Density and Concentration Fluctuations in Poly(styrene-*b*-phenylmethylsiloxane) Copolymers

G. Floudas,* S. Vogt, T. Pakula, and E. W. Fischer

Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany

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ABSTRACT: Small-angle X-ray scattering (SAXS) is employed to study the density and concentration fluctuations near the microphase separation in poly(styrene-*b*-phenylmethylsiloxane) copolymers. The former were calculated from the measured isothermal compressibility and are continuous throughout the transition. The residual SAXS background intensity due to local concentration fluctuations is a sensitive probe of the order–disorder transition. The same results have been obtained by independent computer simulations of dense diblock copolymer melts.

Diblock copolymers have attracted many theoretical and experimental efforts with the aim of understanding the transition from the disordered homogeneous phase into a variety of microstructures composed of periodic ordered phases. In a mean-field theory of the microphase-separation transition (MST), established by Leibler,[1] the phase behavior of diblock copolymer melts was defined by two variables: χN and f, the product of the interaction parameter χ with the total degree of polymerization N ($=N_A+N_B$, with N_A and N_B being the number of segments in blocks A and B, respectively) and the composition f ($=N_A/N$). Accordingly, the structure factor in the disordered state is

$$NS_L^{-1}(Q) = F(x,f) - 2\chi N \quad (1)$$

where $x = Q^2R_G^2$ and $F(x,f)$ is related to Debye pair-correlation functions of a Gaussian diblock copolymer. It has been shown that eq 1 provides a quantitative description of the scattering profiles only at $T > T_{MST}$. Among the predictions of this approach is that the MST is a second-order transition for $f = 0.5$ and a first-order transition for $f \neq 0.5$ and that the $S_L^{-1}(Q)$ should vary linearly with T^{-1}(eq 1) and should become zero at the spinodal ($F(x^*,f) - 2(\chi N)_s = 0$). Fredrickson and Helfand[2] introduced fluctuation corrections to show that the spinodal is suppressed and the order–disorder transition (ODT, in this notation), for symmetric diblocks, is a weakly first-order phase transition. Furthermore, they have identified windows in composition through which it is possible to pass from the disordered phase to each of the ordered microphases with only one controlling parameter: T. These theoretical predictions have been verified experimentally by SANS[3] and rheological investigations[4,5] on poly(ethylenepropylene-*b*-ethylethylene) copolymers by Bates and others.

Small-angle X-ray scattering (SAXS)[6–8] has been used extensively to study the concentration fluctuations which give rise to the maximum of the static structure factor at Q^* (Q^* being the most probable wavevector). Relatively little is known, however, about the behavior of pure density and local concentration fluctuations near the order–disorder transition temperature (T_{ODT}). In this study we evaluate (i) the density, (ii) the concentration fluctuations around Q^*, and (iii) the local concentration fluctuations present in diblock copolymers. The concentration fluctuations at Q^* and the local concentration fluctuations provide evidence for the ODT, whereas the density fluctuations are not influenced by the transition.

The samples used in this study are three poly(styrene-*b*-phenylmethylsiloxane) [P(S-*b*-MPS)] copolymers with molecular weights of 2.8×10^4, 5.5×10^4, and 6.4×10^4 and compositions (in PS volume fraction) $f_{PS} = 0.32$, 0.5, and 0.45, respectively, and with a polydispersity (M_w/M_n) of less than 1.1. The SAXS measurements were performed with a Kratky camera as described in detail elsewhere[9] within the temperature range 219–463 K. The scattered intensity as a function of Q ($=4\pi/\lambda \sin(\theta/2)$, where $\lambda = 0.154$ nm is the wavelength of X-rays and θ is the scattering angle) is shown in Figure 1 for temperatures in the range 298–413 K for the asymmetric diblock ($M_w = 2.8\times10^4$). The peak in the low Q range is due to the "correlation hole" effect,[10] whereas the increasing "background" at higher Q is due to density *and* concentration fluctuations (see below). Notice that the two effects have opposite temperature dependences, and this creates problems in the evaluation of the peak parameters (peak intensity, width, and integral intensity) at high T. The extrapolation to the $I(Q\to0)$ is made using $\tilde{I}(Q) = \tilde{I}(0)\exp(bQ^2)$ as shown in the inset of Figure 1. Data points from the high Q range ($2\ \text{nm}^{-1} \le Q \le 2.8\ \text{nm}^{-1}$) were used which are unaffected by the peak centered at $Q^* = 0.36\ \text{nm}^{-1}$. Other power laws (i.e., $\tilde{I}(Q) = a + bQ^n$ with $n = 4$ and 6) may also fit the data. In fact, in a plot of $\tilde{I}(Q)$ vs Q^4 the experimental data lie on a straight line over a broad Q range and the extrapolated $\tilde{I}(0)$ is ~8% higher than the one shown in the inset of Figure 1. The pure density fluctuations in the block copolymer were computed from the measured isothermal compressibility $\beta(T)$, obtained from pressure–volume–temperature (PVT) measurements on the same sample as described in detail elsewhere.[9] The PVT measurements were made with a pressure dilatometer in the temperature range 296–522 K. Then the measured $\beta(T)$ was converted into $I(0)$ using

$$I(0) = n^2k_BT\beta_T \quad (2)$$

where n is the average electron density, and this facilitates the comparison with the $I(0)$ obtained from SAXS (see Figure 3). We discuss next the temperature dependence (i) of the peak intensity $I(Q^*)$ and (ii) of the background intensity $I(0)$.

