

## Thermotropic Transition from a State of Liquid Order to a Macrolattice in Asymmetric Diblock Copolymers

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The disorder-to-order transition in asymmetric diblock copolymers of polystyrene/polyisoprene is studied using small angle x-ray scattering. In between the homogeneously disordered state at high temperature and the bcc ordered array of spheres we find a stable state of liquidlike order between the spherical domains. Quantitative analysis of this order is possible in the framework of the Percus-Yevick theory for hard sphere liquids. The transition to the ordered state occurs at a sphere volume fraction of 0.47. The size of the spheres may be determined in the disordered as well as the ordered state and is found to increase continuously with decreasing temperature.

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The microphase separation transition in block copolymers combines the properties of a segregation phenomenon and of a disorder-to-order transition. It is therefore of interest in the context of many fields of physics. An important impulse for both theoretical and experimental studies was provided by theory [1], pointing out the similarity of the microphase separation transition in block copolymers and the solidification of a liquid. The latter aspect refers to the ordering of domains on a macrolattice.

In the simplest case of a diblock copolymer these are linear chain molecules consisting of two chemically distinct blocks  $[A]_n$  and  $[B]_m$ . For most pairs of monomers one has a repulsive effective interaction between  $A$  and  $B$  segments. As a consequence the system phase separates on a mesoscopic scale as soon as this interaction outweighs the entropy of mixing. In contrast to the macroscopic phase separation which is generally observed in polymer blends this phenomenon is termed microphase separation transition. It is a disorder-to-order transition (DOT) in the liquid state. For symmetric composition ( $f \approx 1/2$ ) the properties of this transition have been extensively studied theoretically [1–3] and the thermotropic transition could be observed experimentally [4–7].

The picture of the DOT is qualitatively different when one changes the composition of the diblock copolymer from the symmetric to the asymmetric case [8]. The separation of segments  $A$  and  $B$  in the ordered state now leads to cylindrical or spherical domains of an  $A$  rich phase in a matrix of  $B$  rich material. These domains order with two- or three-dimensional periodicity on lattices that are described as hexagonally packed cylinders (hpc) or spheres in a body centered cubic lattice (bcc). The transition from the disordered state to these states of order is expected to occur at considerably larger values of the repulsive interaction between  $A$  and  $B$  as compared to the symmetric diblock copolymer. The disordered state will therefore exhibit much stronger concentration fluctuations.

The results presented in this Letter refer to the DOT in a melt of a strongly asymmetric diblock copolymer.

A full account of this investigation including molecular weight dependence will be given separately [9]. We use small angle x-ray scattering (SAXS) to characterize quantitatively the disordered as well as the ordered state and the temperature driven transition. We will show that the transition to the ordered state is preceded by a microphase separated state of liquidlike order between domains.

The diblock copolymer used in this study is a polystyrene/poly(cis1–4)isoprene of molecular weight  $M_w = 46\,000$  and polydispersity  $M_w/M_n = 1.09$ . The volume fraction of polystyrene  $f$  is 0.11. It was synthesized anionically in our laboratory using standard high vacuum techniques.

The SAXS measurements were carried out in an evacuated Kratky compact camera to reduce background and to avoid degradation of the sample. Temperature stability was better than 0.2 K. The source of radiation was a sealed x-ray tube with a Cu anode, and a graphite monochromator was applied to select the wavelength of Cu  $K\alpha$  radiation  $\lambda = 0.1542$  nm. Data have been desmeared using standard procedures to result in the scattering cross section. The registration of a scattering profile at one temperature takes approximately 120 min, and the sample was annealed after each temperature change for 30 min to make sure that it was in thermal equilibrium. Repeated heating and cooling cycles with fresh samples and varying duration were used to verify the thermal stability of the sample.

In the following we will first discuss the different shapes of the scattering profile obtained for various temperatures. We will then turn to the variation of the structural parameters with temperature and finally discuss the properties of the phase transition leading from a state of liquidlike order to a macrolattice.

The intensity  $I(q)$  at a scattering vector  $q$  in a SAXS experiment is proportional to the Fourier transform of correlations in the concentration fluctuations or the structure factor of the sample. In Fig. 1 we show the three qualitatively different shapes of  $I(q)$  that are observed in different temperature regimes.

