Eur. Phys. J. B **4**, 325–332 (1998)

THE EUROPEAN PHYSICAL JOURNAL B

Phase behavior of binary blends of symmetric polystyrene-polybutadiene diblock copolymers studied using SANS

C.M. Papadakis[1,a], K. Mortensen[1], and D. Posselt[2]

[1] Condensed Matter Physics and Chemistry Department, Risø National Laboratory, P.O. Box 49, 4000 Roskilde, Denmark
[2] IMFUFA (Department of Mathematics and Physics), Roskilde University, P.O. Box 260, 4000 Roskilde, Denmark

Received: 9 February 1998 / Revised: 20 April 1998 / Accepted: 24 April 1998

Abstract. Binary blends of compositionally symmetric diblock copolymers are investigated using small-angle neutron scattering. The study focuses on the miscibility of blends of polystyrene-polybutadiene diblock copolymers as a function of chain length ratio and blend composition, and the results are related to the theoretical phase diagram put forward by M.W. Matsen (J. Chem. Phys. **103**, 3268 (1995)). Three different low molar mass copolymers were blended with a high molar mass copolymer. We find very good coincidence with the theoretical phase diagram obtained. Only for blends having a chain length ratio of 0.06, theory predicts that a larger amount of short copolymers can be dissolved in the matrix of long copolymers, and *vice versa*. With the latter blends and volume fractions of short chains between 0.11 and 0.70, the second-order Bragg-peaks do not vanish, which indicates that the lamellae are asymmetric.

PACS. 61.41.+e Polymers, elastomers, and plastics – 64.60.Cn Order-disorder transformations; statistical mechanics of model systems – 61.12.Ex Neutron scattering techniques (including small-angle scattering)

1 Introduction

Diblock copolymers consist of two chemically distinct polymer blocks joined by a covalent bond. In compositionally symmetric diblock copolymers, both blocks have the same volume. Their phase behavior is usually described in terms of the combined parameter χN, where χ denotes the Flory-Huggins segment-segment interaction parameter, being inversely proportional to temperature, and N the overall chain length [1]. In the bulk, pure systems of symmetric diblock copolymers form a microphase-separated, lamellar structure or a disordered melt with some correlation on the length scale of the order of the overall radius of gyration, depending on whether χN is above or below a threshold value, $(\chi N)_{ODT}$. The order-disorder transition (ODT) is by mean-field theory predicted to be a second-order phase transition located at $(\chi N)_{ODT} = 10.5$ [2]. When fluctuations are included in the calculations, $(\chi N)_{ODT}$ becomes N-dependent and the ODT becomes weakly first-order [3].

Binary blends of chemically identical, symmetric diblock copolymers having different chain lengths have been studied experimentally and have under certain conditions been found to phase-separate macroscopically [4–7]. However, in none of these studies, the conditions for macrophase-separation were systematically investigated as a function of χN_l (N_l denotes the overall chain length of the long copolymers), *i.e.* the results of these studies cannot be related to each other or to theories. In the systems studied so far, macrophase-separation has been encountered for chain length ratios $\alpha = N_s/N_l < 0.2$ (N_s denotes the overall chain length of the short copolymers) and for volume fractions of short copolymers $\phi_s > 0.2 - 0.3$, the location of the phase transition depending on α [4–7]. Macrophase-separation was found to be highly asymmetric in blend composition, *i.e.* the solubility of short copolymers in a matrix of long copolymers is larger than it is *vice versa*. In the lamellar one-phase state with only few short copolymers ($\phi_s = 0.10$) being added to a lamellar sample of long symmetric copolymers, it was found that the short copolymers preferentially reside at the interfaces [8].

