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Synchrotron SAXS Study of the Microphase Separation Transition in Diblock Copolymers

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ABSTRACT: The microphase separation transition (MST) in a nearly symmetric diblock copolymer is studied using time-resolved synchrotron SAXS. The transitions from the lamellar microphase to the isotropic melt and vice versa appear in the form of pronounced singularities in height and width of the main scattering maximum as a function of the temperature. The plot of the reciprocal scattering maximum $S^{-1}(q^*)$ vs the reciprocal absolute temperature T^{-1} can be fitted to the corresponding theoretical function in the Hartree approximation although the present degree of polymerization N is much lower than the usually given limit of $N > 10^4$. The observed scattering functions fit well to the theoretical Leibler-type structure factors, modified to take polydispersity into account. The evaluation of the experimental data yields several parameters of interest to be compared with their theoretical predictions. The observed temperature dependence of the peak position q^* is discussed in relation to a temperature-dependent radius of gyration R_G and a temperature-dependent x^*. A computational error present in a previous paper is corrected in the Appendix.

1. Introduction

Diblock copolymers are of great interest for the development of thermoplastic elastomers and other polymer materials. In the melt, they undergo at a certain temperature a microphase separation transition and form microdomain structures of spatial periodicity. The behavior at this phase transition and the phase diagram in the weak segregation regime are features of general interest.

A mean-field theory of the MST in diblock copolymers has been established by Leibler.[1] He computed the scattering curve as well as the phase diagram for the transition from the disordered melt to the ordered microdomain structures in the framework of the random phase approximation. The phase diagram is completely defined by the composition f and the product χN of the Flory-Huggins interaction parameter χ and the total number of the statistical segments per molecule, i.e., the degree of polymerization N. In this phase diagram the MST is always a first-order transition from the melt to a bcc phase except for the critical point, where the symmetric ($f = 0.5$) diblock undergoes a second-order transition to a lamellar phase.

It has been already pointed out by Leibler[1] that the appearance of a critical point is an artifact of the mean-field description and that it will be necessary to take fluctuations into account. This has been done by Fredrickson and Helfand,[2] based on a self-consistent Hartree approximation by Brazovskiĭ.[3] As a result, the critical point vanishes and well-defined windows for transitions to the hexagonal and lamellar phase open. The mean-field theory is restored in the limit $N \to \infty$.

Experimental results showing the effect of fluctuations in the vicinity of the MST have been obtained using SANS on partially deuterated poly(ethylenepropylene-*b*-ethylethylene) (PEP-PEE) in the nearly symmetrical case[4,5] as well as in the asymmetrical case.[6]

Recently,[7] the influence of polydispersity on the microphase separation transition and on the scattering functions in the disordered phase for one-component and multicomponent systems including mixtures with homopolymers has been investigated. The numerical treatment of the microphase separation transition has been facilitated by means of a reduced phase diagram.

In the present work, a poly(styrene-*b*-butadiene) (PS-PB) diblock copolymer is investigated by synchrotron SAXS over the whole temperature range from below the glass transition temperature of the styrene block via the weak segregation and the MST to the disordered state. Synchrotron SAXS offers a far higher accuracy in comparison to SANS, which is retained in time-resolved measurements. Furthermore, in contrast to PEP-PEE, the system PS-PB is much less compatible. In order to cover the MST point in the experimentally accessible temperature window between the glass transition (nonequilibrium system below T_g) and the degradation temperature (starting with a cross-linking of olefinic double bonds in the butadiene block), diblocks of comparatively low molecular weights have to be used. These correspond to degrees of polymerization well below the limits of validity usually given for the theories.[2] Nevertheless, due to the lack of an applicable theory for these systems, an evaluation along the lines of existing theories is tried. It turns out that the system under consideration is astonishingly well described by this approach. While some theoretical quantities are quite well reproduced, some experimental parameters are found to differ from theory but may be considered as empirical parameters describing the transition. A theoretical justification, e.g., a refinement of the present parameters by renormalization, could be thought of.