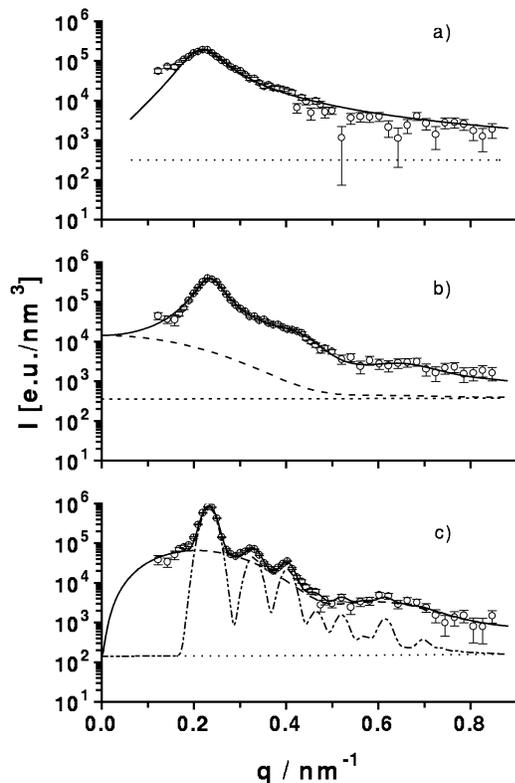


FIG. 1. Comparison of the scattering profiles referring to the homogeneously disordered state [(a)  $T = 458$  K], the state of liquidlike order between spherical domains [(b)  $T = 413$  K], and the bcc ordered state [(c)  $T = 318$  K]. The full lines are fits of structural models for the different states of order (see text).

At high temperature the structure factor displays a broad peak at a position  $q^*$  indicating the existence of a dominating wave vector in the spectrum of concentration fluctuations. In Leibler's random phase approximation theory [1] this wave vector is related to the radius of gyration of the diblock copolymer molecule. The full structure factor is also given by this theory, and the full line in Fig. 1(a) refers to a fit of this structure factor to our data after correction for polydispersity [10]. The dotted horizontal line in Fig. 1(a) marks the contribution of density fluctuations to the scattering. Its value is determined from the flat background at large  $q$  [10].

At lower temperatures a different shape of the structure factor is observed as is shown in Fig. 1(b). Besides the strong maximum at small  $q$  two more peaks are seen in this profile. Obviously the system has reached a significantly larger degree of order. The increase of the repulsive segmental interaction with lowering temperature as described by  $\chi$  is known to give rise to concentration fluctuations also for symmetric diblock copolymers [5,11]. They show up in the temperature dependence of the scattering intensity at  $q^*$  [2]. The situation is different in the case of strongly asymmetric copolymers. The expected ordered state [1,3] consists

of spheres that arrange on a bcc lattice. However, a separation of polystyrene and polyisoprene segments may also be achieved by local demixing and formation of spherical domains without the additional loss of entropy due to the arrangement of the spheres on a lattice [8]. This micellar type of order has been observed in solutions of diblock copolymers [12,13] as well as in blends of block copolymers and homopolymers [14], which are thermodynamically similar to the pure melt.

In the present case of a diblock copolymer melt we assume a partial demixing which leads to polystyrene spheres in a matrix of polyisoprene and some remaining molecules that are not bound to the sphere. The polydispersity of the block copolymer supports this mechanism. The structure factor of such a system will exhibit intraparticle as well as interparticle interferences. The intraparticle interference is described by the structure factor of a homogeneous sphere with radius  $R_{sp}$  and volume  $v_{sp}$  as

$$\Phi(qR_{sp}) = \left\{ v_{sp} \frac{3}{(qR_{sp})^3} [\sin(qR_{sp}) - qR_{sp} \cos(qR_{sp})] \right\}^2. \quad (1)$$

In order to account for the distribution of sphere sizes that will be present in our sample we average Eq. (1) with a Gaussian distribution of  $R_{sp}$  and a second moment  $\sigma_{sp}^2$  to result in  $\bar{\Phi}(qR_{sp})$ . For distances that are in between  $R_{sp}$  and the end-to-end distance of the polymer molecules the interaction between spheres will be dominated by a repulsive potential which results from the presence of the polyisoprene chains bound to the sphere surface. The pair correlation function of a fluid of hard spheres has been obtained in closed form for the Percus-Yevick (PY) model [15]. Although there is no phase transition predicted by this model we use it to describe the interparticle interference factor

$$S(q) = \{1 + 24\eta G(x)/x\}^{-1}, \quad (2)$$

with  $x = 2qR_{hs}$ .

