the melt state; $M_{e,PMMA} \approx$ 10 kg/mol, and we anticipate $M_{e,PtBS} > M_{e,PS} \approx$ 18 kg/mol, where M_e is the entanglement molecular weight.[48] Dynamic mechanical spectroscopy (DMS) data obtained as a function of frequency and temperature from

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lower (N = 168) and higher (N = 411) molar mass samples were used to establish the Williams–Landel–Ferry (WLF) time–temperature–superposition (TTS) shift factors, $a_T(T)$, for this system.[47] (These materials are characterized by essentially a single glass transition temperature, $T_g \approx 130$ °C, making application of the TTS method particularly robust.)

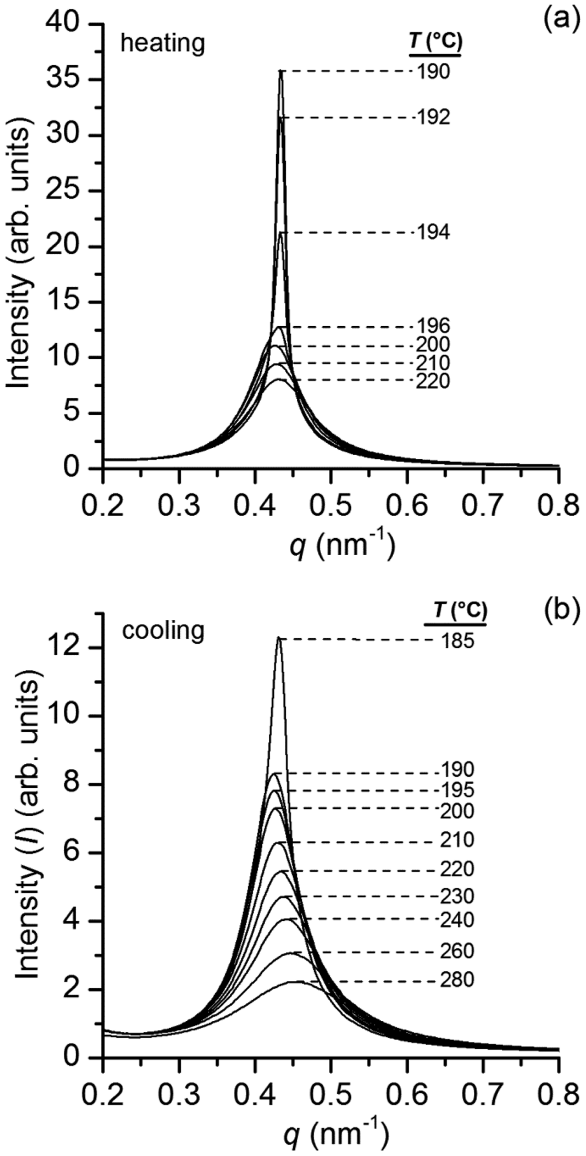

Figure 1. SAXS patterns for PtBS-PMMA-236 obtained while (a) heating and (b) cooling through the T_{ODT}. The dashed lines identify the peak intensity at q^* for the indicated temperatures.

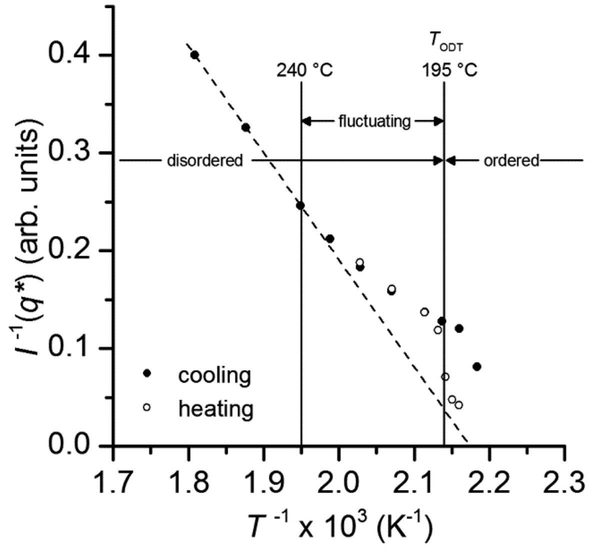

Figure 2. Inverse peak intensity, $I(q^*)$, versus inverse temperature obtained while heating (open symbols) and cooling (closed symbols) PtBS-PMMA-236 showing the fluctuation regime between T_{ODT} = 194 (±1) °C and 240 °C where deviation from linearity (dashed line) occurs.