2. Theory

According to Leibler,[1] the reciprocal structure factor for the isotropic melt in the mean-field approximation is given by

$$NS_0^{-1}(q) = F(x,f) - 2\chi N \qquad (1)$$

where $x = R_G^2q^2$ and $f = N_A/N$ describes the block composition. The function $F(x,f)$ has been calculated by Leibler[1] in the framework of the random phase approximation and is given in terms of Debye functions in the monodisperse case. The corresponding expression for polydisperse systems and also for mixtures, based on the appropriate weight averages, has been obtained recently.[7]

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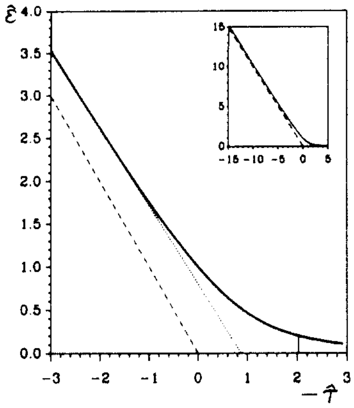

Figure 1. Plot of $\hat{\epsilon}$ vs $-\hat{\tau}$ (solid line) according to eq 4. The dotted asymptotic representing the usual approach to extrapolate to $S^{-1}(q^*) = 0$ obviously leads to an erroneous spinodal, the correct value being $\hat{\tau} = 0$. The correct asymptotic (dashed line) corresponding to the equation $\hat{\epsilon} = \hat{\tau}$ neglecting the fluctuation correction can only be obtained by extrapolation if a very large portion of the function is given (see inset). The vertical solid line at $\hat{\tau} = -2.03$ represents the microphase separation transition to the lamellar phase.

The function $F(x,f)$ reaches its minimum at x^*, corresponding to a maximum in the scattering curve at nonzero scattering vector q^*, in contrast to the situation for homopolymer mixtures. At the spinodal the scattering maximum diverges. Accordingly, we have $F(x^*,f) = 2(\chi N)_s$.

For polymers without specific interactions and with comparable coefficients of expansion, it is common to describe the temperature dependence of the Flory–Huggins interaction parameter χ by

$$\chi(T) = a + b/T \tag{2}$$

Since $F(x,f)$ in eq 1 does not depend on χ and, thus, on the temperature, a plot of the reciprocal scattering intensity at the maximum $S_0^{-1}(q^*)$ versus the reciprocal absolute temperature should show a linear relationship. Furthermore, an extrapolation to $S_0^{-1}(q^*) = 0$ should reveal the reciprocal spinodal temperature T_s^{-1}.[8-14]

Going beyond the mean-field picture, Fredrickson and Helfand[2] introduced a fluctuation correction based on earlier work of Brazovskiĭ.[3] Approximating the mean-field scattering curve (eq 1) by a shifted Lorentzian restores the Hamiltonian considered by Brazovskiĭ, and the problem can be analytically solved in the Hartree approximation. The fluctuation correction for the structure factor $S(q)$ reads as follows:

$$NS^{-1}(q) = F(x,f) - 2\chi N + \frac{c^3 d\lambda}{N} S^{1/2}(q^*) \tag{3}$$

where c, d, and λ are constants defined in ref 2. It should be noted that in the Hartree approximation, the scattering curve retains its shape and the position of the maximum q^*; it is only the peak height that is affected. If eq 3 is valid, a plot of $S^{-1}(q^*)$ vs T^{-1} should exhibit a pronounced deviation from the linear relationship expected for the mean-field case. It has been found to be convenient to introduce reduced parameters[7] so that eq 3 can be rewritten

$$\hat{\epsilon} = \hat{\tau} + \hat{\epsilon}^{-1/2} \tag{4}$$

where essentially $\hat{\epsilon} \sim S^{-1}(q^*)$ and $\hat{\tau} \sim T_s^{-1} - T^{-1}$, and the exact definitions are given in ref 7. Figure 1 shows a plot of $\hat{\epsilon}$ vs $-\hat{\tau}$ according to eq 4, essentially reproducing the features of a plot of $S^{-1}(q^*)$ vs T^{-1}. The dotted line in Figure 1 represents the classical approach to determine the spinodal temperature by linear extrapolation from the high-temperature region to $S^{-1}(q^*) = 0$. Clearly, an incorrect value is obtained by this method since the spinodal corresponds to $\hat{\tau} = 0$. The correct asymptotic (dashed line) corresponding to $\hat{\epsilon} = \hat{\tau}$ neglecting the fluctuation correction can only be obtained if the extrapolation starts at very high values of $S^{-1}(q^*)$, i.e., very high temperatures.

