

Observation of a Discontinuity in the Value of I_m^{-1} at the Order–Disorder Transition in Diblock Copolymer/Homopolymer and Diblock Copolymer/Diblock Copolymer Blends

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The order–disorder transition (ODT) of block copolymers has attracted substantial interest due to the industrial and scientific importance of these materials. Block copolymers and their blends are used in an array of industrial products. In addition, the nature of the ODT is an interesting problem in polymer physics. Initial studies of diblock copolymers in the weak segregation limit (close to the ODT) concentrated on the deviation from linearity in the dependence of the reciprocal of the peak scattered intensity, I_m^{-1} , on $1/T$, the reciprocal of temperature.^{1–7} The temperature at which this deviation occurred was considered the ODT temperature. This criteria arose from the predictions of the mean-field theory of Leibler⁸ and such calculations were extended to blends as well.⁹

Mean-field theory predicts that the scattered intensity $I(q)$ at a scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$ (λ is the wavelength of the X-ray beam, and θ , the scattering angle) is given by the relation $[I(q)]^{-1} \sim F(q) - 2\chi$ where $F(q)$ is a function that depends on the blend composition, radius of gyration of the block copolymer, R_g , and nature of the polymers (volume fraction of each block and molecular weight) and χ is the Flory interaction parameter.^{8,9} $F(q)$ has a minimum, and hence $I(q)$, a maximum at a particular value of q , q_m . In the mean-field theory, the value of q_m is considered constant with respect to temperature although it does weakly depend on temperature through the temperature dependence of R_g . The value of χ changes with temperature, T , and is usually described by an equation of the form $\chi = A + B/T$ where A and B are constants. Under the condition $\chi = F(q_m)/2$ the value of $[I(q_m)]^{-1}$ is zero, and the value of $I(q_m)$ diverges, which marks the mean-field spinodal point of the system. In the disordered state, the value of I_m^{-1} changes linearly with $1/T$.

It has been pointed out that the mean-field description of Leibler does not take into account the effect of thermal noise (fluctuations).^{8,10} A fluctuation correction has been calculated by Fredrickson–Helfand (FRH), though only for high molecular weight copolymers.¹⁰ The FRH theory predicts a deviation from linear behavior in the plot of I_m^{-1} vs. $1/T$. Experimentally, it has recently been observed that the order-disorder transition of pure diblocks shows the effects of thermal fluctuations

in the form of nonlinearity in the plot of I_m^{-1} vs. $1/T$ and, more dramatically, a discontinuity in the plot of I_m^{-1} or σ_q , the half-width at half-maximum (HWHM) for the scattering maximum, against $1/T$.^{11–17} This sharp discontinuity has also been identified as indicating the ODT. These results are important, as they suggest that the effect of thermal fluctuations in pure diblock copolymers is substantial. Also, it shows that there are at least two characteristic temperatures for these systems: T_{ODT} , which is characterized by the discontinuity in I_m^{-1} vs. $1/T$, and T_{MF} , the mean-field-to-non-mean-field crossover temperature, which is characterized by deviation from linear behavior in I_m^{-1} vs. $1/T$ and the onset of experimentally observed fluctuation effects.¹⁶

To our knowledge, similar observations for diblock copolymers blended with either homopolymer or other diblock copolymers have not yet been reported. Such a point is important, as it would show experimentally the failure of the mean field theory, which may suggest fluctuations are universally important in understanding the behavior of these systems. Also, such data would promote deeper understanding of fluctuation effects. Furthermore, it would suggest that there also exist two characteristic temperatures for these blends parallel to that seen in pure diblock; an ODT and a crossover from non-mean-field-to-mean-field behavior. Here, we present data on a series of diblock copolymer blends with homopolymer and another diblock copolymer that *clearly* show a discontinuity in the value of I_m^{-1} vs. $1/T$ and σ_q^2 vs. $1/T$ similar to that seen in neat diblock copolymers. We expect this observation of the discontinuity will stimulate ongoing theoretical efforts by showing experimentally the universality of a discontinuity at the ODT and experimental efforts by pointing out a more appropriate criteria for the ODT, which until now, has not appeared in the literature for blends.

