Asymmetric diblock copolymers near the microphase separation: limitations of mean field theory

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The microphase separation transition in five asymmetric diblock copolymers {poly(styrene-block-isoprene)} is studied using small angle X-ray scattering. In the disordered phase Leibler's random phase approximation together with a polydispersity correction yields a quantitative description of the scattering profiles. Close to the microphase transition we find strong deviations from mean field theory. The peak intensity and the apparent interaction parameter are smaller than expected. The Frederickson–Helfand theory explains these effects only qualitatively in terms of concentration fluctuations. The polymer coil size is found to increase when approaching the microphase transition.

(Keywords: small angle X-ray scattering; block copolymers; microphase transition; random phase approximation)

INTRODUCTION

The ability of block copolymers to phase separate on a microscopic scale opens the way for many valuable technical applications of these materials[1]. It has consequently been of great interest to determine the dependence of morphology in such systems on parameters like molecular architecture and thermal history. More recently the so-called weak segregation limit has raised considerable interest: if the repulsive interaction between the different constituents of the block copolymer chain is small enough, the material undergoes a phase transition from the ordered into a disordered, homogeneous phase at the microphase separation temperature (MST). This phase transition as well as the properties of the homogeneous phase were first treated by Leibler[2] using a generalization of de Gennes' random phase approximation (RPA)[3]. The theory interprets the microphase separation as a first-order phase transition quite similar to the crystallization of a liquid.

A second important result is the calculation of correlation functions for concentration fluctuations in the homogeneous phase. They are related to the strength of the monomer–monomer interaction as well as to the structure and size of the polymer chain. This correlation function may be measured using scattering techniques like neutron or X-ray scattering.

In this paper we briefly discuss Leibler's results for X-ray scattering from the homogeneous phase of a block copolymer melt. More recent improvements of the theory that take into account the effects of polydispersity are incorporated. For the transition regime close to the MST it is important to consider the contribution of concentration fluctuations to obtain the correct structure factor.

Small angle scattering experiments on block copolymers in the homogeneous phase have been reported in the literature for a variety of systems[4–8]. Comparison of the measured structure factors with Leibler's theory in general gave good agreement and made it possible to determine the interaction parameter χ and its temperature dependence. It was found that in approaching the MST the measured intensities were lower than those expected from RPA theory[7] and the interaction parameter deviated from its expected temperature dependence[5]. Other authors reported a shift of the peak in the structure factor with temperature[4,7].

In this paper we present small angle X-ray scattering (SAXS) data for five styrene–isoprene diblock copolymers that differ in either composition or molecular weight distribution (*Table 1*). The static structure factor in the homogeneous phase will be compared to the prediction of mean field theory. A quantitative analysis allows the determination of interaction and chain size parameters.

Of particular interest are the strong deviations from theory found in the transition regime. We systematically study these effects and discuss their origin.

Table 1 Characterization of the polymers used

No.	$M_N{}^b$	f^c	$P=M_W/M_N{}^d$	Block A, M_W, P
1	24 000	0.78	1.05	–
2	14 600	0.25	1.05	Polystyrene, 4100, 1.01
3[a]	18 700	0.76	1.04	Polyisoprene, 4000, 1.03
4	9200	0.26	1.5	–
5	22 800	0.28	1.5	–

[a] Styrene block deuterated
[b] Osmometry
[c] Volume fraction of styrene from ^{1}H n.m.r.
[d] By g.p.c.

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EXPERIMENTAL

Synthesis and characterization

Polymer 3 was purchased from Polymer Laboratories Ltd, Shawbury, UK. It had already been used in a previous study[6] and its styrene block is perdeuterated.

In the synthesis of the other polymers conventional high vacuum methods were employed for the purification and degassing of solvents and monomers. The polymerization was carried out in cyclohexane under a nitrogen atmosphere at room temperature with sec-butyllithium as initiator. The monomers were sequentially added to the solvent starting with styrene. In some cases a sample of polystyrene was taken before addition of the isoprene monomer. The gel permeation chromatography (g.p.c.) molecular weight characterization of this block is given in *Table 1*. The reaction was terminated with methanol. After precipitating the polymer it was freeze dried from benzene.

The microstructure of the diblock copolymers was determined using ^{13}C nuclear magnetic resonance (n.m.r.). The *trans* content of the isoprene block was found to be 15%. ^{1}H n.m.r. gave the volume fraction (f) of polystyrene (*Table 1*). The molecular weight distribution was obtained from g.p.c. and the number average molecular weight from osmotic pressure measurements (cf. *Table 1*).

Small angle X-ray scattering

For the scattering experiments a Kratky compact camera (Paar, Graz, Austria) in the conventional slit collimation was used. Data were collected using either a position-sensitive detector or a scintillation counter in the usual step scanning mode. The samples were contained in brass holders with acetate windows. This allowed precise temperature control with fluctuations <0.5 K. All experiments were performed in an evacuated camera.

Further data treatment involves subtraction of background scattering and accounting for the slit type beam geometry using Strobl's desmearing algorithm[9]. In order to obtain the scattering cross-section of the sample without any arbitrary prefactors we measured the intensity of the incoming beam with a 'moving slit device' (Paar).