Various theories have been put forward to describe the phase behavior of binary blends of diblock copolymers [9–13], all being mean-field theories. The most pronounced differences to pure copolymer systems are the following: on the one hand, dissolving short copolymers in a lamellar matrix of long copolymers means that the long copolymers must stretch through the layer of short copolymers residing at the interface and thus assume a "mushroom conformation", which corresponds to a considerable loss of entropy and may cause precipitation of a certain amount of short copolymers, *i.e.* macrophase-separation. On the other hand, dissolving long copolymers in a lamellar matrix of short copolymers means that the

---

[a] e-mail: `Christine.Papadakis@risoe.dk`

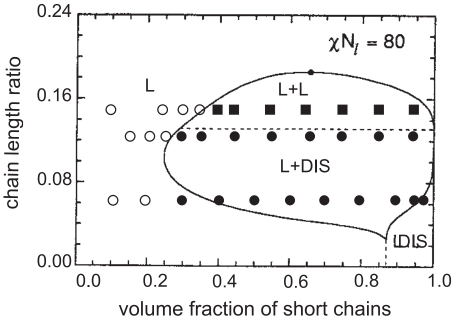


Fig. 1. Theoretical phase diagram for binary blends of symmetric diblock copolymers for $\chi N_l = 80$, as calculated by Matsen (see [13]). The full lines denote binodals and the dashed lines continuous transitions. The symbols indicate the blends studied in the present work. Blends which were found to be in the lamellar one-phase state (○), macrophase-separated blends consisting of lamellar and disordered domains (●), and macrophase-separated blends with coexisting lamellar domains (■).

long copolymers loose a significant amount of entropy due to the confinement in a narrow lamellar domain. These entropy losses are included in all the approaches cited above, and all of them, except the one described in reference [13], fail in predicting macrophase-separation. This means that macrophase-separation cannot only be due to the entropic changes compared to the pure system, but is more subtle. The latter approach [13] uses self-consistent field theory in order to calculate the phase diagram as a function of α, ϕ_s and χN_l (Fig. 1). The block junctions are not confined to the lamellar interfaces and the copolymers' trajectories are allowed to fluctuate around straight paths [13]. The two different segments are assumed to have equal volumes and lengths. The phase states predicted by this theory are (i) a lamellar one-phase state with most of the short copolymers residing at the interfaces of the lamellar structure formed by the long copolymers, (ii) a disordered one-phase state, and (iii) a macrophase-separated state, where a lamellar phase rich in long copolymers coexists with a phase rich in short copolymers, which can either be lamellar or disordered, depending on χN_s (Fig. 1). For $\chi N_l = 80$ (the case studied in the present publication), macrophase-separation is predicted for $\sim 0.02 < \alpha < 0.2$ and $0.25 < \phi_s < 1$, with the exact locations of the phase boundaries depending on α. For $\alpha < 0.02$, no macrophase-separated state is predicted, but a direct transition from the lamellar to the disordered one-phase state takes place at $\phi_s \simeq 0.87$. The transitions between the lamellar and the disordered one-phase state encountered upon changing α or ϕ_s (the dashed lines in Fig. 1) are in the field-theoretical framework predicted to be continuous; however, due to fluctuations (which have not been included), they are in real systems expected to be first-order phase transitions [13].

In the present study, we investigate systematically the conditions for macrophase-separation in binary blends of symmetric diblock copolymers, which are equal in chemical structure and only differ in their overall chain length. Even though macrophase-separation has been observed in binary blends of symmetric diblock copolymers in a few studies [4–7], we are not aware of a systematic test of the predictions from reference [13]. We study blends of symmetric polystyrene-polybutadiene (SB) diblock copolymers, which all previously have been characterized thoroughly [14–16]. As we have determined the χ-parameter of the polystyrene-polybutadiene pair experimentally, we are able to compare our results quantitatively with the phase diagram from reference [13]. For this purpose, we have prepared three series of blends: copolymers with three different low molar masses were blended with the same high molar mass copolymer. The latter has $\chi N_l \simeq 80$ at the measuring temperature chosen and is thus strongly segregated, *i.e.* its concentration profile is close to rectangular with narrow interfaces between the two parts of the lamellae [16]. The three series have the chain length ratios $\alpha = 0.15$, 0.12 and 0.06 and consist of blends with different volume fractions of short copolymers, ϕ_s (Fig. 1). As $\alpha < 0.2$ for all three series, we expect blends with large values of ϕ_s to macrophase-separate. With the series having $\alpha = 0.15$, we have the possibility of identifying the transition from the lamellar one-phase state to the macrophase-separated state with coexisting domains of thick and thin lamellae. With the two other series, we can study the transition from the lamellar one-phase state to the macrophase-separated state with a lamellar phase rich in long copolymers coexisting with a disordered phase being nearly pure in short copolymers. With the series with $\alpha = 0.06$, we also expect to access the transition from the macrophase-separated to the disordered one-phase state, predicted at $\phi_s \simeq 0.96$. The sample structures were studied using small-angle neutron scattering (SANS).

