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Communications to the Editor

Signatures of the Order−Disorder Transition in Copolymers with Quenched Sequence Disorder

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Systems with quenched disorder such as spin glasses, proteins, and synthetic random copolymers are of broad interest in condensed matter physics, and our understanding of their phase behavior continues to evolve.[1−6] In this communication, we describe an experimental study that sheds light on the nature of phase transformations in a soft material composed of molecules carrying quenched disorder.

Amphiphilic molecules have proven to be excellent materials for studying the physics that underlie the phase behavior of complex systems.[7−10] For example, studying the phase behavior of block copolymers with ordered sequences and well-defined molecular architectures has yielded deep insights into the spontaneous formation of ordered microphases including lamellae, hexagonally packed cylinders decorated with rings, etc. This understanding has, in turn, provided rules for the molecular design of materials with desired morphologies and properties.

Random copolymers, wherein two or more kinds of monomers are connected together in a disordered sequence, are a class of amphiphilic molecules with quenched disorder.[3−6,11−15] A large number of high volume and commercially important materials, such as styrene−butadiene rubber (SBR), acrylonitrile−butadiene-styrene copolymers (ABS), Nafion, and polyurethanes, belong to this category. In addition to their commercial importance, random copolymers seem to be ideal systems for studying the behavior of soft materials with quenched disorder. Field theoretic predictions of phase diagrams of this class of systems clearly demonstrate the possibility of obtaining a wide variety of ordered phases.[3−6,11,12] While evidence for the presence of order has been obtained in some cases,[14] experimental data that probe the thermodynamic properties of copolymers with quenched disorder do not exist. We are not aware of any random copolymer system wherein the order−disorder transition (ODT) has been determined experimentally. The existence of a well-defined transition between two phases (one ordered and the other disordered) is by no means a foregone conclusion because these copolymers are complex multicomponent mixtures composed of different kinds of molecules. This can in some cases lead to coexistence of numerous phases over a broad range of temperatures as predicted in ref 6. Our purpose is to present the first experimental data set that establishes the existence of order−disorder transitions in copolymers with quenched disorder. We also demonstrate that the signatures of the order−disorder transition in these copolymers differ dramatically from those seen in copolymers with well-defined architectures.

A polybutadiene-*graft*-polystyrene copolymer (BgS) with a 77 kg/mol polybutadiene backbone and 10 kg/mol polystyrene branches was synthesized and characterized by methods described in ref 15. The average number of branches per backbone was determined to be 14.2. The volume fraction of the polybutadiene backbone in our randomly grafted copolymer (RGC) melt is 0.39. Both the backbone and branches were synthesized by living anionic polymerization, and they are thus nearly monodisperse. The quenched randomness arises only because the branch points are located randomly along the backbone. The polydispersity indices of the backbone, branches, and the RGC were determined to be 1.02, 1.04, and 1.17, respectively. Our sample has considerable sequence disorder: the number of different molecules that are obtained by randomly locating 14 branches on our polybutadiene backbone is approximately 10^{50}. We studied the properties of the RGC melt as well as concentrated solutions of the RGC in dioctyl phthalate (DOP), a nonselective solvent for polystyrene and polybutadiene. Our samples are labeled BgS[x], where the number in brackets denotes the weight percentage of DOP ($0 \leq x \leq 50$). Since we are interested in the thermodynamic properties of graft copolymers, we do not discuss data obtained below the glass transition temperatures (T_g's) of our samples determined by differential scanning calorimetry (T_g's of BgS[0] and BgS[7] were 68 and 41 °C, respectively). The optical birefringence of the samples was determined using an instrument described previously.[16,17] The fraction of the incident power (wavelength 633 nm) reaching the detector after passing through the sample held between crossed polarizers (P/P_0) was recorded as a function of increasing temperature. Small-angle X-ray scattering (SAXS) experiments were performed at beamline 1-4 at the Stanford Synchrotron Radiation Laboratory. We report the absolute SAXS intensity, I, as a function of scattering vector q ($q = 4\pi \sin(\theta/2)/\lambda$, where θ is the