The source of radiation was a copper anode together with a Siemens generator (Kristalloflex 710H). We operated at wavelength $\lambda = 0.154$ nm using Cu Kα radiation. The $K\beta$ contribution was reduced using Ni filters. In an accessible scattering angle interval of $0.15° \leqslant 2\theta \leqslant 4.2°$ we covered a range of wave vectors $q = 4\pi/\lambda \sin\theta$ between 0.1 nm^{-1} and 3 nm^{-1}.

SCATTERING THEORY

Here we provide the relationship between the experimentally determined X-ray scattering curve and the thermodynamic and structural properties of the sample. In general X-ray scattering is caused by the existence of electron density fluctuations in the sample. For a two-component system like a diblock copolymer the main source of such fluctuations is variations in concentration as long as there exists a difference in the electron number densities η_a and η_b for the respective components a and b. The styrene–isoprene system is quite favourable in this respect with an electron density difference of 10%. This part of the X-ray scattering, the contrast scattering, is then given as

$$I_c = (\eta_{Is} - \eta_{St})^2 V S(q) \qquad (1)$$

with V the volume of a polymer chain and $S(q)$ the static structure factor for concentration fluctuations. Equation (1) holds in the same form for other scattering methods like neutron scattering with the electron densities being replaced by the scattering length densities of the components isoprene (Is) and styrene (St).

Another source of electron density fluctuations is the variation of density. They give rise to a q independent scattering component. Statistical mechanics relate this intensity to the compressibility κ_T of the sample:

$$I_\kappa = \langle \eta \rangle^2 k_B T \kappa_T \qquad (2)$$

Here $\langle \eta \rangle$ denotes the average electron density of the system and k_B is Boltzmann's constant.

The contribution of equation (2) to the total X-ray scattering cannot be neglected (*Figure 1*), as it would lead to a significant misinterpretation of the structure factor $S(q)$. I_κ is found experimentally from measurements at large scattering angles where $S(q)$ has decayed to practically zero.

STRUCTURE FACTOR OF A DISORDERED DIBLOCK COPOLYMER

Here we present some results of Leibler's RPA and give an expression for $S(q)$ including the effects of polydispersity. We begin by considering a monodisperse block copolymer melt in its homogeneous phase.

Each molecule is comprised of N_{St} styrene and N_{Is} isoprene segmental units. The units must refer to the same volume per segment. The block length ratio $f = N_{St}/(N_{St} + N_{Is})$ will be the only parameter describing the specific geometry of the molecule. It is obvious that there are no concentration fluctuations on a large length scale compared to the radius of gyration R_g of a polymer, because the styrene and isoprene blocks cannot diffuse independently and f is a fixed quantity. Correspondingly the X-ray scattering must vanish in the limit $qR_g \ll 1$. Going to shorter scales that refer to distances within a molecule, strong concentration fluctuations are to be found because of the block structure of the copolymer. They will no longer be felt on the very short, segmental

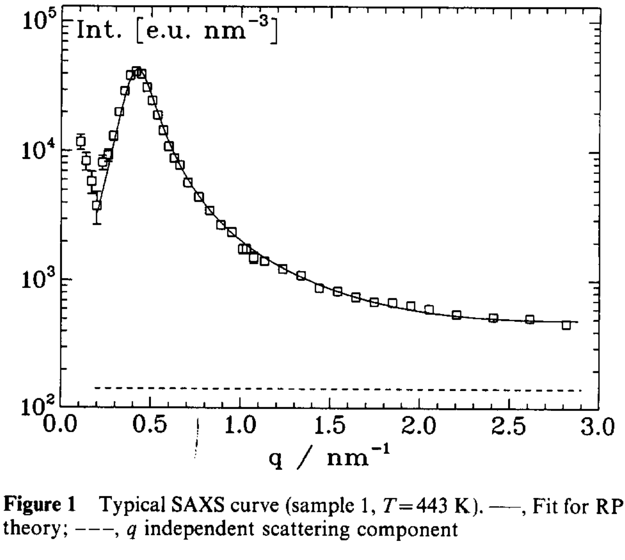

Figure 1 Typical SAXS curve (sample 1, $T = 443$ K). ——, Fit for RPA theory; – – –, q independent scattering component

scale where all segments are essentially surrounded by like ones. The X-ray scattering curve therefore exhibits a maximum around $qR_g \approx 1$ which is primarily due to the correlation hole effect[3].

The specific interaction between polymer segments was accounted for by Leibler[2] in a mean field type theory, the RPA. Assuming a Gaussian coil conformation in the absence of interactions he finds for the structure factor $S(q)$

$$\frac{N}{S(q)} = F(f,[qR_g]^2) - 2\chi N$$
$$N = N_{St} + N_{Is} \tag{3}$$

Equation (3) describes a modification of the pure correlation hole scattering. The peak remains at the same position q^* but gains in height with increasing values of the Flory–Huggins parameter χ. In a lattice model χ is used in a phenomenological manner to describe the local free energy per lattice point G_{loc}

$$\chi = -\frac{1}{2k_B T}\frac{\partial^2 G_{loc}}{\partial f^2} \tag{4}$$

As long as the major contribution to G_{loc} comes from contact interaction between segments, χ displays the simple temperature behaviour

$$\chi \propto \frac{1}{T} \tag{5}$$

The study of phase diagrams in polymer blends however, suggests in general a more complex temperature and even composition dependence of χ (refs. 10 and 11). In the latter case equation (4) is no longer valid.