The function  $G(x)$  is explicitly given in Ref. [16]. The parameters entering this equation are the volume fraction of hard spheres  $\eta$  and the hard-sphere radius  $R_{hs}$ . We note that  $R_{hs}$  marks the range of the repulsive interaction between spheres and is therefore larger than the geometric size of the polystyrene domain  $R_{sp}$  appearing in  $\Phi$ .

The scattering profile for the hard-sphere fluid is then given as

$$I_{hs}(q) = K\bar{\Phi}(qR_{sp})S(q). \quad (3)$$

The scaling factor  $K$  depends on the electron density difference between the polystyrene spheres and the matrix. The full curve in Fig. 1(b) corresponds to a fit of Eq. (3) to the scattering data. The dotted line indicates the shape of the scattering profile without interparticle interference as described by  $\bar{\Phi}(qR_{sp})$ . It shows that the polystyrene spheres are not only visible in the diffuse scattering at large  $q$  but in the full scattering profile. The

agreement is extremely good and allows us to determine  $R_{hs}$ ,  $\eta$ , and  $R_{sp}$ . The fit shown in Fig. 1(b) was obtained with a width of the distribution for  $R_{sp}$  of  $\sigma_{sp} = 1.5$  nm.  $\sigma_{sp}$  is nearly independent of temperature.

At even lower temperatures the system develops solid-like order as is seen in the scattering profile of Fig. 1(c). The reflections observed in this state of order may all be identified as belonging to a bcc lattice ( $Im\bar{3}m$ ). Our scattering pattern contains 14 reflections. For an isotropic ensemble of bcc ordered domains the scattering intensity at a Bragg position is modulated by the Lorentz factor ( $1/q^2$ ) and the form factor of the scattering particle as given in Eq. (1):

$$I_{\text{Bragg}}(q) = \sum_{\{hkl\}} \bar{\Phi}(q_{hkl}R_{sp}) \frac{j_{hkl}}{q^2} G_{hkl}(q; \sigma) \times \exp\{-q_{hkl}^2 u^2/3\}. \quad (4)$$

$G_{hkl}(q; \sigma)$  denotes a normalized Gaussian centered at the Bragg position  $q_{hkl}$  with width  $\sigma$  and  $j_{hkl}$  is the multiplicity of the set  $\{hkl\}$  of equivalent reflections.

Equation (4) alone does not adequately describe our data. We need to take diffuse scattering into account, which is caused by the deviation of the actual position of the spheres from their mean in the bcc lattice. We assume the disorder to be isotropic and describe it with the help of a single mean squared deviation  $u^2$ . The disorder has the effect of decreasing the Bragg intensities in Eq. (4) and at the same time generating an additional diffuse scattering component which carries essentially the  $q$  dependence of the  $\bar{\Phi}$ ,

$$I_{\text{diff}} = \bar{\Phi}(qR_{sp})(1 - \exp\{-q^2 u^2/3\}). \quad (5)$$

The total intensity at a given scattering vector  $q$  then is the weighted sum of the components given in Eqs. (4) and (5). Density fluctuations are taken into account as a  $q$ -independent contribution to the scattering intensity. The full line in Fig. 1(c) is a fit of this model to the data, and again the agreement is good. The diffuse scattering component is indicated as a broken line in the figure and is seen to contribute significantly to the overall scattering. We are thus able to extract from this analysis the lattice constant  $a$ , the mean squared displacement  $u^2$ , as well as the sphere radius  $R_{sp}$ .