However, the informational content of the spinodal temperature should not be overestimated since, taking fluctuations into account, the spinodal only serves as a classical limit for the expansion and, in particular, has no longer the meaning of a stability limit. The value of $(\chi N)_s$ is further affected by the proper treatment of the cut-off dependent part of the one-loop integral implied by Brazovskiĭ's approach, which becomes increasingly important for low degrees of polymerization.

The power of the concept of reduced variables lies in the ability to predict the transition points for the microphase separation transition and for the transitions within the ordered phases by means of a reduced phase diagram.[7] For example, the reduced temperature variable for the transition from the melt to the lamellar phase is expected to be $\tau^* = \hat{\tau}_t = -2.0308$, valid independent of the sample composition. This point has been indicated in Figure 1. The transitions to the cylindrical and spherical microphases depend on the composition and can be calculated as given in ref 7.

Figure 1 will serve as a useful means to experimentally test the fluctuation correction in the Hartree approximation. The curve is clearly distinguished from the expected mean-field linear relationship. However, considering the mean-field approach as a zero-order approximation and the Hartree approximation as a first-order approximation, the question arises whether higher-order contributions also have to be taken into account. This could be expected for low molecular weight diblock copolymers as used for experiments since fluctuation effects increase with decreasing degree of polymerization.

3. Experimental Section

The sample investigated in this work is a poly(styrene-*b*-butadiene) diblock copolymer, synthesized via anionic living polymerization. The molecular weight characteristics as obtained by GPC are as follows: total molecular weight $M_{w,sb}$, 18 000; molecular weight of the styrene block $M_{w,s}$, 9000; total polydispersity U_{sb}, 0.09; polydispersity of the styrene block U_s, 0.070, where the polydispersity U is defined as $U = M_w/M_n - 1$. The polydispersity of the butadiene block is obtained assuming independent statistics of the two block lengths. From these data one derives a degree of polymerization $N = 229$ and a composition $f_s = 0.47$, based on the volume fraction of the styrene block. Hence, we are dealing with a nearly symmetric diblock copolymer for which a lamellar morphology is to be expected.

The time-resolved synchrotron SAXS measurements were performed at DESY in Hamburg. The combination of synchrotron radiation and a linear position-sensitive detector is necessary to follow the kinetics of the process. Ionization chambers before and after the sample have been found to be necessary for an absorption correction of the measured intensities. Starting at 60 °C, the sample was heated in vacuum up to 220 °C and then cooled down again to 60 °C. The heating rate of 10 °C/min is justified by the quick response due to fast relaxation of the system in the disorderd state, indicated by the absence of hysteresis in the structure factor of the melt.

During this heating/cooling cycle a complete scattering curve was recorded every 15 s.

4. Results and Discussion

Figure 2 shows the measured structure factor $S(q)$, plotted vs the scattering vector $q = 4\pi\lambda^{-1} \sin \theta$ and the time of experiment t, corresponding to increasing and

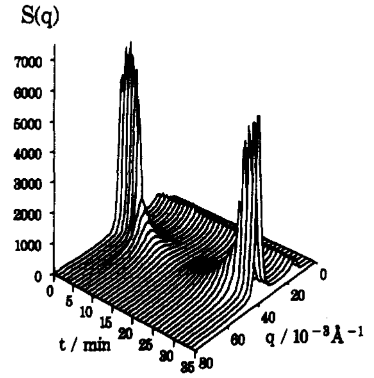

Figure 2. Plot of the measured intensity $S(q)$ as a function of scattering vector q and time of experiment t, the latter corresponding to a temperature ramp. Shown is the whole heating cooling cycle (60 °C → 220 °C → 60 °C, rate 10 °C/min).