The effect of the interaction obviously lies in an enhancement of fluctuations with wavevector q^*. At the spinodal value $(\chi N)_s = \frac{1}{2}F(f,[q^*R_g]^2)$ the amplitude of these fluctuations diverges and the block copolymer has gone through its microphase separation. The RPA theory gives an explicit expression for $F(f,[qR_g]^2)$ in terms of Debye functions[2] $g(f, x)$

$$F(f, x) = \frac{g(1,x)}{g(f,x)g(1-f,x) - \frac{1}{4}[g(1,x) - g(f,x) - g(1-f,x)]^2} \tag{6}$$

with

$$g(f, x) = \frac{2}{x^2}[fx + e^{-fx} - 1]$$

The theory may of course be generalized to account for more complex molecular architecture like multiblock copolymers and stars[12–15]. The form of equation (3) remains unchanged with F being replaced by an expression describing the particular structure of the molecule.

Polydispersity correction

The assumption of monodispersity is of course highly unrealistic. However, in the spirit of a mean field theory a distribution of molecular weight may be incorporated in the theory in a straightforward manner[16] because the correlation functions entering equation (3) in terms of Debye functions already involve an average over molecular weight. The influence of a molecular weight distribution was discussed by Leibler and Benoit[16] for the symmetric case $f = \frac{1}{2}$ and has later[4,8] been generalized for arbitrary f. It is assumed that the number of monomers in both blocks as well as in the block copolymer is distributed according to a Schulz–Flory density

$$\varphi(N) = \frac{\nu^{k+1}}{\Gamma(k+1)} N^k e^{-\nu N} \tag{7}$$

k and ν are parameters of the distribution and are related to the number average $\langle N \rangle_N$ and weight average $\langle N \rangle_W$ via

$$P \equiv \frac{\langle N \rangle_W}{\langle N \rangle_N} = \frac{k+2}{k+1} \qquad \langle N \rangle_N = \frac{k+1}{\nu} \tag{8}$$

The notations $\langle h \rangle_W$ and $\langle h \rangle_N$ symbolize

$$\langle h \rangle_N \equiv \int h(N)\varphi(N)\mathrm{d}N$$
$$\langle h \rangle_W \equiv \int h(N) \cdot N\varphi(N)\mathrm{d}N / \langle N \rangle_N$$

As a further simplification we assume that the polydispersity P and therefore k is the same for both the blocks and the total polymer. Following Hong and Noolandi[17] we use weight averages to compute the correlation functions in equation (6) and obtain

$$\langle Ng(1, x) \rangle_W = \langle N \rangle_N \left\{ \frac{2}{x^2}\left[x - \left(1 - \left\{ 1 + \frac{x}{k+1} \right\}^{-(k+1)} \right) \right] \right\}$$

$$\begin{aligned} \langle Ng(f, x) \rangle_W = \langle N \rangle_N \Bigg\{ & \frac{1}{x}\frac{f}{1-f} F(1, k+3; 2k+5; z_0) \\ & - \alpha F(1, k+2; 2k+4; z_0) \\ & + \alpha\left(1 + \frac{fx}{k+1} \right)^{-(k+2)} F(1, k+2; 2k+4; z_1) \Bigg\} \end{aligned}$$

$$\begin{aligned} \langle Ng(1-f, x) \rangle_W = \langle N \rangle_N \Bigg\{ & \frac{1}{x} F(1, k+2; 2k+5; z_0) \\ & - \alpha F(1, k+2, 2k+4, z_0) \\ & + \alpha\left(1 + \frac{1-f}{k+1}x \right)^{-(k+1)} \\ & F(1, k+2; 2k+4; z_1') \Bigg\} \end{aligned}$$

with

$$\begin{aligned} \alpha &= \frac{2}{x^2} \times \frac{1}{1-f} \times \frac{k+1}{2k+3} \\ z_0 &= \frac{1-2f}{1-f} \\ z_1 &= 1 - \frac{f}{1-f}\left(1 + \frac{fx}{k+1} \right)^{-1} \\ z_1' &= 1 - \frac{f}{1-f}\left(1 + \frac{(1-f)x}{k+1} \right) \\ x &= (qR_g)^2 \end{aligned} \tag{9}$$

where F is the hypergeometric function[18] and equation (9) is written for $f \leqslant \frac{1}{2}$. It is similar to the results obtained by Bates and Hartney[4] and Mori *et al.*[8] but it uses weight averages as was pointed out by Hong and Noolandi[17]. In view of the complex structure of the true molecular weight distribution however, equation (9) can only be

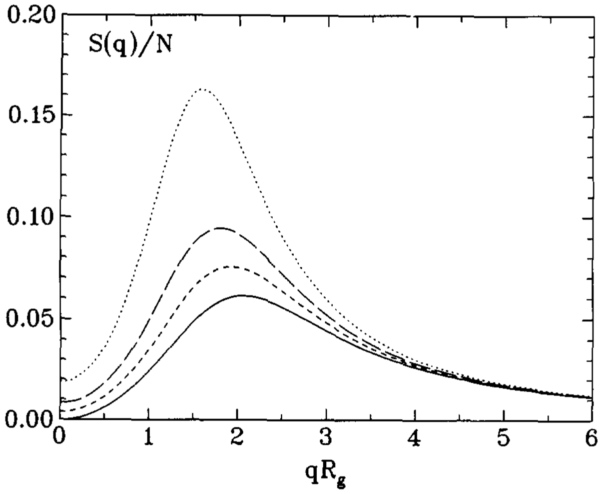

Figure 2 Influence of polydispersity P on the scattering function of an asymmetric diblock copolymer ($f=0.25$) with $\chi N=10$. P: —, 1.00; ---, 1.05; — —, 1.10; ····, 1.20

considered as a model which allows the study of the effects of a molecular weight distribution.