Azimuthally averaged synchrotron SAXS patterns obtained from PtBS-PMMA-236 are shown upon heating (Figure 1a) and cooling (Figure 1b, and in the Supporting Information) as scattering intensity $I(q)$ (arbitrary units) versus scattering wavevector ($q = 4\pi\lambda^{-1}\sin(\theta/2)$, where λ = 0.073 nm is the radiation wavelength and θ is the scattering angle). The transition between lamellar order and disorder is signaled by a sudden increase in width and decrease in intensity of the principal diffraction peak centered at q^*. Using this criterion T_{ODT} = 195 ± 1 °C based on the SAXS data acquired while heating, consistent within experimental error with the previous assignment.[47] Figure 2 illustrates how the inverse peak intensity varies with inverse temperature. Between 280 and 240 °C, $I^{-1}(q^*)$ decreases linearly with T^{-1} and then curves (concave up) down to 196 °C, followed by a jump down between 196 and 194 °C during heating (open symbols) coincident with the T_{ODT}. The jump in intensity upon cooling (solid symbols) occurs between 190 and 185 °C, which we attribute to hysteresis associated with the first-order nature of the phase transition. This behavior mimics what has been reported elsewhere,[27] and we associate the curvature in $I^{-1}(q^*)$ between 240 and 195 °C with the presence of composition fluctuations.

DMS experiments were conducted on a TA Instruments ARES Rheometer with 25 mm parallel plates maintained under a blanket of nitrogen. Dynamic elastic (G′) and loss (G″) moduli were acquired between 185 and 250 °C using strain amplitudes within the regime of linear response at frequencies $0.01 \leq \omega \leq 100$ rad/s (see Supporting Information). The data were superposed using the previously determined WLF parameters[47] (C_1 = 6.1, C_2 = 128, T_{ref} = 200 °C), and the resulting master plot is presented in Figure 3. Here we emphasize that this master plot was prepared without any adjustable fitting parameters. Above a critical reduced frequency (ω_c) the G′ and G″ data collapse onto individual master curves, while for $\omega < \omega_c$ two distinct branches are evident. Within experimental uncertainty the temperature associated with the transition between these low-frequency branches is coincident with T_{ODT}. Most significantly, the transition to terminal behavior ($G' \sim \omega^2$ and $G'' \sim \omega^1$) at low frequencies varies with temperature over the entire range of measurements in the disordered state, i.e., 194–250 °C. These results duplicate findings presented in previous reports dealing with diblock copolymer melts near T_{ODT}.[32,33] In fact, the low-frequency discontinuous change in G′ provides the most straightforward way to identify the ODT in block polymers. Figure 4 plots the phase angle, $\delta = \tan^{-1}(G''/G')$, versus the reduced frequency, $\log(a_T\omega)$, illustrating an alternative method for exposing the rheological effects of order, disorder, and composition fluctuations in block polymer melts.[34] In the absence of fluctuations the disordered state data in Figures 3 and 4 would