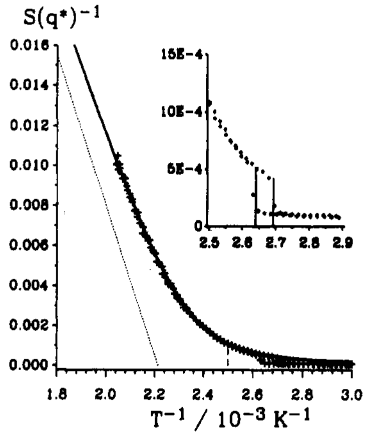

Figure 3. Plot of the reciprocal scattering maximum $S^{-1}(q^*)$ vs reciprocal absolute temperature T^{-1}. Solid line: fit according to eq 3. Dotted line: asymptotic corresponding to the mean-field approximation. Dashed vertical line: theoretical microphase separation transition. Solid vertical lines (see inset): experimentally observed microphase separation transition.

Table I
Summary of All Obtained Parameters

	theor	from fit	exptl
T_s/°C		178.6	
T_t/°C		126.8	105.6
$(\chi N)_s$	10.08	9.30	
$(\chi N)_t$	14.92	10.53	11.43
λ	64.60	8.31	

$\chi(T) = -9.6 \times 10^{-4} + 18.78/T$

decreasing temperature, respectively, during the heating/cooling cycle. The narrow peak in the low-temperature region (strong segregation regime) is the first Bragg reflection of the lamellar microphase-separated two-phase system while in the high-temperature region (weak segregation regime) the broader Leibler type peak corresponding to eq 1 or eq 3 is found. The microphase separation transition from the ordered structure to the isotropic melt and vice versa appears as a pronounced discontinuity in the peak's shape and height.

The plot of $S^{-1}(q^*)$ vs T^{-1} discussed in section 2 is shown in Figure 3. One recognizes a close resemblance of the experimental result in Figure 3 with the theoretical prediction shown in Figure 1. Remapping the plot scale to the reduced variables $-\hat{\tau}$ and $\hat{\epsilon}$ according to eq 4, the experimentally observed MST temperature (solid vertical lines in Figure 3) can immediately be compared to the theoretically predicted one ($\tau^* = \hat{\tau}_t$, dashed vertical line). In fact, the transition is found in close vicinity to the theoretically expected position. The observed hysteresis in the MST position for the heating and cooling cycle can be attributed to the kinetics of the first-order phase transition since in the latter case we probably have a supercooled melt.

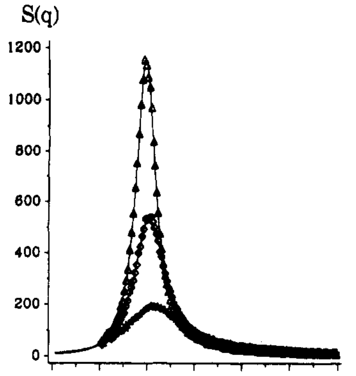

Figure 4. Experimental scattering curves $S(q)$ for three temperatures (upper curve, 119.2 °C; middle curve, 148.6 °C; lower curve, 208.6 °C). Solid lines: fit to the modified form of eq 1 or eq 3, averaged with respect to the molecular weight distribution.[7]

Inspection of eqs 3 and 2 shows that the plot in Figure 3 should enable us to obtain numerical values for various parameters of interest. The solid line in Figure 3 represents the result of a nonlinear fit of the experimental data to eq 3. Of course, only the part above the transition temperature has been taken into account. The fitting parameters were the spinodal temperature T_s, the parameter b in eq 2, and the prefactor $c^3d\lambda$ in eq 3. The parameter a in eq 2 cancels due to $\tau \sim \chi_s - \chi$ and cannot be obtained by this fit. Since c and d are taken from the scattering curve (see below), it is essentially λ which is obtained from the third fitting parameter. The resulting parameters are summarized in Table I and will be discussed below.