2 Experimental

2.1 Sample preparation

The blends were prepared from compositionally symmetric polystyrene-polybutadiene diblock copolymers, which were polymerized anionically under inert atmosphere [17] and have narrow molar-mass distributions. The characterization of the parent copolymers is given in references [15, 16]. Using ^{1}H NMR, the volume fractions of polybutadiene have been found to be 0.49±0.01 for all samples. The overall chain lengths, N, were calculated based on the segment of polybutadiene. The χ-parameter at 150 °C (the temperature chosen for all preparations and measurements) was determined to be 0.033 ± 0.007. The chain lengths, the ODT temperatures and the χN-values at 150 °C are given in Table 1.

Blends of a high molar mass diblock copolymer ($N_l = 2511$) with three low molar mass diblock copolymers (N_s = 156, 310 and 374) were prepared by dissolving the different copolymers in toluene at concentrations of 25-30 mg/ml together with 1 weight-% (relative to the polymer mass) of the antioxidant Irganox 1010. In the following, we neglect the difference between volume and weight fraction of the different copolymers. The solutions

Table 1. Characteristics of the parent polystyrene-polybutadiene diblock copolymers: the overall chain lengths N based on the polybutadiene monomer volume, the order-disorder transition temperatures, and the χN-values at 150 °C [16]. (a) Outside the experimentally accessible temperature range.

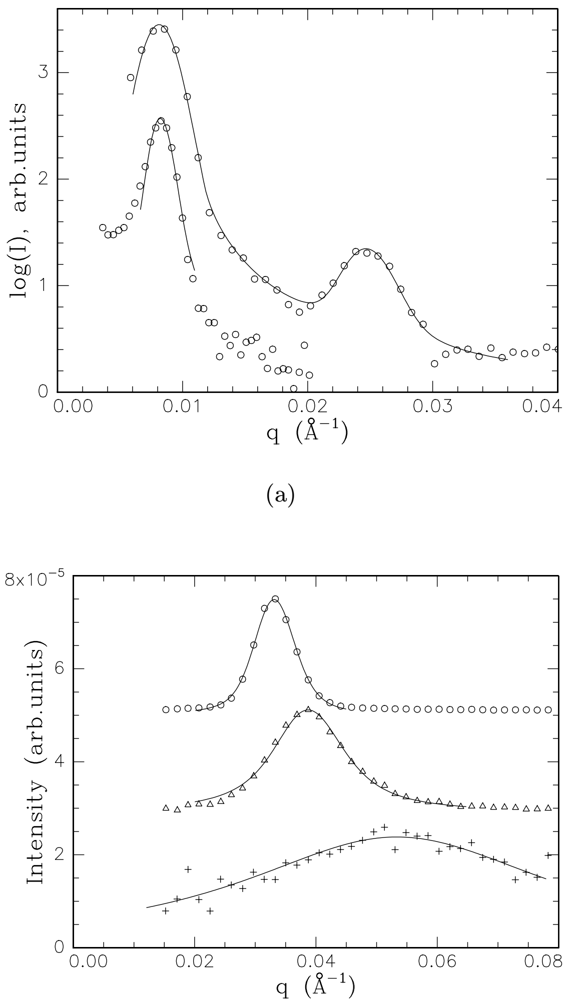
Sample	N	T_{ODT} (°C)	χN at 150 °C
SB07	2511	(a)	81
SB12	374	181 ± 1	12
SB11	310	130 ± 1	10
SB05	156	(a)	5

were stirred until the polymer was dissolved and were then left to dry at room temperature for 1-6 days. The samples were further dried in a vacuum oven at 140-160 °C at a pressure of 0.04 mbar for one day, *i.e.* above the highest glass transition temperature of the copolymers (∼ 100 °C) and above the ODT temperatures of the samples with $N = 156$ and 310 (Tab. 1). The blends containing short copolymers with $N = 374$ were heated to 200 °C for 10 min right before the SANS measurements, *i.e.* above the ODT temperature of the pure short copolymers.

A minor degree of crosslinking of the long chains (below 2%) occured during preparation, as indicated by size exclusion chromatography.