The peak intensity is plotted in Figure 2 as a function of inverse temperature. The two sets of data correspond to the $I(Q^*)^{-1}$ with (filled circles) and without (open circles) background subtraction. In the former set of data the background due to pure density fluctuations was evaluated from the measured isothermal compressibility according to eq 2. At $T < 300$ K, $I(Q^*)$ is largely unaffected by the subtraction of the background because of the high peak

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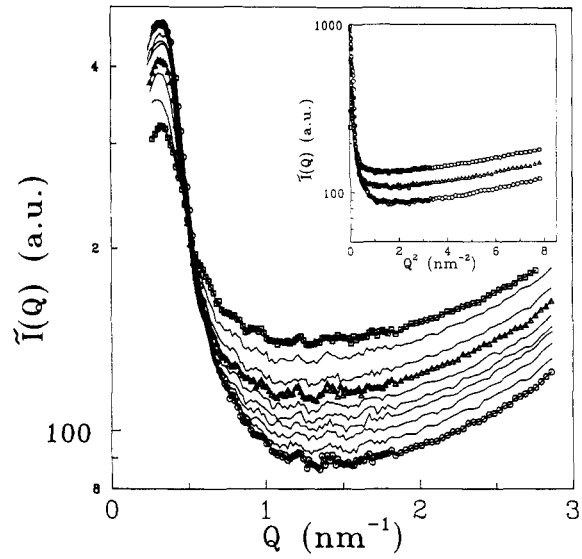

Figure 1. Semilogarithmic plot of the slit-smeared intensity $\tilde{I}(Q)$ as a function of Q, plotted for different temperatures in the range 298–413 K. In the inset, data from three temperatures [(○) 298 K, (△) 363 K, and (□) 413 K] are plotted vs Q^2.

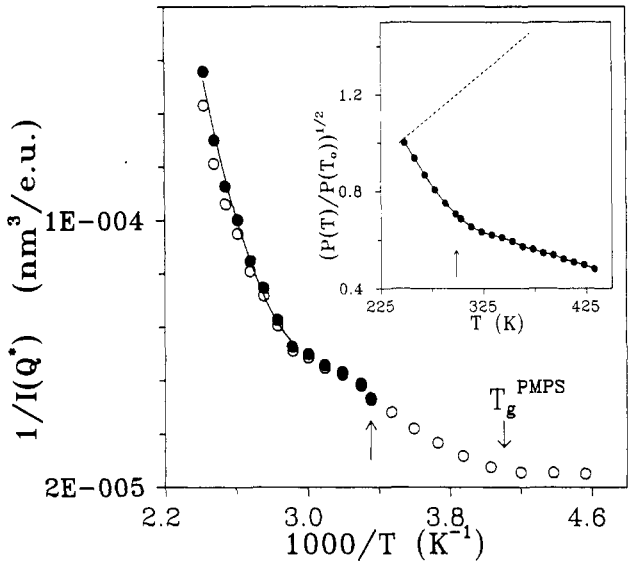

Figure 2. Inverse peak intensity vs reciprocal temperature with (●) and without (○) background correction. Notice that the correct evaluation of the background intensity results in a curvature at high T. In the inset the square root of the scattering power P, which has been corrected for the background due to density fluctuations, is plotted as a function of T. The dashed line gives the calculated scattering power according to eq 4. The arrow indicates the transition temperature.

intensity, but at $T > 300$ K this situation is no longer true and the subtraction of the density fluctuations leads to a pronounced curvature at higher T. The nonlinearity of $I(Q^*)^{-1}$ vs T^{-1} is a direct consequence of fluctuation effects present in the disordered state well above T_{ODT} and can be described by an additional term in the mean-field structure factor ($c^3d\lambda S^{1/2}(Q^*)/N$; ref 2). The T_{ODT} is identified in Figure 2 by the small discontinuity occurring at $T = 298$ K (arrow in Figure 2). The constancy of $I(Q^*)^{-1}$ at lower temperatures is a result of the glass transition T_g of the PMPS component ($T_g^{PMPS} \sim 251$ K) and signifies the freezing of all possible rearrangements below this temperature. A second T_g—due to the PS block—could not be resolved in the DSC curves (taken with heating rates of 10 and 20 K/min and after annealing for 12 h at 333 K), and this is consistent with the continuous behavior of the $\beta_T(T)$ (see Figure 3). However, it has been shown[11] that a coupling between ODT and T_g can occur when the