We now turn to a discussion of the temperature dependence of the concentration fluctuations. In Fig. 2 we show the reciprocal intensity at the position  $q^*$  of the first maximum in the scattering profile. Within Leibler's theory it should depend linearly on reciprocal temperature, and such a regime is indeed found above  $T \approx 460$  K. The extrapolation of this linear behavior defines a spinodal temperature  $T_s = 450$  K. We find no significant change of the scattering pattern at this temperature which is in agreement with observations made on symmetric diblock copolymers [5]. However,  $I(q^*)^{-1}$  clearly bends off the linear line in the range of  $T_s$ , which is taken as an indica-

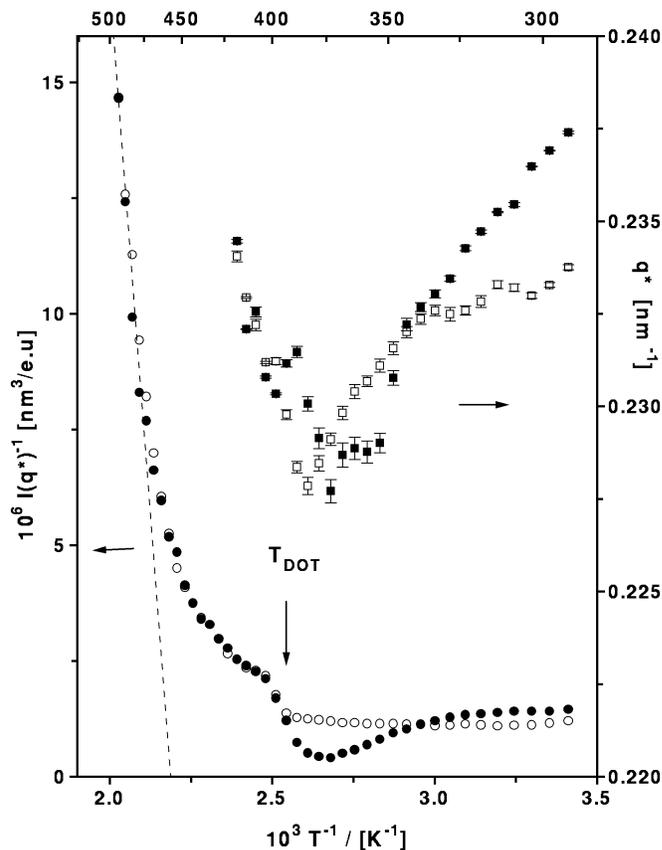


FIG. 2. The reciprocal intensity and the position of the maximum of the first peak in the scattering profile. The reciprocal temperature is directly proportional to the repulsive interaction between the blocks. Open symbols: heating, filled symbols: cooling. The system is completely reversible above  $T_{\text{DOT}}$ .

tion for the contribution of concentration fluctuations [11]. At a well-defined temperature  $T_{\text{DOT}} = 393$  K  $< T_s$ , the intensity  $I(q^*)$  increases abruptly, and at the same point the shape of the scattering profile changes from the PY form in Fig. 1(b) to the form shown in Fig. 1(c).  $T_{\text{DOT}}$  marks the transition from a state of liquid order between spheres for  $T > T_{\text{DOT}}$  to a bcc ordered array in the regime  $T < T_{\text{DOT}}$ . Below  $T_{\text{DOT}}$  the intensity decreases because of the glass transition of the polystyrene spheres. Their density remains essentially constant, whereas the density of the polyisoprene matrix keeps increasing with lowering temperature thus reducing the scattering contrast between the spheres and the matrix.

The phase behavior is completely reversible for  $T > T_{\text{DOT}}$ . Below  $T_{\text{DOT}}$ , however, we find different intensities in the heating and in the cooling run.

Also included in Fig. 2 is the temperature dependence of the position  $q^*$  of the first maximum in the scattering profile. It is seen to decrease with lowering temperature, which in the disordered state indicates a stretching of the polymer chains. At the transition to the ordered state this trend is reversed and  $q^*$  shifts to larger values. This