It is important to note that the composition f is no fixed quantity in a polydisperse sample. It becomes obvious from the qualitative discussion above that concentration fluctuations over large distances will then be possible and will give rise to X-ray intensity at small angles. This effect is observed in *Figure 2*. The theoretical curve, which is obtained by inserting equation (9) into equations (6) and (3) does not extrapolate to zero for $q=0$. The figure shows the qualitative changes of the structure factor $S(q)$ for several degrees of polydispersity P.

With increasing P the peak gains in height and shifts to smaller values of wavevector. The microphase separation is therefore reached at smaller values of χN compared to the monodisperse case. In other words, polydispersity shifts the critical $(\chi N)_s$ to smaller values.

Furthermore it is seen that neglecting polydispersity leads to significantly incorrect values for the peak position q^* and therefore the radius of gyration of the polymer.

Concentration fluctuations

The divergence of $S(q^*)$ as described by equation (3) needs closer inspection. In the theory of linear response $S(q^*)$ is proportional to the susceptibility of the system and is obtained as the inverse of the coefficient of the quadratic term in an expansion of the free energy density with respect to the order parameter[2] (cf. equation (10)). The order parameter $\psi(r)$ is defined as the difference between the reduced local density of styrene segments and its average value f:

$$\psi(r)=\rho_{\mathrm{St}}(r)/\bar{\rho}-f$$

where $\bar{\rho}$ is the average density of polymer segments. Close to the MST $\psi(r)$ will be dominated by components of wavevector q^*. If one assumes a lamellar structure for the ordered phase (i.e. $f\simeq\frac{1}{2}$) then[19]

$$\langle\psi(r)\rangle\propto 2A\cos(q^*\vec{r}\cdot\vec{n})$$

with $\vec{n}$ a unit vector describing the orientation of the lamellae. The Landau expansion for a reduced free energy density then reads

$$f_{\mathrm{L}}(\tilde{A})=\tau\tilde{A}^2+\frac{u}{4}\tilde{A}^4$$

with

$$\tau=2N(\chi_s-\chi)=\frac{N}{S(q^*)} \tag{10}$$

$\tilde{A}$ is proportional to the amplitude A of the order parameter. The parameter u depends on f and is of the order $1/N^{\frac{1}{2}}$. It is defined by Binder and Frederickson[19]. Obviously the Landau expansion gives exactly Leibler's result (cf. equation (3)). However, it is known to break down near the phase transition because of the contribution of higher order terms to the free energy. Leibler points out that the block copolymer problem belongs to a class of systems that were discussed by Brazosvskii[20]. In this formalism one obtains a Hartree expansion of the free energy density analogous to equation (10) with renormalized parameters $\tau_{\mathrm{R}}, u_{\mathrm{R}}, w_{\mathrm{R}}$[19]

$$f_{\mathrm{H}}=\tau_{\mathrm{R}}\tilde{A}^2+\frac{u_{\mathrm{R}}}{4}\tilde{A}^4+\frac{w_{\mathrm{R}}}{36}\tilde{A}^6 \tag{11}$$

For τ_{R} one has the following implicit equation[19,21]

$$\tau_{\mathrm{R}}=2N(\chi_s-\chi)+\frac{c(f)}{(N\tau_{\mathrm{R}})^{\frac{1}{2}}} \tag{12}$$

$c(f)$ is a constant depending on the copolymer composition f, but f is assumed to be close to 1/2.

As a consequence of equation (12) the X-ray intensity at q^* will no longer diverge but remain at a finite limit.

Following Frederickson and Helfand[21] the full structure factor (cf. eq. (3)) neither changes its shape nor the location of its maximum q^*. The parameter χN however, is renormalized and will be called an apparent interaction parameter $(\chi N)_{\mathrm{app}}$. They find

$$(\chi N)_{\mathrm{app}}=\chi N-\frac{1}{2}\frac{c(f)}{(N\tau_{\mathrm{R}})^{\frac{1}{2}}} \tag{13}$$

The temperature dependence of the interaction is carried by the parameter χN.

RESULTS AND DISCUSSION

The data obtained from the SAXS experiment in general are the sum of three components:

1. the scattering caused by concentration fluctuations (eq. (1));
2. a flat background due to density fluctuations (eq. (2));
3. parasitic scattering at small angles.

In some cases (sample 1) the parasitic scattering was negligible. For others it produced a substantial background and was phenomenologically taken into account by a Porod term constant/q^4. The physical origin of this scattering is not clear. One possible reason could be the abundance of homopolymer in the sample[6]. This assumption is not confirmed by g.p.c. measurements. Other authors ascribed the effect to 'domain scattering'[4] or simply neglected it. We were unable to detect a systematic dependence of this intensity on temperature, molecular weight or composition of the block copolymer.