EXPERIMENTAL AND METHODS

Diblock copolymers, polystyrene-*block*-polyisoprene (SI), were synthesized by living anionic polymerization with *sec*-butyllithium as an initiator and cyclohexane as a solvent. The polymer was characterized by GPC. Polystyrene homopolymer was obtained from Tosoh Corporation and has a number average molecular weight of 6100. The polymer characteristics are tabulated in

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Table I. Characteristics of polymers used in this study

Name	M_n	M_w/M_n	Volume fraction PS
SI-11/9	19600	<1.05	0.51
SI-7/8	14600	<1.05	0.48
S-6 (b)	6100	<1.05	1 (homopolymer)
SI-10/10	20000	<1.05	0.47

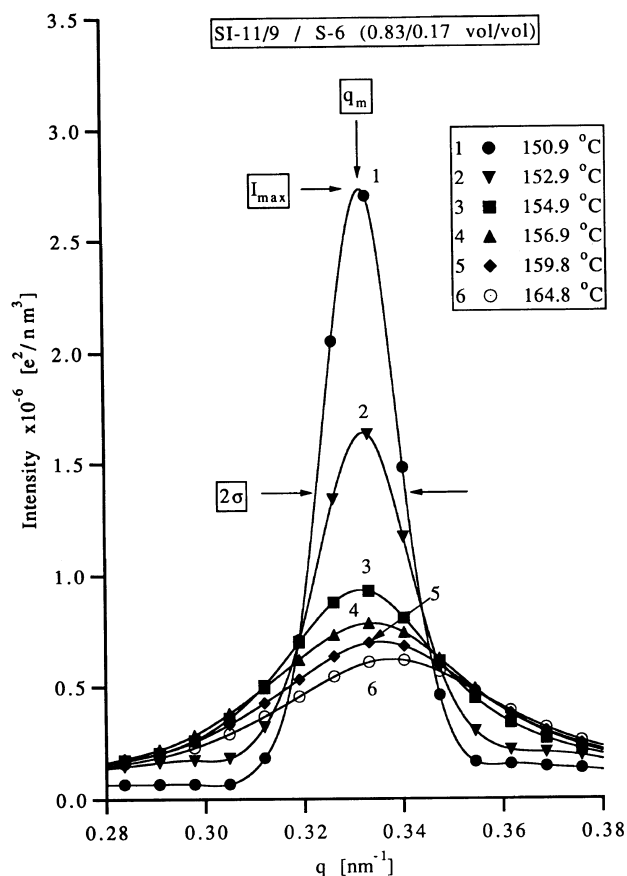
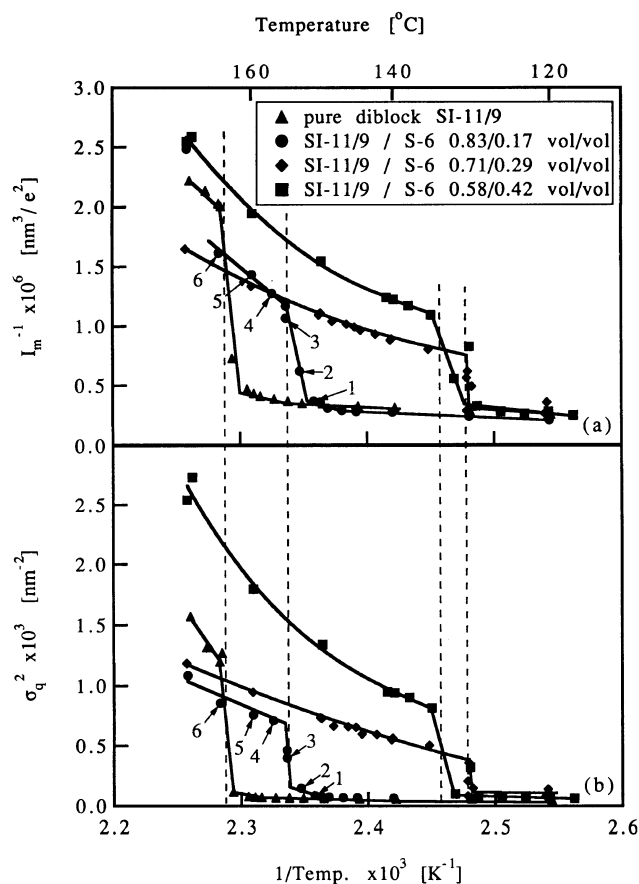
**Figure 1.** Desmeared scattered intensity from a blend of 0.83 volume fraction diblock SI-11/9 and homopolystyrene S-6 at temperatures above and below T_{ODT} (157°C). The number assigned to each profile corresponds to that assigned to each point in Figures 2a and 2b.

Table I and designated according to the scheme presented by Winey *et al.*¹⁸ Samples were cast from toluene solution and annealed before measurement.

Temperature-dependent small-angle X-ray-scattering, SAXS, was measured *in-situ* with a SAXS apparatus described elsewhere, except for the replacement of the X-ray generator with a new one (MAC Sciences M18X HF operated at 16 kW) for some experiments.^{19–21} All measurements were conducted in an evacuated chamber to reduce thermal degradation. At each measuring temperature the samples were held for about 45 min and measured for about one hour. SAXS profiles were desmeared for slit-width and slit-height smearing, and corrected for air scattering, absorption, and thermal diffuse scattering.^{19–21} Measurements were performed while the samples were both heated and cooled.