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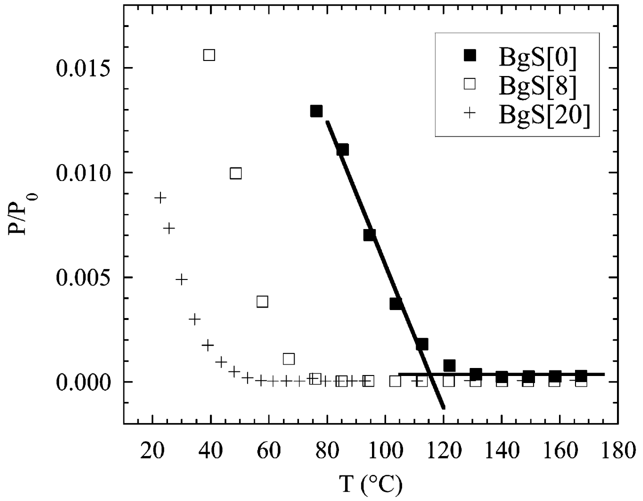

Figure 1. Birefringence signal from BgS[0], BgS[8], and BgS[20] as a function of temperature. The lines through the BgS[0] data represent the results of the two-line least-squares method for determining the order–disorder transition temperature T_{ODT}, as described in the text.

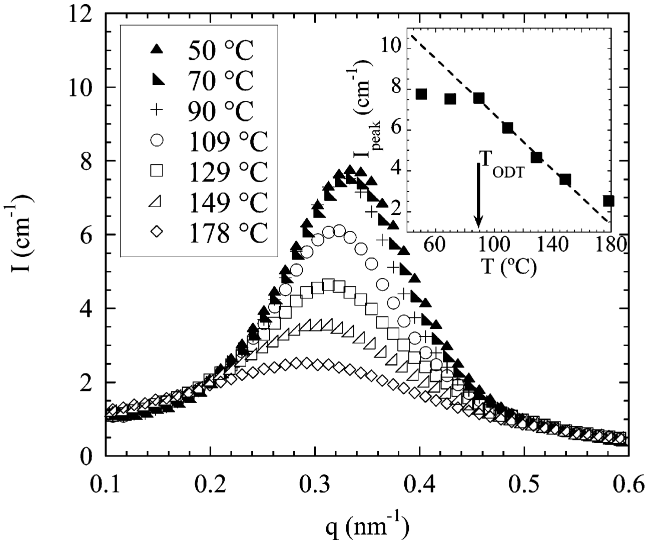

Figure 2. SAXS intensity profiles for BgS[7] upon heating. The inset shows the peak SAXS intensities for BgS[7] upon heating. The dashed line is a guide to the eye and represents an extrapolation of the disordered data. The arrow denotes the T_{ODT} as determined by birefringence.

scattering angle and λ is the wavelength of the incident X-rays). Thin sections (ca. 50 nm) of BgS[0] stained with osmium tetroxide were studied by transmission electron microscopy (TEM) at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory.

Typical birefringence data are shown in Figure 1, where P/P_0 for samples BgS[0], BgS[8], and BgS[20] is plotted vs temperature. In all cases we see a finite birefringence signal at low temperatures, which is a signature of an ordered phase,[16,17] and zero birefringence at high temperatures, which is a signature of a disordered phase. It is clear from Figure 1 that the birefringence signals of all three samples decrease continuously to zero. This suggests that the order–disorder transition in these systems is continuous, as predicted by mean-field theory.[11,12] This is very different from molecules with well-defined architectures such as diblock copolymers, where the decrease in the birefringence signal at the ODT is discontinuous.[9,16,17] The order–disorder transition temperatures (T_{ODT}) of our samples were determined by locating the intersection of the two least-squares linear fits through the birefringence data, as shown for the BgS[0] data in Figure 1. T_{ODT} of BgS[0], BgS[8], and BgS[20] thus determined were 117 ± 5, 74 ± 7, and 44 ± 5 °C, respectively.

Typical SAXS data from our samples are given in Figure 2, which shows data obtained from BgS[7] recorded as a function of increasing temperature. A scattering peak, which could arise from either the presence of a weakly ordered phase or the presence of disordered concentration fluctuations, is seen in the entire temperature window. In the inset of Figure 2 we plot the SAXS peak intensity I_{peak} vs temperature for BgS[7]. We see a clear break in the temperature dependence of I_{peak} in the vicinity of $T = 89$ °C, the order–disorder transition temperature of the sample determined independently from birefringence measurements. Similar breaks in the temperature dependence of I_{peak} were noted for the other samples in the vicinity of the T_{ODT} determined by birefringence.