For both other components listed above an explicit theoretical description is available (see earlier). It is therefore straightforward to fit the theory to the experimental data using a standard least squares algorithm. The finite angular resolution of the Kratky camera is accounted for by convoluting the theoretical scattering curve with the vertical primary beam profile

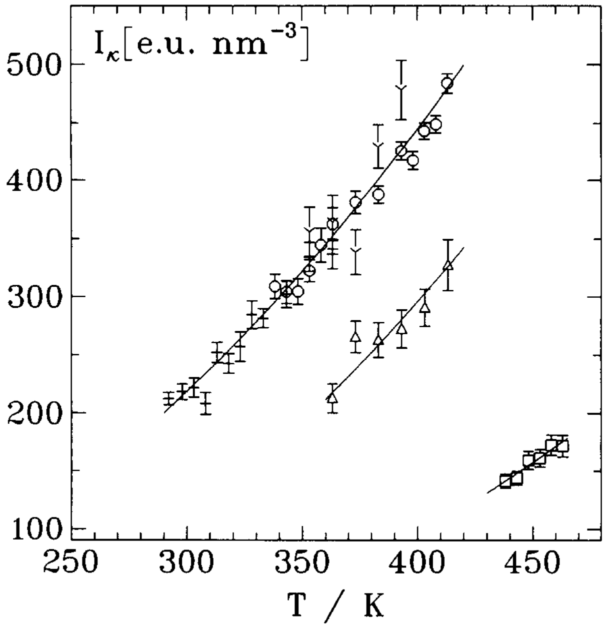

Figure 3 Temperature dependence of the scattering component I_κ. —, Computed from the compressibility κ (see text). Sample no.: □, 1; ○, 2; △, 3; +, 4; Y, 5

in the plane of registration. The effect of finite resolution may not be neglected.

Polydispersity enters this procedure as a fixed input parameter which is obtained from g.p.c. measurements. Parameters calculated in the fit then are:

1. the compressibility κ_T of the sample from the flat background;
2. the radius of gyration of the chain R_g essentially given by the peak position q^*;
3. the interaction parameter χN from peak height and width.

Finally it is of course difficult to estimate the contrast $(\eta_{St}-\eta_{Is})^2$ and its temperature variation from thermodynamic data. We have therefore treated this quantity as an additional fit parameter and compared it with tabulated values for the density and its temperature variation[22]. The fitted contrast factors were in all cases in accordance with those calculated from thermodynamic data.

Figure 3 displays the results for the temperature dependence of the density fluctuation component. The data for samples 2, 4 and 5 fall on one universal curve. Indeed these polymers are of the same composition but differ in molecular weight. Using known data for the compressibilities of the homopolymers polyisoprene[22] and polystyrene[23] one expects a quadratic law $I_\kappa = \alpha T + \beta T^2$ with α and β depending on the composition of the block copolymer. Our data confirm this T dependence quantitatively. An exception is sample 1 whose apparent compressibility is too low.

In a preliminary procedure we evaluated the SAXS profiles independent of the specialities of RPA theory. Expanding F in equation (3) around its extremum at q^* one finds[14]

$$S(q) = \frac{S(q^*)}{1+\xi^2(q-q^*)^2} \tag{14}$$

Equation (14) is similar to the Ornstein–Zernicke type expressions found in the theory of critical phenomena. The main difference lies in the existence of a finite wavevector q^* for which $S(q)$ reaches its maximum. The correlation length ξ denotes the typical distance over which the correlation of fluctuations decays. In RPA theory ξ and the peak height $S(q^*)$ are related to the interaction parameter χ via

$$\xi^2 = \frac{F''}{4N(\chi_s-\chi)}, \quad S(q^*) = \frac{1}{2(\chi_s-\chi)} \tag{15}$$

At the spinodal point $(\chi \rightarrow \chi_s)$ the correlation length diverges, i.e. the Lorentzian in equation (14) has zero width. At the same time $S(q^*)$ goes to infinity.

The advantage of using equation (14) over the full RPA theory lies in its simplicity and the direct interpretation of peak shape parameters in terms of thermodynamic properties. It is of course only applicable in the immediate vicinity of q^*. As long as $\chi \ll \chi_s$ the peak shape deviates clearly from a Lorentzian. We use equation (14) for a determination of $S(q^*)$ and its temperature dependence. Assuming $\chi(T) \propto \frac{1}{T}$ we have

$$\frac{1}{S(q^*)} \propto \frac{1}{T_s} - \frac{1}{T} \tag{16}$$

When approaching the phase transition however, one expects deviations from the simple $1/T$ law of equation (16) because of the fluctuation correction discussed earlier.

The SAXS profiles of all four diblock copolymers described in *Table 1* exhibit a pronounced variation with temperature which is shown in *Figure 4* for sample 2. Lowering T one finds a strong increase in peak intensity. At the same time the peak narrows and shifts to smaller q values. This behaviour is found for all samples. The SAXS curves are fully reproduced in heating and cooling runs if a minimum of 30 min is allowed for the sample to equilibrate at each temperature.

As an example we plot in *Figure 5* the reciprocal peak intensity $1/S(q^*)$ *versus* $1/T$ for sample 2. The linear extrapolation to infinite intensity as suggested by equation (16) leads to a spinodal temperature T_s. However, for all samples one finds the experimental points to bend off the linear law when approaching the MST.