RESULTS AND DISCUSSION

The desmeared scattered intensity from a diblock copolymer (SI-11/9) blended with homopolymer (S-6) is

**Figure 2.** Summary of scattering results for neat diblock, SI-11/9 and blends of various compositions with homopolystyrene, S-6. (a) Reciprocal of maximum scattered intensity I_m^{-1} vs. reciprocal of absolute temperature, $1/T$. (b) square of peak half-width at half-height, σ_q^2 , vs. reciprocal of absolute temperature, $1/T$. The number assigned to each point corresponds to that assigned to each profile in Figure 1.

shown in Figure 1, with particular attention being drawn to the first-order scattering peak measured above and below the ODT temperature. We note that there is a large increase in peak height and a substantial decrease in peak width as the sample becomes ordered. Thus, for a series of peaks, we can summarize the behavior of each with the parameters of I_m^{-1} and σ_q^2 , the square of the peak half-width at half-height. While σ_q^2 is not independent of I_m^{-1} , it is a useful parameter as it is free from error in the absolute intensity measurement, and thus serves as an important check on the experimental data. From the location of the maximum, q_m , we can obtain the wavelength of the dominant mode of the fluctuations, $D = 2\pi q_m^{-1}$, which we will discuss in future work.²²

In Figure 2, we show plots of the reciprocal maximum scattered intensity, I_m^{-1} (Figure 2a), and the square of the peak HWHM, σ_q^2 (Figure 2b), against reciprocal temperature, $1/T$, for the pure diblock copolymer SI-11/9 and its blends with homopolystyrene S-6. As expected, I_m^{-1} and σ_q^2 show parallel temperature dependent behavior. Furthermore, we observe a sharp discontinuity in the values of I_m^{-1} and σ_q^2 at a particular reciprocal temperature corresponding to the ODT for each blend composition. From Figures 1 and 2 we note the following for the ODT behavior for the blend of SI-11/9/S-6 (0.83/0.17) vol/vol: onset of the ODT above 150.9°C and completion of the ODT below 156.9°C; the data in between the two temperatures show the coexistence of

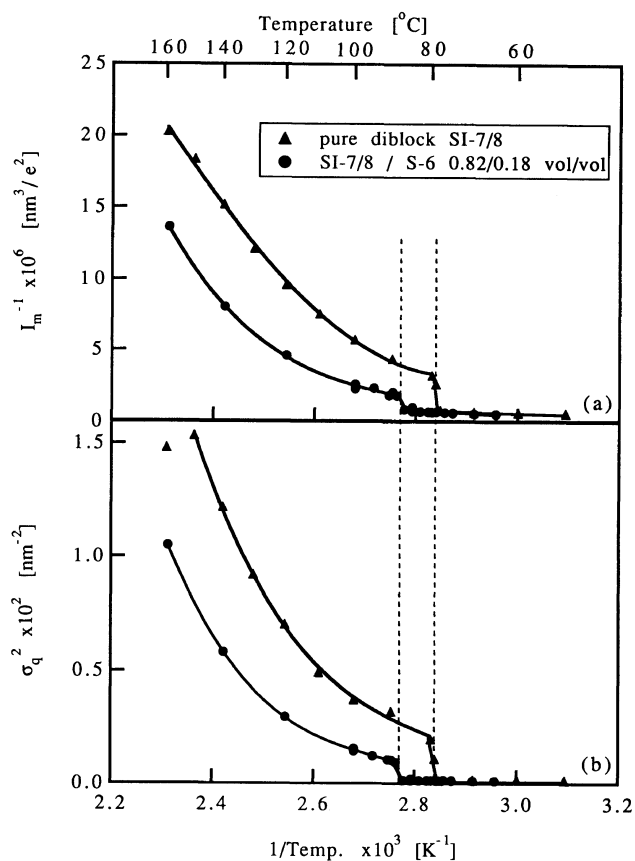


Figure 3. Summary of scattering results for neat diblock SI-7/8 and 0.82 volume fraction diblock blend with homopolystyrene, S-6. (a) Reciprocal of maximum scattered intensity, I_m^{-1} vs. reciprocal of absolute temperature, $1/T$. (b) square of peak half-width at half-height, σ_q^2 , vs. reciprocal of absolute temperature, $1/T$.

the ordered and disordered phases. The temperature interval of this coexistence depends on the time scale of observation. The data for the other samples should be interpreted similarly.