2.2 SANS

SANS measurements were carried out at Risø National Laboratory. Each sample was measured using three different settings in order to cover a large q-range. The following neutron wavelengths and sample-detector distances were used: 14.8 Å/6 m, 6.98 Å/6 m and 6.98 Å/3 m. In this way, q-ranges of ∼ 0.004-0.020, ∼ 0.006-0.040 and ∼ 0.015-0.08 Å^{-1} were covered. The copolymer samples were pressed into pills of ∼ 1.5 mm thickness and were mounted between aluminum foil in a furnace which was under vacuum or surrounded by air. For all measurements, a temperature of 150 °C was chosen. The temperature was controlled with a stability better than 0.5 °C. Before the measurements, the samples were left to equilibrate at 150 °C for at least 10 min. The measuring times were 10 min for 6.98 Å and 30 min for 14.8 Å. The two-dimensional spectra show Debye-Scherrer rings from the lamellar domains and, in some cases, broad rings corresponding to correlation peaks from disordered domains. Because of air bubbles in the samples, the amount of material in the beam varied significantly, and we have therefore not brought the intensities to an absolute scale. Data analysis was made using standard Risø software. The spectra were azimuthally averaged and the background from aluminum foil and the dark current were subtracted. In order to determine the peak positions, q^*, Lorentz-functions were convoluted with the instrumental resolution and fitted to the peaks [18] both in the ordered and the disordered state, for reasons of consistency. When two peaks are present, two Lorentz-functions were fitted simultaneously.



(a)

(b)

Fig. 2. Azimuthally averaged SANS spectra of the parent copolymers with Lorentz-functions (convoluted with the instrumental resolution) fitted to the peaks. (a): $N = 2511$, measured at two different settings: 6.98 Å/6 m (upper curve), 14.8 Å/6 m (lower curve), semi-logarithmic representation. (b): $N = 374$, 310 and 156 (from top to bottom), all measured at 6.98 Å/3 m. For clarity, the intensities were scaled and shifted by arbitrary amounts.

Size exclusion chromatography showed that, in the course of the SANS experiments with the sample surrounded by air, the amount of crosslinked material was substantial (up to 17 %). Both the formation of dimers and trimers and deterioration of the high molar mass copolymer are observed. Therefore, additional experiments were made with the samples under vacuum during the SANS experiments, especially with those samples which are close to the phase boundaries identified. The samples measured under vacuum had a lesser degree of crosslinking: typically less than 7 % of crosslinked material. The peak positions found in these latter measurements were used for establishing the phase boundaries.

3 Results and discussion

3.1 Parent diblock copolymers

SANS spectra of the pure high molar mass copolymer ($N_l = 2511$), measured at 150 °C are given in Figure 2a. The χN-value of this sample at the measuring temperature of 150 °C is $\sim 81 \gg (\chi N)_{ODT}$, the sample is in the so-called strong-segregation regime [14]. The absence of the second-order Bragg-peak shows that the lamellae are close to symmetric (*e.g.* [16]), and the presence of a relatively well-developed third-order Bragg-peak indicates that the concentration profile is close to rectangular, as expected for a sample in the strong-segregation regime [19]. SANS spectra of the three low molar mass samples measured at 150 °C are given in Figure 2b. At that temperature, the sample with $N = 374$, having $\chi N \simeq 12$, is lamellar. The two other samples are disordered [14]: the sample with $N = 310$ has $\chi N \simeq 10$ and is thus close to the ODT. The sample with $N = 156$ has $\chi N \simeq 5.1$ and is thus quite deep in the disordered state. The deeper the sample is in the disordered state, the flatter and broader is the correlation peak, because the amplitude of the concentration fluctuations decreases with decreasing χN.