In a next step the interaction parameter χ and the radius of gyration R_g are extracted from the SAXS profiles. To this end equation (9) is used for the

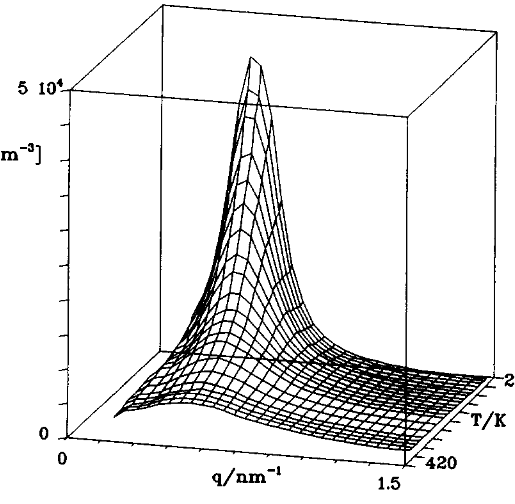

Figure 4 Temperature dependence of the SAXS curve for sample 2

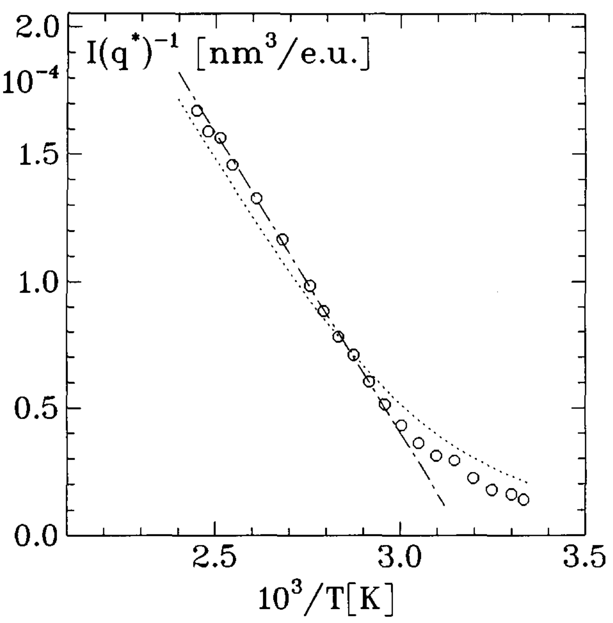

Figure 5 Inverse peak intensity defining the spinodal temperature T_s (—-) for sample 2. ····, Computed from the Frederickson–Helfand theory (see text)

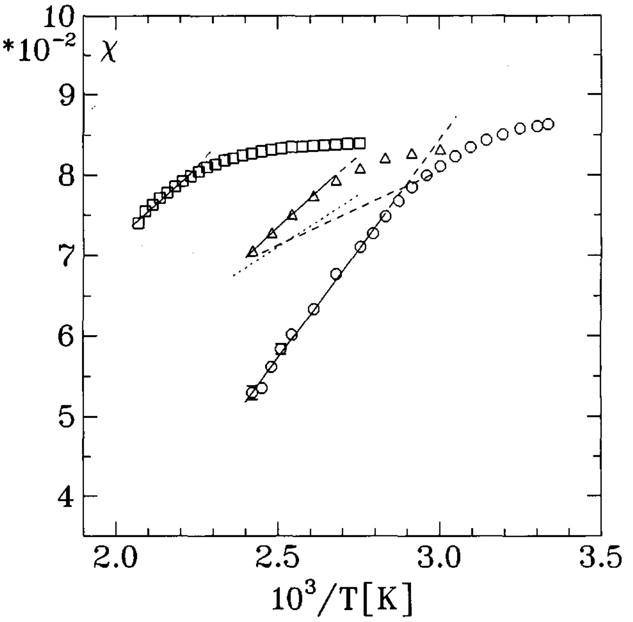

Figure 6 Flory–Huggins parameter for styrene–isoprene diblock copolymers with different styrene fraction f. □, Sample 1, $f=0.78$; ○, sample 2, $f=0.25$; △, sample 3, $f=0.76$; – – –, Mori *et al.*[8], $f=0.05$; ····, Owens *et al.*[7], $f=0.5$

correlation functions in equations (6) and (3). The resulting profile is fitted to the data and the excellent quality of these fits is shown in *Figure 1*. It turns out however, that only for rather narrow molecular weight distribution (samples 1–3) does the model of a Schulz–Flory distribution lead to correct results. Our 'polydisperse' samples 4 and 5 deviate from this model. As a consequence the location of the maximum q^* cannot be predicted by the molecular weight although this is possible for the other samples. In the following we therefore restrict attention to those samples with $P \leqslant 1.05$. A more detailed analysis of the g.p.c. results on polydisperse samples and their quantitative use in a description of the SAXS profiles is currently in progress.

Figure 6 collects the results of the temperature dependence of the χ parameter. Here χ refers to the interaction per average molar volume $v=(\hat{\rho}_{\mathrm{Is}}\hat{\rho}_{\mathrm{St}})^{-\frac{1}{2}}$, where $\hat{\rho}_{\mathrm{Is}}$ and $\hat{\rho}_{\mathrm{St}}$ are the molar densities of polystyrene and polyisoprene, respectively. The quantity χN entering equation (9) is therefore reduced to χ using

$$N = N^*_{\mathrm{St}}\sqrt{\frac{\hat{\rho}_{\mathrm{Is}}}{\hat{\rho}_{\mathrm{St}}}} + N^*_{\mathrm{Is}}\sqrt{\frac{\hat{\rho}_{\mathrm{St}}}{\hat{\rho}_{\mathrm{Is}}}} \qquad (17)$$

$$= N_{\mathrm{St}} + N_{\mathrm{Is}} \qquad (18)$$

The N_i^* are the degrees of polymerization for each block.