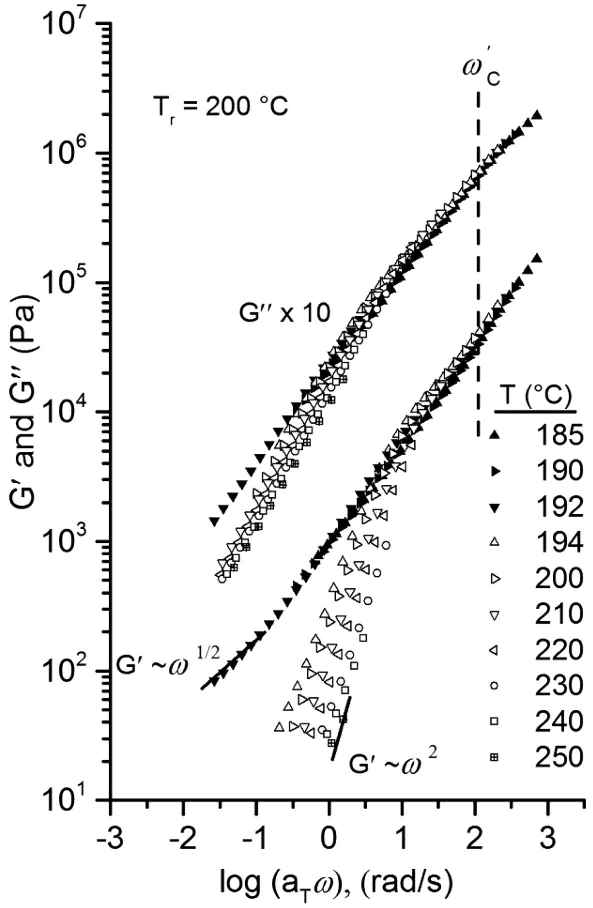

Figure 3. TTS master curves for PtBS-PMMA-236 near the order−disorder transition (T_{ODT} = 193 ± 1 °C) show the effect of composition fluctuations on low frequency ($\omega < \omega_c$) viscoelastic properties as much as 50 °C above T_{ODT}. Shift factors (a_T) were applied without adjustable parameters and are directly obtained from the previously determined WLF equation with a reference temperature of 200 °C and C_1 = 6.4 and C_2 = 128.

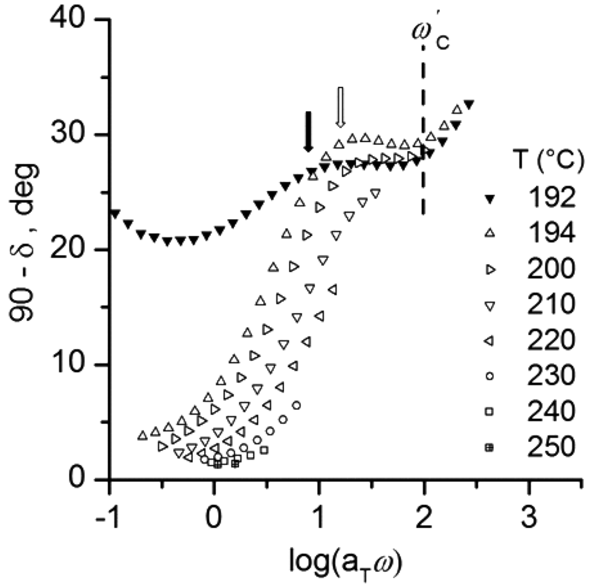

Figure 4. Phase angle as a function of shifted frequency for PtBS-PMMA-236 in the disordered (open symbols) and ordered (solid symbols) states. Development of composition fluctuations with decreasing temperature results in a peak in the phase angle at $\omega < \omega_c$. The associated time τ_{fluc} required to relax locally stored stresses is identified by open (disordered state) and solid (ordered state) arrows just above and below T_{ODT}, respectively.

collapse onto single master curves; ω_c is associated with the frequency in Figure 4 below which the data fail to superimpose. These results provide unambiguous evidence that the rheological signature of disordered state composition fluctuations does not derive from the coupling of entanglements and finite amplitude local (ca. $D \approx 2\pi/q^*$) variations in block concentration.

We believe that the low-frequency features associated with G′ (and to a lesser extend G″) for $T > T_{ODT}$ and $\omega < \omega_c$ reflect interfacial relaxation in transient correlated clusters of locally segregated but globally disordered composition fluctuations. As the disordered melt is cooled toward $T_{ODT,}$ the associated time (τ_{fluc}) required to relax locally stored stresses within the strained clusters shifts to lower reduced frequency. Interestingly, evidence for this relaxation mode persists at $T < T_{ODT}$, i.e., in the lamellar state, as evidenced by intermediate curvature in G′ at $\omega_{lam} < \tau_{fluc}^{-1} < \omega_c$, where G′ ~ $\omega^{1/2}$ for $\omega < \omega_{lam}$, and more prominently in Figure 4 where the mode of relaxation of fluctuations in the ordered and disordered states is identified with solid and open arrows, respectively. All the results reported here for unentangled PtBS-PMMA-236 precisely duplicate G′(ω) and G″(ω) results reported more than 25 years ago for well-entangled poly(1,4-butadiene-*b*-1,2-butadiene) (1,4PB-1,2PB)[32] and poly(ethylenepropylene-*b*-ethylethylene) (PEP-PEE).[33]