Figure 4 shows experimental scattering curves for three different temperatures above the microphase separation transition; i.e., the system exists in the isotropic melt regime and the scattering curves should be described by the Leibler type structure factor. The solid lines represent a fit of the experimental data to a modified form of eq 1 or eq 3 which is averaged with respect to the molecular weight characteristics of the diblocks.[7] The fit parameters were the radius of gyration R_G, mapping the q-axis to the x-scale, and a parameter α, defined as $\alpha = -2\chi N + c^3d\lambda N^{-1}S^{1/2}(q^*)$ so that eq 3 for the structure factor simply reads

$$NS^{-1}(q) = F(x,f) - \alpha \qquad (5)$$

The parameter α enables us to draw a plot of the reciprocal scattering maximum which exhibits a linear relationship in the region accessible to the experiment. Figure 5 shows a plot of $NS^{-1}(q^*)$ vs α. The extrapolation of this linear relationship leads, according to eq 5, to $F(x^*,f) = 2(\chi N)_s$, i.e., the spinodal for $N \rightarrow \infty$. Since the parameter b in eq 2 and the spinodal temperature T_s are known from the evaluation of the plot in Figure 3, it is now possible to obtain the parameter a in eq 2. The results are summarized in Table I. This determination of the parameters a and b characterizing the temperature dependence of the Flory–Huggins interaction parameter appears to be more reliable than former approaches.[8-14]

The parameter R_G mapping the experimental q-scale to the theoretical x-scale as obtained from the fit mentioned above is shown in Figure 6, upper curve. It is shown in Figure 2 that the position q^* of the Leibler maximum shifts to larger values with increasing temperature. Mean-field theory[1] as well as fluctuation theory[2] in the Hartree

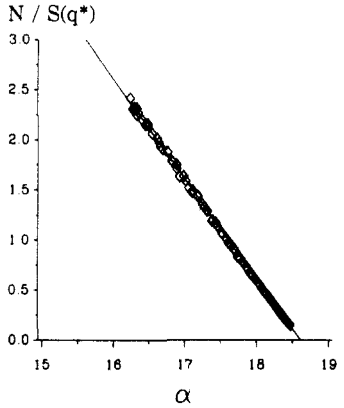

Figure 5. Plot of the product $NS^{-1}(q^*)$ of the degree of polymerization and the reciprocal scattering maximum vs the parameter α defined in eq 5. The extrapolation of this linear relationship to $S^{-1}(q^*) = 0$ yields a value of $(\chi N)_s = 9.30$.

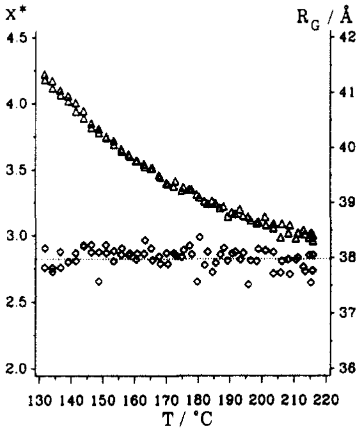

Figure 6. Plot of x^* (lower curve, left axis) and R_G (upper curve, right axis), respectively, vs temperature for the heating cycle.

approximation with a wave vector independent quartic coefficient λ predicts temperature independence of x^* so that the observed shift of q^* would have to be attributed to the temperature dependence of R_G. The independently determined values of q^* and R_G produce the values of x^* plotted in Figure 6, lower curve. Since there is only a slight dependence of x^* on the temperature, a constant average value of x^* has been used, e.g., for the calculation of the transition point in Figure 3. However, recent theoretical investigations,[15,16] taking into account the wave vector dependence of the quartic coefficient λ corresponding to Leibler's Γ_4, predict a temperature dependence of x^*, interpreted as a stretching of the coils when approaching the transition point from the melt. A transition of Gaussian to stretched coils has been observed experimentally to exist above the MST in the system PEP–PEE.[17] The effect of such a transition is, however, not observable in the temperature dependence of R_G for the PS–PB sample studied here.