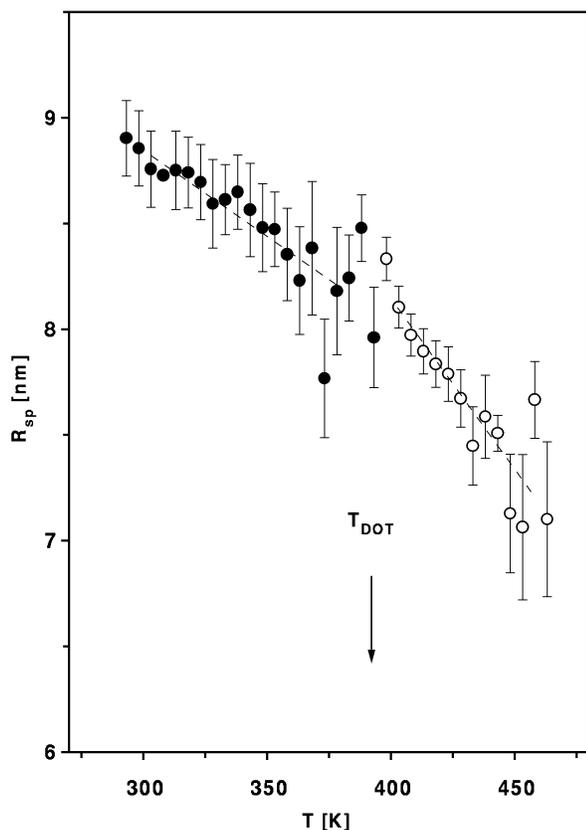


FIG. 3. The radius  $R_{sp}$  of the polystyrene spheres obtained from a fit of Eq. (3) above  $T_{DOT}$  (open symbols) and Eq. (4) below (filled symbols).  $R_{sp}$  varies continuously through both regimes thus demonstrating the applicability of the structural models.

behavior is in accordance with theory for the transition to a bcc lattice [3,8].

The detailed analysis of the PY regime and the bcc ordered state both allow the determination of the sphere radius  $R_{sp}$ . The temperature dependence of  $R_{sp}$  is given in Fig. 3 for both regimes.

The smallest observed polystyrene sphere is of radius  $R_{sp} = 7$  nm at  $T = 470$  K. This amounts to a stretching of the molecule by 1.4 over its unperturbed dimension. The model of Ref. [8] compares well with a calculated stretching of 1.24.

There is no discontinuity at the ordering transition, and  $R_{sp}$  is consistently determined by the application of PY model equation (3) at high temperatures and from the ordered state using Eqs. (4) and (5).  $R_{sp}$  increases monotonically with decreasing temperature. Above  $T_{DOT}$  the subsequent implementation of molecules with increasing interaction  $\chi$  into the polystyrene sphere may be responsible for the strong variation of sphere size with temperature.

The situation is different for the range of the interaction between spheres. It is defined in the PY regime as the hard sphere radius  $R_{hs}$ . Above  $T_{DOT}$  we find the hard sphere radius to be proportional to the sphere radius  $R_{sp}$

(see Fig. 3),  $R_{hs} \approx 1.8R_{sp}$ . In the ordered state, however,  $R_{sp}$  continues to increase with lowering temperature, but at the same time the lattice constant and therefore the distance between spheres decreases.

The mean squared displacement of the spheres in the ordered state is nearly independent of temperature and  $\sqrt{u^2} \approx 4.5$  nm.

The parameter that controls the ordering transition in a hard sphere fluid is the volume fraction of spheres  $\eta$ . We find  $\eta$  to increase linearly from 0.37 at  $T = 450$  K to 0.47 at the ordering transition.  $\eta = 0.494$  is indeed expected for the transition to occur in a hard sphere liquid [17].  $\eta$  is related to the volume fraction of polystyrene spheres  $\Phi_v$  as  $\Phi_v = \eta(R_{sp}/R_{hs})^3$  in the PY regime. In the bcc ordered state we calculate  $\Phi_v$  as  $\Phi_v = 8/3\pi(R_{sp}/a)^3$ . Again we find a continuous increase of  $\Phi_v$  with lowering temperature and this quantity extrapolates correctly to  $f$  at low  $T$ .

In summary, we have observed an equilibrium state of microphase separated spherical domains with liquidlike order in the melt of an asymmetric diblock copolymer. Lowering temperature leads to an increase of the domain size as more chains become integrated into the spheres. Their volume fraction consequently increases, and at a volume fraction that is close to the critical value for the phase transition in a hard sphere system a DOT to a bcc lattice occurs.

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