Curiously, several previous studies describing the rheological properties of unentangled, or weakly entangled, diblock copolymer melts near the ODT have not identified the fluctuation behavior found in Figure 3. Stühn et al.[40] and subsequently Choi et al.[43] investigated the viscoelastic properties of a nearly symmetric poly(styrene-*b*-isoprene) (PS-PI) sample (M_n = 15.7 and 20 kg/mol) and reported terminal behavior in G′ just a few degrees above the T_{ODT}. Yet SAXS measurements on the same materials confirmed curvature in $\Gamma^{-1}(q^*)$ versus temperature up to 40 °C above $T_{ODT.}$[40] Gehlsen and Bates[41] studied PS-PI (M_n = 17 kg/mol, f_{PS} = 0.46) and the fully saturated counterpart, poly(cyclohexylethylene-*b*-ethylene propylene) (PCHE-PEP), and obtained similar DMS results. All these materials were essentially unentangled ($M_{e,PI} \cong 6$ kg/mol, $M_{e,PCHE} \cong 40$ kg/mol, $M_{e,PEP} \cong 2.7$ kg/mol). (The PCHE-PEP case is somewhat ambiguous since the two blocks have such disparate values of M_e.) The following critical assessment of the application of the TTS technique to rather sparse sets of data in diblocks may help explain these seemingly contradictory results.

Construction of master plots in all the previous rheological investigations (entangled and unentangled) has relied on establishing the TTS shift factors based on frequency scans obtained above and below ω_c. However, unless the results at a given temperature extend sufficiently above ω_c, this process may obscure the true reduced viscoelastic behavior in the terminal regime; i.e., terminal G′ and G″ data can always be made to superimpose notwithstanding the true underlying relaxation times. This issue is germane to the results reported by Gehlsen and Bates[41] and may influence the G′ master plot presented by Stühn et al.[40] ($a_T(T)$ values were not reported in ref 40.) Moreover, the TTS method cannot be rigorously applied to thermorheologically complex block copolymers characterized by widely varying glass transition temperatures (e.g., T_{gPS} = 100 °C and $T_{\mathrm{g,PI}}$ = −70 °C and T_{gPCHE} = 140 °C and $T_{\mathrm{g,PEP}}$ = −60 °C) which necessarily produce very different individual $a_{\mathrm{T}}(T)$ functions. In addition, changing temperature influences the local state of mixing, which also influences the actual T_{g} values and associated shift factors.

To reiterate, we chose the PtBS-PMMA system with these considerations in mind. Similar glass transition temperatures, $T_{\mathrm{g,PtBS}} \cong T_{\mathrm{g,PMMA}}$, justify application of the TTS technique above and below the ODT as demonstrated in an earlier publication.[47] Use of these independently determined WLF parameters circumvents problems associated with shifting isothermal frequency data that may or may not bridge ω_{c}. Figures 3 and 4 were prepared without any adjustments to $a_{\mathrm{T}}(T)$.

Finally, the findings of several elegant tracer diffusion measurements with lamellae forming (entangled) PEP-PEE[49,50] and unentangled poly(styrene-*b*-2-vinylpyridine) (PS-PVP)[49,51] diblock copolymers also contributed to the conclusion that entanglements are a necessary ingredient in explaining the rheological feature attributed to disordered state fluctuation effects. Self-diffusion of diblock chains in ordered lamellae was shown to be strongly influenced by the state of entanglement. Unentangled PS-PVP appears to be unimpeded by a periodic lattice, displaying equivalent diffusion capability perpendicular and normal to the lamellar phase boundary and almost no change in diffusivity across the T_{ODT}. In contrast, diffusion perpendicular to the PEP-PEE lamellae is significantly retarded relative to molecular motion in the parallel direction. A seemingly logical extrapolation of these results led to speculation that locally pseudoperiodic composition fluctuations coupled with the localization of entangled diblock chains at the interfaces impede chain movement thus shifting the longest relaxation time of the melt to beyond the unimpeded single chain reptation time. The results presented here do not support this interpretation of the rheological properties of disordered diblock copolymers as $T \rightarrow T_{\mathrm{ODT}}$ in the disordered state.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Contains additional parameters associated with the rheology and SAXS analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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