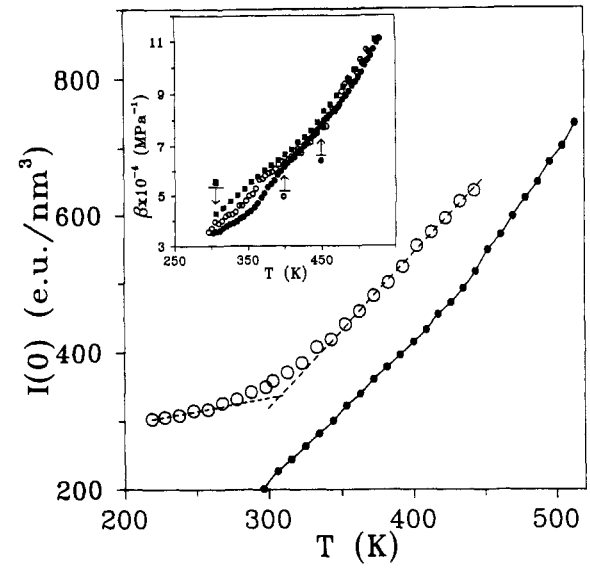

Figure 3. Temperature dependence of the desmeared intensity $I(0)$ as a function of T: (○) obtained from SAXS; (●) calculated from the measured isothermal compressibility according to eq 2. The inset gives the temperature dependences of the isothermal compressibilities of the three P(S-b-MPS) copolymers: (●) $M_w = 6.4 \times 10^4$ ($f_{PS} = 0.45$), (○) $M_W = 5.5 \times 10^4$ ($f_{PS} = 0.5$), and (■) $M_W = 2.8 \times 10^4$ ($f_{PS} = 0.32$). Arrows indicate the transition temperatures.

T_{ODT} is below the T_g of the hard block.

The integrated scattered intensity P, which gives the scattering power of the medium (also called invariant) is calculated from

$$P = \frac{1}{2\pi^2}\int_0^\infty Q^2 I(Q)\, dQ \tag{3}$$

by subtracting the correct background due to density fluctuations and by normalizing to the scattering power at the lowest measurement temperature. The square root of this quantity is plotted in the inset of Figure 2, and it is compared with the same ratio calculated for an ideal two-phase system (sharp boundaries) according to[12,13]

$$\left(\frac{P(T)}{P(T_0)}\right)^{1/2} = 1 + \frac{\alpha_1 - \alpha_2}{\Delta\rho(T_0)}(T - T_0) \tag{4}$$

where T_0 is the reference temperature, α_1 and α_2 are the thermal expansion coefficients of the homopolymers and $\Delta\rho(T_0)$ is the density difference at the selected reference temperature T_0. At the selected T_0 (=248 K), the value of P (eq 3) is only moderately below the calculated one for an ideal two-phase system. The theoretical curve and the experimental points, however, display opposite temperature dependences as a result of the dissolution process. At $T \approx 370$ K, i.e., 70 K above T_{ODT}, the experimental $P(T)$ values are significantly higher than zero, and this is consistent with the observed second Bragg peak (not shown here) up to this temperature. This second peak is centered at $Q/Q^* \approx \sqrt{3}$, indicating the presence of a hexagonal structure well within the "disordered" state, and this is also verified from the transmission electron micrographs (TEM) taken from the same specimen at room temperature. The kink in the temperature dependence of the experimental points indicates the T_{ODT}, and it is shown in the $I(Q^*)^{-1}$ vs T^{-1} plot with an arrow.

Going now from the peak into the base line, we plot in Figure 3 the extrapolated and the calculated $I(0)$ from the SAXS and PVT measurements, respectively, as a function of T for the asymmetric diblock. The pertinent features of Figure 3 are as follows: (i) the $I(0)$ obtained from SAXS

is higher when compared with the calculated $I(0)$ from the pure density fluctuations,[14] (ii) the former changes slope at T_{ODT}, and (iii) the temperature dependences of the specific volume (not shown here) and of the isothermal compressibility (inset of Figure 3) show no discontinuity within the T range and for the time scale of the PVT measurements (heating rate ~ 0.5 K/min). Starting from this last observation, we have made additional compressibility measurements on the higher molecular weight P(S-*b*-MPS) copolymers with T_{ODT} well above ambient temperature, and the results are plotted in the inset of Figure 3. The $\beta_T(T)$ is continuous throughout the transition temperatures which are indicated by arrows. The specific volume and the compressibility of simple molecular crystals are discontinuous at the melting point. However, unlike low molecular weight ordered compounds, the ODT is a very weak first-order transition due to effects of fluctuations which makes the direct observation of changes in certain state properties very difficult.[15]