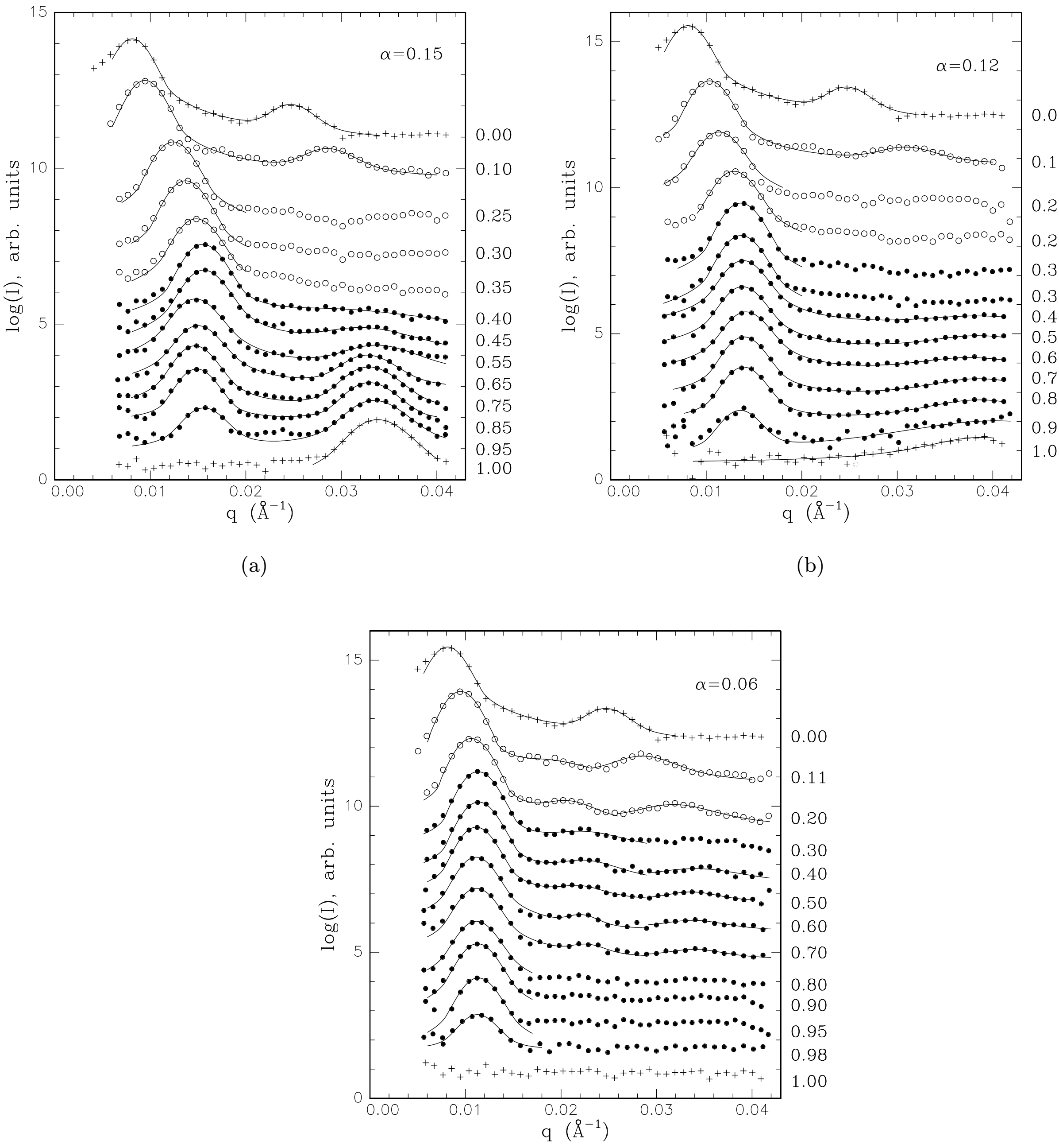
3.2 Copolymer blends

Azimuthally averaged SANS spectra of the three series of blends (all measured at 150 °C) are shown in Figures 3a–c. The spectra display Bragg-peaks from the lamellar domains and/or correlation peaks from the disordered domains. The peak at low q is the first-order Bragg-peak from the lamellar phase rich in long copolymers. The position of this peak increases with ϕ_s, which is reasonable because the more short copolymers are contained in the lamellae, the smaller is the resulting lamellar thickness. The peak positions remain constant when the amount of short copolymers, ϕ_s, is between 0.40 and 0.95 for $\alpha = 0.15$, between 0.30 and 0.95 for $\alpha = 0.12$ and between 0.30 and 0.98 for $\alpha = 0.06$ (for the peak positions as a function of ϕ_s see Figs. 5a–c). The fact that the position of the first-order Bragg-peak of the domain rich in long copolymers remains constant is taken as the criterion for macrophase-separation because the peaks from the domains rich in short copolymers are often difficult to detect. In some of the spectra, third-order peaks (and in some cases, also second-order peaks, see below) from the lamellar domains are observed as well, indicating a relatively narrow interface of the concentration profile.