5. Conclusions

In the present work it has been shown that even low molecular weight diblock copolymers are, at least empirically, well described by a simple fluctuation theory in the Hartree approximation.[2,3,7] The plot of the reciprocal scattering maximum $S^{-1}(q^*)$ vs reciprocal absolute temperature seems to be a crucial test for the validity of the approximations employed. In the mean-field picture[1] this plot would show a straight line with negative slope ending at the spinodal. The MST is expected in the form of a singular deviation from this line to occur before the spinodal is reached, according to the physical interpretation of the latter.

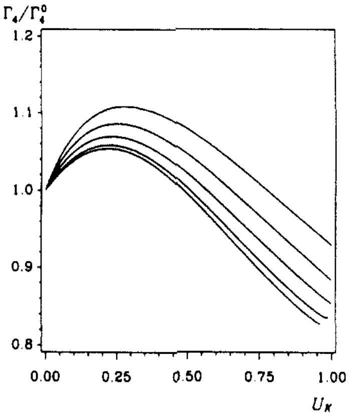

Figure 7. Plot of the ratio $\Gamma_4(0,0)/\Gamma_4^0(0,0)$ for a one-component system as a function of U_K, values of f varying from 0.1 (lower curve) to 0.5 (upper curve) in steps of 0.1, independent variances of N_K, and $U_A = U_B$.

Considering the mean-field approach as the zero-order approximation, the corresponding first-order correction can be obtained by a diagram expansion taking only one-loop integrals into account, known as the Hartree approximation. As has been discussed before, this leads to an additive fluctuation correction to the reciprocal structure factor, changing the plot in question to a cubic curve with characteristic shape; see Figure 1. Further, the MST is shifted to lower temperatures, and the spinodal has lost its physical significance, merely serving as a mathematical origin for the expansion of the theory.

While the validity of mean-field theories can in general only be expected for infinitely large systems, i.e., infinitely large polymer chains in the present case, it has been estimated[2] that the Hartree approximation should only be valid for degrees of polymerization larger than 10^4. This is well beyond $N \approx 10^2$–10^3 accessible by the common experimental systems. Going beyond the Hartree approximation would mean to take higher order diagrams into account which would change the nature of the fluctuation correction from a simple additive term and would change the appearance of the plot under consideration from its simple cubic form. However, such a computation seems to be rather difficult.

Returning to the experiment, it has been shown in Figure 3 that the measured data are very well fitted by the first-order theory. Obviously, the mean-field description, still widely applied, is not sufficient, but, on the other hand, there seems to be no need to include higher order corrections. Also, the exact point of the MST corresponds surprisingly well to the theoretical prediction. It is interesting to note that the parameter λ as obtained empirically from the fitting procedure is much smaller than the value predicted by the theory. Since the diagram expansion essentially consists of a power series in λ, this would indicate that higher order terms are much less important than originally estimated.[2]

It may be concluded that taking into account the angular dependence of Γ_4 leading to the shift of x^* will be more important and more fruitful for future work than trying to compute higher order corrections to the present theory.

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Appendix

During the present work it has been kindly brought to our attention by Prof. C. D. Han that there was an error in the computation of the coefficient $\Gamma_4(h_1,h_2)$ in ref 7. The error involved the computation of the quantity $S_{ij}^{-1}(0)$ which equals $1/N$ in the monodisperse case[1] and, due to the scaling $S \sim O(N)$, will appear as unity in a monodisperse calculation. It turns out that, taking polydispersity into account, there is no longer a comparatively simple expression but the result has to be obtained by a thorough matrix inversion. It is only the coefficient Γ_4 and quantities derived thereof that are affected. The correct dependence of the coefficient $\Gamma_4(0,0)$ on the polydispersity is shown in Figure 7.

This also leads to a slight shift of the transition windows (original Figures 12 and 13 of ref 7) but the overall conclusion stated there remains intact.

The calculation of all relevant parameters characterizing the MST has been carried out by means of a computer program (written in Pascal, running on a PC or VAX). The program can be obtained from the authors.[18]

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