The SAXS signature of the order–disorder transition in RGCs, seen in Figure 2, is qualitatively different from that observed in systems with ordered sequences and well-defined architectures. In diblock copolymers I_{peak} increases discontinuously at the disorder-to-order transition due to long-range order. In contrast, I_{peak} obtained from ordered RGCs (temperatures below 89 °C in Figure 2) are lower than that expected from extrapolation of data in the disordered state (Figure 2 inset). This suggests that it is difficult to achieve long-range order in RGCs. In Figure 3 we show a typical transmission electron micrograph obtained from BgS[0], which was annealed 10 °C below T_{ODT} for several hours and then cooled slowly to room temperature where the polystyrene vitrifies. A highly defective lamellar phase with limited long-range order is seen in Figure 3. All of our experiments—TEM, SAXS, and birefringence—suggest that the self-assembly of RGCs into ordered structures is affected by severe kinetic barriers. We propose that this is due to the complex molecular architecture of RGCs. The formation of ordered grains in RGCs requires molecules with similar or complementary architectures to be near each other. This, in turn, requires molecular diffusion on length scales comparable to the grain size. In contrast, order formation in melts of copolymers with ordered sequences only requires motion on molecular length scales.[18] The formation of large grains in RGC melts is also hindered by the slow reptation of entangled molecules containing branch points.

The location of the order–disorder transition in RGC melts can be predicted using a mean-field theory.[11,12] In this theory, the value of the Flory–Huggins interaction parameter, χ, at the ODT is given by

$$\chi_{\mathrm{ODT}} = (N + pM)[M_{11}(x_c) + 2M_{12}(x_c) + M_{22}(x_c)]/2[M_{11}(x_c)\,M_{22}(x_c) - M_{12}(x_c)^2]$$

where N and M are the number of repeat units in the backbone and branches, respectively, p is the average number of branches per backbone, and the functions M_{ij} are $M_{11}(x) = N^2g_2(Nx)$, $M_{22}(x) = pM^2g_2(Mx) + p(p - 1)M^2g_1(Mx)^2g_2(Nx)$, and $M_{12}(x) = M_{21}(x) = pNMg_1(Mx)g_2(Nx)$. The functions $g_1(x)$ and $g_2(x)$ are the well-known Leibler and Debye functions, respectively,

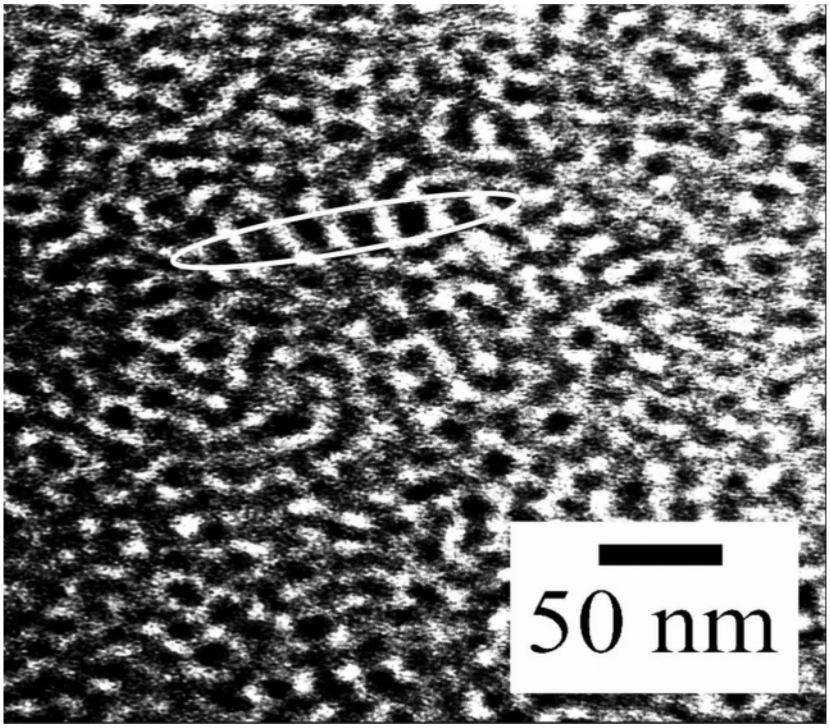

Figure 3. Typical transmission electron micrograph of BgS[0] at room temperature showing a highly defective lamellar phase. Dark regions are polybutadiene-rich. Lamellae are more coherent in some localized regions (e.g., within the oval).