For $\alpha = 0.15$, Bragg-peaks at a position close to the one of the lamellar structure of the short parent copolymer are observed for $\phi_s \geq 0.40$ (Fig. 3a), indicating the coexistence of two lamellar phases, one being rich in long and one being rich in short copolymers, as expected from the theoretical predictions (Fig. 1) [13]. The intensity of these peaks relative to those from the domain rich in long copolymers increases with ϕ_s, indicating that the domain rich in short copolymers grows upon addition of short copolymers, which is reasonable. Note that this peak is not a second-order Bragg-peak from the domain rich in long copolymers, because the ratio of the position of this peak and the first-order Bragg-peak from the domains rich in long copolymers is typically 2.2 ± 0.03, which is significantly larger than 2.0. The peaks observed at $q \simeq 0.033$ Å^{-1} are thus not second-order Bragg-peaks from the domain rich in long copolymers, but first-order Bragg-peaks from the domain rich in short copolymers.

For $\alpha = 0.12$ and the setting 6.98 Å/6 m, broad correlation peaks close to the one of the pure short copolymer are observed for $\phi_s \geq 0.45$ (Fig. 3b), indicating coexistence of a lamellar domain rich in long copolymers and a disordered domain rich in short copolymers, as expected from Figure 1. As this correlation peak is relatively broad, it cannot be distinguished from the background for $\phi_s = 0.30$ and 0.35 with the setting 6.98 Å/6 m, because for these values of ϕ_s the domain rich in short copolymers is still small and, with this setting, the statistics are not good enough. The correlation peak can with these blends only be distinguished from the background in the spectra measured with 6.98 Å/3 m (not shown). The ratio of positions of the peaks from the domain rich in short copolymers and the first-order Bragg-peaks from the domain rich in long copolymers are typically 2.8 ± 0.04, which is significantly different from 3.0, showing that this peak is not a third-order Bragg-peak from the lamellar domain rich in long copolymers, but indeed the correlation peak from the disordered domain rich in short copolymers.

The same general behavior as for the other two blends is observed with the blends having $\alpha = 0.06$. By means of blends having a very high content of short copolymers ($\phi_s = 0.90$, 0.95 and 0.98), we attempted to detect the phase boundary between the macrophase-separated state and the disordered one-phase state, which is predicted at $\phi_s \simeq 0.96$ (Fig. 1). However, the spectra of these blends still display first-order Bragg-peaks from the lamellar structure rich in long copolymers (Fig. 3c), *i.e.* macrophase-separation persists up to $\phi_s = 0.98$. With this series measured at the setting 6.98 Å/3 m, broad and flat peaks close to the one of the pure short copolymer can only be distinguished from the background for $\phi_s \geq 0.90$ (Fig. 4). The peak from the domain rich in short copolymers from the blend with $\phi_s = 0.98$ has a higher position than the ones from blends with $\phi_s = 0.90$ and 0.95 and the pure short copolymer (Fig. 4), the reason being unclear. The sample was left to equilibrate at 150 °C for one day under vacuum and at the same temperature for 15 min right before the measurement. The parent short copolymers are disordered at that temperature. We therefore believe that the sample is near equilibrium in spite of the fact that equilibrium can only be attained by heating the blends over the long copolymers' ODT temperature, which is not possible with the present system.



(a)

(b)

(c)

Fig. 3. Semi-logarithmic representation of azimuthally averaged SANS spectra of the blends with $\alpha = 0.15$ (a), 0.12 (b) and 0.06 (c), measured at 6.98 Å/6 m: parent copolymers (+), blends in the one-phase state (○), macrophase-separated blends (●). The curves are shifted by arbitrary amounts. The lines are fits of Lorentz-functions, convoluted with instrumental resolution.