It is seen in *Figure 6* that $\chi(T)$ *versus* $\frac{1}{T}$ displays a linear regime which coincides with the linear relation between $\frac{1}{S(q)}$ and $\frac{1}{T}$. In the case of sample 1 this regime is only approximately reached. It is this temperature interval which may safely be treated as the homogeneously disordered phase. Approaching the MST the observed χ values are smaller than those extrapolated from the linear behaviour at higher T. The presence of concentration fluctuations diminishes the number of contacts between the isoprene and styrene blocks compared to the homogeneously disordered phase. The lattice model therefore overestimates their contribution to the local free energy (eq. (4)). This effect is compensated by a reduced value of the interaction parameter χ.

We could not find a quantitative description of our data in the transition regime using equation (13). Using a linear law for $\chi(T)$ in equation (12) the dotted line in *Figure 5* is obtained.

$$\chi = A + \frac{B}{T} \qquad (19)$$

The parameters A and B however, are not the same as those obtained from the data in *Figure 6* (cf. *Table 2*). Bates *et al.*[24] report a quantitative correspondence between their data on a symmetric diblock copolymer and equation (13). Our polymers are strongly asymmetric in composition (cf. *Table 1*) and the theory would therefore only be expected to be qualitatively correct.

Taking only the linear regime in *Figure 6* into account there still remain marked differences between the three polymers studied that lie outside the limits of experimental error. Also included in the figure are data from Mori *et al.*[8] and Owens *et al.*[7] on styrene–isoprene block copolymers. Although we cannot exclude the possibility that our polymer 1 has not completely reached its homogeneous state there seems to be a strong dependence of χ on the composition of the copolymer. In view of the phenomenological significance of χ this finding is not surprising.

The Gaussian radius of gyration R_g^0 is calculated from the known segment lengths of polystyrene

Table 2 Coil size, transition temperatures and interaction parameter ($\chi = A + B/T$)

No.	N	R_g^0 (nm)	T_s (K)[a]	$A \times 10^3$[a]	B[a]
1	275	4.35	417 (17)	−6 (5)	39 (1)
2	179	3.64	315 (6)	−79 (2)	55 (1)
3	215	3.85	347 (7)	−17 (4)	36 (1)
4	113	2.90	245 (36)	–	–
5	279	4.54	324 (7)	–	–

[a] Errors are given in parentheses

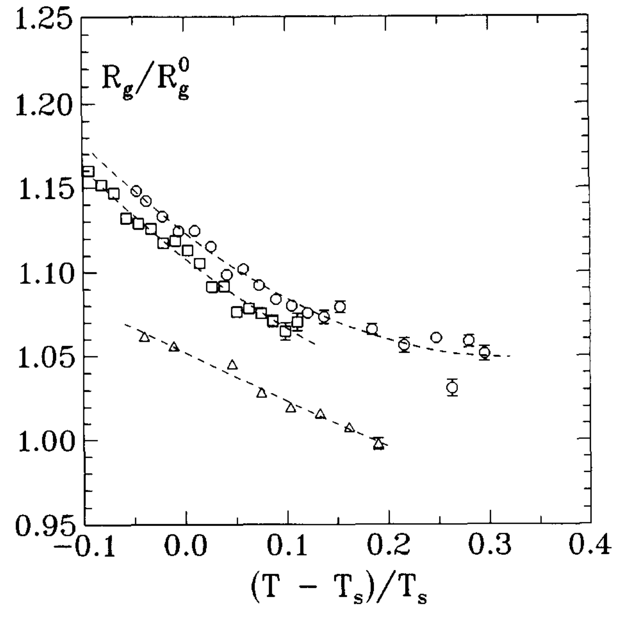

Figure 7 Radius of gyration divided by its Gaussian value. Sample no.: □, 1; ○, 2; △, 3

($a_{St}=0.68$ nm)[25] and polyisoprene ($a_{Is}=0.63$ nm)[26] and the degrees of polymerization N_{St} and N_{Is} (*Table 1*). In *Figure 7* the experimentally determined R_g is divided by its Gaussian value and plotted *versus* the reduced temperature. There is a clear temperature dependence indicating a stretching of the coil when approaching the MST. This effect is shown for polymer 2 in more detail in *Figure 8*. In addition to using the RPA structure factor to obtain R_g as a parameter for the overall shape of the profile one can separately obtain the segment length a from the Kratky regime $qR_g \gg 1$. For the homogeneous system above the MST one simply has

$$S(q) \rightarrow \frac{12f(1-f)}{q^2a^2} \tag{20}$$

On both scales, segmental and radius of gyration, the same T dependence is found. Numerical simulations of block copolymer melts have also shown an increase of R_g over its Gaussian value of the same order[27].

CONCLUSIONS

The concentration fluctuations in the homogeneous melt of diblock copolymers are found to be well described by Leibler's RPA. The correct interpretation of SAXS experiments however, affords the introduction of a distribution of molecular weight into the theoretical structure factor. Including the scattering from density fluctuations we have a precise description of the SAXS experiment in the range $0.9 \leqslant qR_g \leqslant 15$.

It is then possible to derive values for the interaction parameter χ and study its dependence on temperature and composition. We find the temperature variation of χ in the homogeneous phase to be consistent with the linear law equation (19), and χ appears to depend on the composition of the block copolymer.