Due to the observation of a discontinuity in I_m^{-1} and σ_q^2 vs. $1/T$ at the ODT, which clearly indicates that the ODT is a thermally induced first-order phase transition, we do not expect mean-field analysis to be meaningful close to the ODT. However, at higher temperatures above T_{MF} (further from the ODT temperature), beyond those measured here, we expect that such an analysis remains useful.

In Figure 3, we show similar data for a lower molecular weight diblock SI-7/8 and its blend with homopolymer S-6. Again, the values of I_m^{-1} and σ_q^2 have a similar temperature dependence and show sharp discontinuities at a particular temperature. This is evidence that the behavior observed for the blends in Figure 2 is not unique to one particular diblock copolymer molecular weight, but may be a general phenomena. The results shown in Figures 2 and 3 reveal that T_{ODT} depends on both the composition of the blends and the molecular weight of the constituent polymers.

In defense of the mean-field approach, we should point out that the mean-field treatment qualitatively predicts the change in the T_{ODT} with composition and molecular weight observed here. However, there are no quantitative theories at present which predict the T_{ODT} and its variation with composition and molecular weight. We note

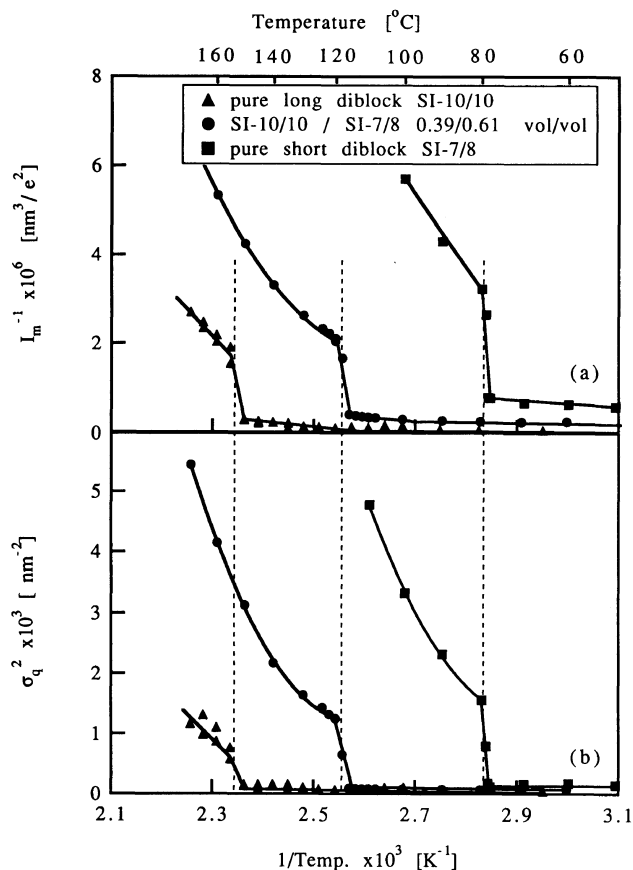


Figure 4. Summary of scattering results for neat diblocks SI-10/10 and SI-7/8 and a blend of the two with 0.61 volume fraction diblock SI-7/8. (a) Reciprocal of maximum scattered intensity, I_m^{-1} vs. reciprocal of absolute temperature, $1/T$. (b) square of peak half-width at half-height, σ_q^2 vs. reciprocal of absolute temperature, $1/T$.

that the FRH theory correctly describes the nature of the ODT transition, but is expected to be appropriate only for higher molecular weight polymers.

So far, we have discussed results from blends of a diblock copolymer and homopolymer. Results from a series of measurements on a diblock copolymer SI-10/10 as well as its blend with another, shorter diblock copolymer SI-7/8 (used above) are shown in Figure 4. Again, for both the pure diblock copolymer and its blend we observe a discontinuity in the values of I_m^{-1} and σ_q^2 which mark the ODT. Since the ODT temperature of the blend is between that of either of the neat diblock copolymers, we conclude that this blend forms a single phase system. These results are further evidence that such a discontinuity is seen in a broad array of diblock copolymer systems.

The above results show that the previous observations regarding pure diblock copolymers also hold for their blends¹⁶: fluctuation effects may be quite important in attempting to describe the behavior of diblock copolymer blends as well as neat diblocks. Furthermore, it points out that an experimental attempt to describe the phase behavior of these systems should consider this discontinuity in I_m^{-1} vs. $1/T$ or σ_q^2 vs. $1/T$ as indicating the onset of ordering. Finally, it implies that the mean-field treatment is not appropriate for describing the behavior of these materials close to the order-disorder transition. In the future, the relationship between the ODT and the mean-field-to-non-mean-field crossover for

blends as well as neat diblocks is a topic worth examining. The discontinuity may also result from order-order transitions, though this is not the case in our systems here. The details along this line will be described elsewhere.²²

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