The observed higher $I(0)$ from SAXS as compared to the calculated $I(0)$ from density fluctuations is due to local concentration fluctuations which exist in two-component systems. In a recent study[16] of a plasticized polymer we have shown that such concentration fluctuations exist not only at small Q but also at higher Q values and create higher background intensities when compared to the pure density fluctuation background. The change in slope observed in the SAXS $I(0)$ at $T \approx T_{ODT}$ shows that local concentration fluctuations within each of the microdomains are enhanced by lowering the temperature. Consequently, one is able to observe the order–disorder transition by properly accounting for the changes in the SAXS background. On the basis of the higher density (and therefore electron density) difference between the homopolymers, we expect this effect for the local concentration fluctuations to be more pronounced for asymmetric block copolymers of low molecular weight. The SAXS and PVT measurements from the higher molecular weight symmetric P(S-*b*-MPS) copolymers revealed higher $I(0)$ as obtained from SAXS than the $I(0)$ calculated from the measured isothermal compressibility (shown in the inset of Figure 3) by 8% in the temperature range $T_g^{PS} < T < T_{ODT}$.

Similar results have been obtained in computer-simulated systems of dense diblock copolymer melts. The simulation has been performed by the cooperative motion algorithm (CMA), the application of which to some block copolymer systems has been presented in detail elsewhere.[17] It was demonstrated earlier that the simulation of symmetric diblock copolymers of partially miscible components allows the determination of the temperature of the order-disorder transition (from the maximum in the temperature dependence of the specific heat) and the related structural changes both above and below the transition. Here, for the same systems as studied before[17,18] only some fragmentary results are presented which are closely related to the experimental observations. Figure 4 shows a comparison between the simulated temperature dependence of the structure factor at Q^* and of the mean-squared concentration fluctuations, determined locally for the nearest-neighbor shell of each monomer [$(\Delta c)^2 = \langle (c - c_0)^2 \rangle / c_0$, where c and c_0 are the local and nominal concentrations of a single component, respectively]. In the inset, the structure factor $S(Q)$ is plotted at temperatures above and below T_{ODT}. As with other simulations,[19] it has been observed that eq 1 well describes the form of the structure factor above T_{ODT}. The two temperature dependences shown are very similar and show that local concentration fluctuations increase remarkably already far above T_{ODT} and change stepwise at the T_{ODT}. These changes are well reproduced in the temperature dependence of the structure factor at Q^*. Both results agree very well qualitatively with the experimental results shown in Figures 2 and 3.

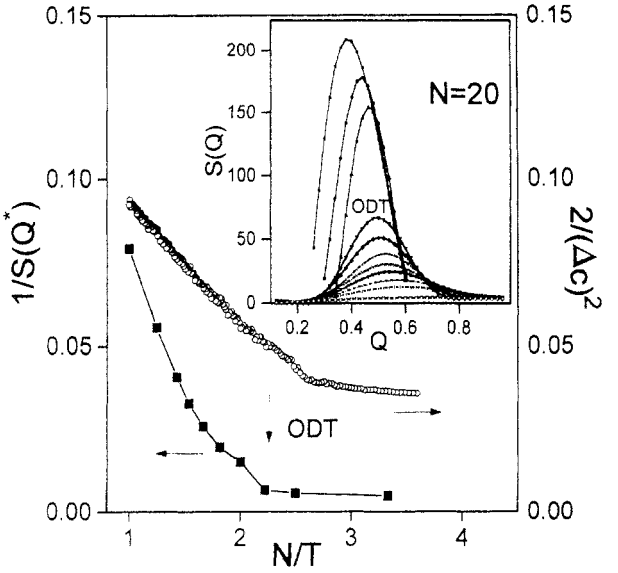

Figure 4. Comparison between the temperature dependence of the structure factor at Q^* and of the mean-squared concentration fluctuations within volume elements of the size of the nearest-neighbor shell of a monomer, determined from a computer-simulated system of a diblock copolymer melt (chain length $N = 20$, composition A:B = 1:1). The inset shows the structure factor determined at various temperatures below and above T_{ODT}. The position of the ODT (vertical arrow) is determined from the temperature dependene of the specific heat.

It has been shown here, for the first time, that the local concentration fluctuations present in the SAXS background of the block copolymers are also influenced by the ODT. We suggest that the only possible way of separating the pure density fluctuations from the local concentration fluctuations is by measuring directly the isothermal compressibility as a function of T. Not correcting for the background or subtracting any other background is likely to result in errors in the interpretation of the composition fluctuations, especially for asymmetic low molecular weight block copolymers.

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