The microphase transition takes place in a rather broad temperature range. This regime is characterized by a reduction of the number of contacts between the blocks and an increase of the polymer coil size. Both observations demonstrate the necessity to incorporate composition fluctuations into a theory for the microphase separation[21]. So far the only theory available treats composition fluctuations for a nearly symmetric diblock copolymer. Its major conclusions concerning the structure factor are qualitatively supported by our data.

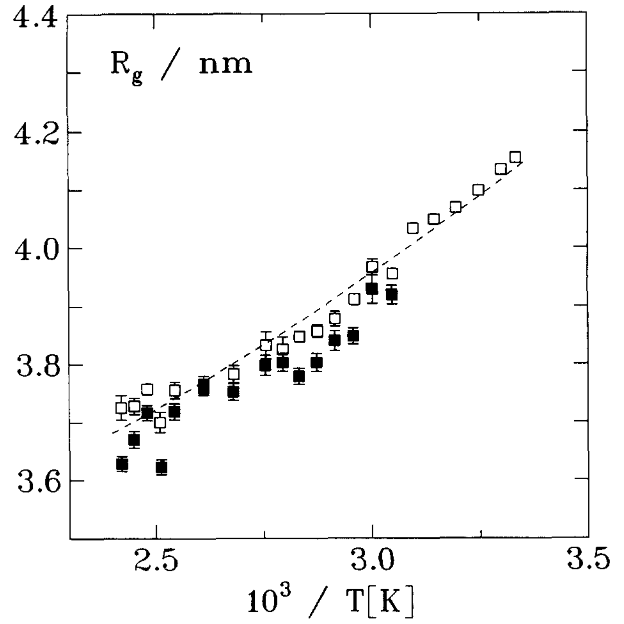

Figure 8 Comparison of coil expansion obtained from the peak position (→R_g) and from the large q scattering (→R_g (Kratky)) for sample 2. ■, R_g (Kratky); □, R_g

In approaching the MST we find an increase of the polymer coil size. It is reflected by a shift of the maximum q^* as well as by an expansion of the segment length as obtained from the scattering at large scattering vectors. The observed swelling of the polymer coil is not described by the theory. It is expected from scaling considerations because the ideal coil relation $R_g \propto N^{0.5}$ in the homogeneous phase is replaced by $D \propto N^{0.636}$ for the period of the ordered phase[28]. Monte Carlo simulations show the swelling in the transition regime[27].

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REFERENCES

1 Goodman, I. 'Developments in Block Copolymers', Applied Science, London, 1982
2 Leibler, L. *Macromolecules* 1980, **13**, 1602
3 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, 1979
4 Bates, F. S. and Hartney, M. A. *Macromolecules* 1985, **18**, 2478
5 Mori, K., Hasegawa, H. and Hashimoto, T. *Polymer J.* 1985, **17**, 799
6 Stühn, B. and Rennie, A. R. *Macromolecules* 1989, **22**, 2460
7 Owens, J. N., Gancarz, I. S. and Koberstein, J. T. *Macromolecules* 1989, **22**, 3380
8 Mori, K., Tanaka, H., Hasegawa, H. and Hashimoto, T. *Polymer* 1989, **30**, 1389
9 Strobl, G. R. *Acta Cryst.* 1970, **A26**, 367
10 Roe, R. J. and Zin, W. C. *Macromolecules* 1980, **13**, 1221
11 Koningsveld, R., Kleintjens, L. A. and Schoffeleers, H. M. *Pure Appl. Chem.* 1974, **39**, 1

12 Benoit, H. and Leibler, L. *Polymer* 1981, **22**, 195
13 Mori, K., Tanaka, H. and Hashimoto, T. *Macromolecules* 1987, **20**, 381
14 de la Cruz, M. O. and Sanchez, I. C. *Macromolecules* 1986, **19**, 2501
15 Benoit, H. and Hadziioannou, G. *Macromolecules* 1988, **21**, 1449
16 Leibler, L. and Benoit, H. *Polymer* 1981, **22**, 195
17 Hong, K. M. and Noolandi, J. *Polym. Commun.* 1984, **25**, 265
18 Abramowitz, M. and Stegun, I. A. 'Handbook of Mathematical Functions', Dover Publications Inc., New York, 1972
19 Binder, K. and Frederickson, G. H. *J. Chem. Phys.* 1990, **10**, 6195
20 Brazovskii, S. A. *Zh. Eksp. Teor. Fiz.* 1975, **68**, 175
21 Frederickson, G. H. and Helfand, E. *J. Chem. Phys.* 1987, **87**, 697
22 Brandrup, J. and Immergut, E. H. 'Polymer Handbook', John Wiley and Sons, New York, 1975
23 Hellwege, K. H., Knappe, W. and Lehmann, P. *Kolloid Z. Z. Polym.* 1962, **182**, 110
24 Bates, F. S., Rosedale, J. H. and Frederickson, G. H. *Phys. Rev. Lett.* 1988, **61**, 2229
25 Ballard, D. G., Wignall, G. D. and Schelten, J. *Eur. Polym. J.* 1973, **9**, 965
26 Wagner, H. L. and Flory, P. J. *J. Am. Chem. Soc.* 1952, **74**, 195
27 Minchau, B., Dünweg, B. and Binder, K. *Polym. Commun.* 1990, **31**, 348
28 Ohta, T. and Kawasaki, K. *Macromolecules* 1986, **19**, 2621