$x = q^2b^2/6$ (b is the statistical segment length of the chains), and x_c is the value of x at the theoretical scattering peak. For BgS[0] ($N = 1578$, $M = 172$, and $p = 14.2$) the theory obtains $\chi_{ODT} = 0.030$.[19] Data from polybutadiene−polystyrene diblock copolymers[20] indicate that χ at 117 °C, the experimentally determined ODT of BgS[0], is 0.036. The agreement between theory and experiment is reasonable, considering the uncertainty in χ and that the comparison is made without using any adjustable parameters.

The peaks in the SAXS profiles obtained from the RGCs in the disordered state clearly indicate the presence of large concentration fluctuations (e.g., BgS[7] in Figure 2). These fluctuations are “announcements” of the impending disorder-to-order transition. As seen in Figure 2, the increase in SAXS intensity at $q > q_{peak}$ is considerably more pronounced than the increase in the SAXS intensity at $q < q_{peak}$. This indicates the amplification of concentration fluctuations with *smaller* length scales as the ODT is approached, leading to an *increase* of q_{peak}. In the inset of Figure 4 we plot q_{peak} vs temperature for BgS[0], BgS[7], and BgS[22]. We find that q_{peak} vs temperature behaviors of the three samples differ substantially; the sensitivity of q_{peak} to temperature increases with increasing solvent concentration. In Figure 4 we plot q_{peak} as a function of reduced temperature, T_{ODT}/T. The data from the three different samples collapse onto a single master curve, indicating that the characteristic length scale of the concentration fluctuations is controlled by the thermodynamic proximity of the systems to their respective ODTs. Note the T_{ODT}s of the samples vary by as much as 84 °C.

For diblock copolymers, q_{peak} decreases as T_{ODT} is approached from the disordered state.[9] This is due to the increased repulsion between the blocks as the ODT is approached. There is no doubt that the repulsion (χ) between the branches and backbone in our RGCs also increases as the ordering transition is approached.

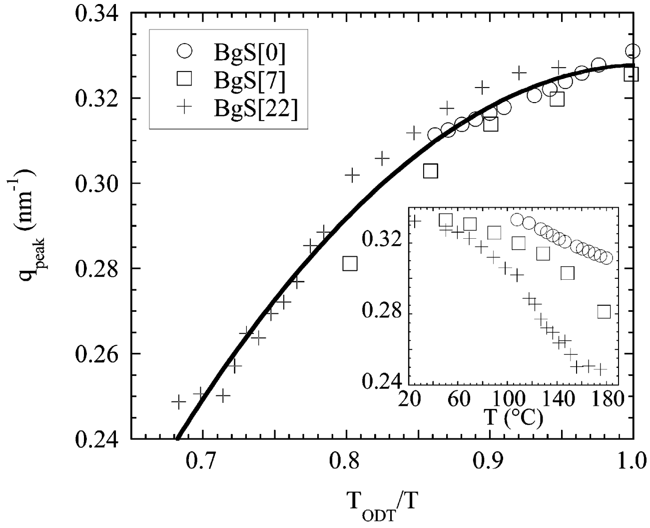

Figure 4. Scattering vector of the SAXS peak, q_{peak}, as a function of reduced temperature, T_{ODT}/T, for BgS[0], BgS[7], and BgS[22]. The curve represents the least-squares quadratic fit through the data. The inset shows q_{peak} vs T.

There is, however, another effect in RGCs that not only compensates for this but also reverses the temperature dependence of q_{peak}. It arises due to the fact that the branch points in our RGCs are distributed randomly along the backbone and that the branch length is much shorter than the backbone. Thus, near the ODT, the concentration fluctuations are dominated by the runs of backbone segments (L) between branch points. As temperature is lowered, shorter runs of backbone segments can participate in microphase separation since it is the product χL that must exceed a threshold for microphase separation.[4,5,11,12]

In summary, we have established the existence of a transition from order to disorder in a copolymer with quenched disorder. It is worth noting that identifying a system with an accessible ODT requires precise knowledge and control over four molecular parameters: N, M, p, and χ. The ODT is announced by subtle and continuous changes in both birefringence and SAXS signals. Kinetic barriers arising due to the presence of quenched disorder and architectural complexity limit the extent of long-range order in these systems. The characteristic length scale of the concentration fluctuations in disordered RGCs decreases as the ordering transition is approached and is a universal function of T_{ODT}/T. The experimentally determined location of the ODT is in reasonable agreement with field theoretic predictions made with no adjustable parameters. These signatures of the ODT of copolymers with sequence disorder are, however, dramatically different from those seen in copolymers without sequence disorder.

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