The peak positions found by fitting Lorentz-functions (which were convoluted with the resolution function of the instruments) to the peaks are given in Figures 5a–c. The expected increase of the positions of the first- and third-order Bragg-peak (and the second-order peaks for $\alpha = 0.06$) with increasing ϕ_s and the subsequent flattening-off is seen for all three series. Also given are the peak positions from the domains rich in short copolymers. For $\alpha = 0.15$ and 0.12, they are very similar to the ones from the short parent copolymers, indicating that only a very small amount of long copolymers is dissolved in this domain. Only the peak position for $\alpha = 0.15$ and $\phi_s = 0.40$ is somewhat lower than for larger ϕ_s. This may be an artifact caused by the low intensity of this peak. For

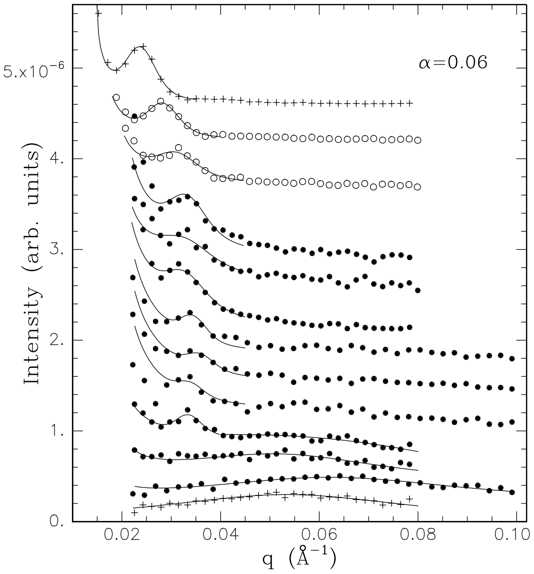


Fig. 4. High q-range of the azimuthally averaged SANS spectra of blends with $\alpha = 0.06$, measured at 6.98 Å/3 m or at 6.98 Å/2.32 m ($\phi_s = 0.60$, 0.70, 0.80 and 0.98). The intensities are scaled with arbitrary factors and the curves are shifted. Same symbols as in Figure 3. The lines are fits of Lorentz-functions, convoluted with instrumental resolution.

$\alpha = 0.06$, the peak from the domain rich in short copolymers can only be detected for $\phi_s \geq 0.90$, as discussed above.

We have added Matsen's predictions for the transition between the one-phase and the macrophase-separated state [13] to these diagrams (see also Fig. 1). The theoretical predictions coincide very well with our experimental findings for $\alpha = 0.15$ and 0.12, which is amazing, since no molecular details are incorporated into this theory. A slight discrepancy is found for $\alpha = 0.06$: theory predicts that a larger amount of short copolymers can be dissolved in the lamellar structure formed by the long copolymers. Possible reasons for the discrepancy are inaccuracies in the theory as well as experimental errors in determining ϕ_s, α, and χ, the polydispersity of the parent copolymers and the conformational asymmetry of the polystyrene-polybutadiene copolymers, which are not included in the theory [13].

With the blends having $\alpha = 0.06$, we observe that the short copolymers are preferentially dissolved in the polystyrene or the polybutadiene domains of the lamellae formed by the long copolymers, as indicated by the appearance of the second-order Bragg-peaks from the domain rich in long copolymers observed with this series (Fig. 3c): the presence of second-order Bragg-peaks indicates that the thick lamellae are slightly asymmetric, *i.e.* the polystyrene and the polybutadiene part are not equally thick, as is the case with the parent long copolymer (Fig. 2a). (Very weak second-order peaks are also observed in the spectra of blends with $\alpha = 0.15$ and $\phi_s = 0.10$ and 0.95, Fig. 3a, and with $\alpha = 0.12$ and $\phi_s = 0.15$, Fig. 3b.)

In order to quantify the asymmetry observed, we have derived a relationship between the ratio of thicknesses of the polystyrene and the polybutadiene lamellae, Φ, and the ratio of peak heights of the second- and the first-order Bragg peak, I_2/I_1. We assume that the lamellae have a rectangular profile (*i.e.* very narrow interfaces) and use standard methods [20]. Then, the intensity scattered by a polycrystal of stacks of N_s lamellae having an overall lamellar thickness D with the two parts of the lamellae having thicknesses ΦD and $(1-\Phi)D$ can be written as [16]

$$I(q) = \frac{(\Delta\rho)^2}{\pi q^4} \sin^2\left(\frac{qD\Phi}{2}\right) \frac{\sin^2(qDN/2)}{\sin^2(qD/2)} \cdot \qquad (1)$$

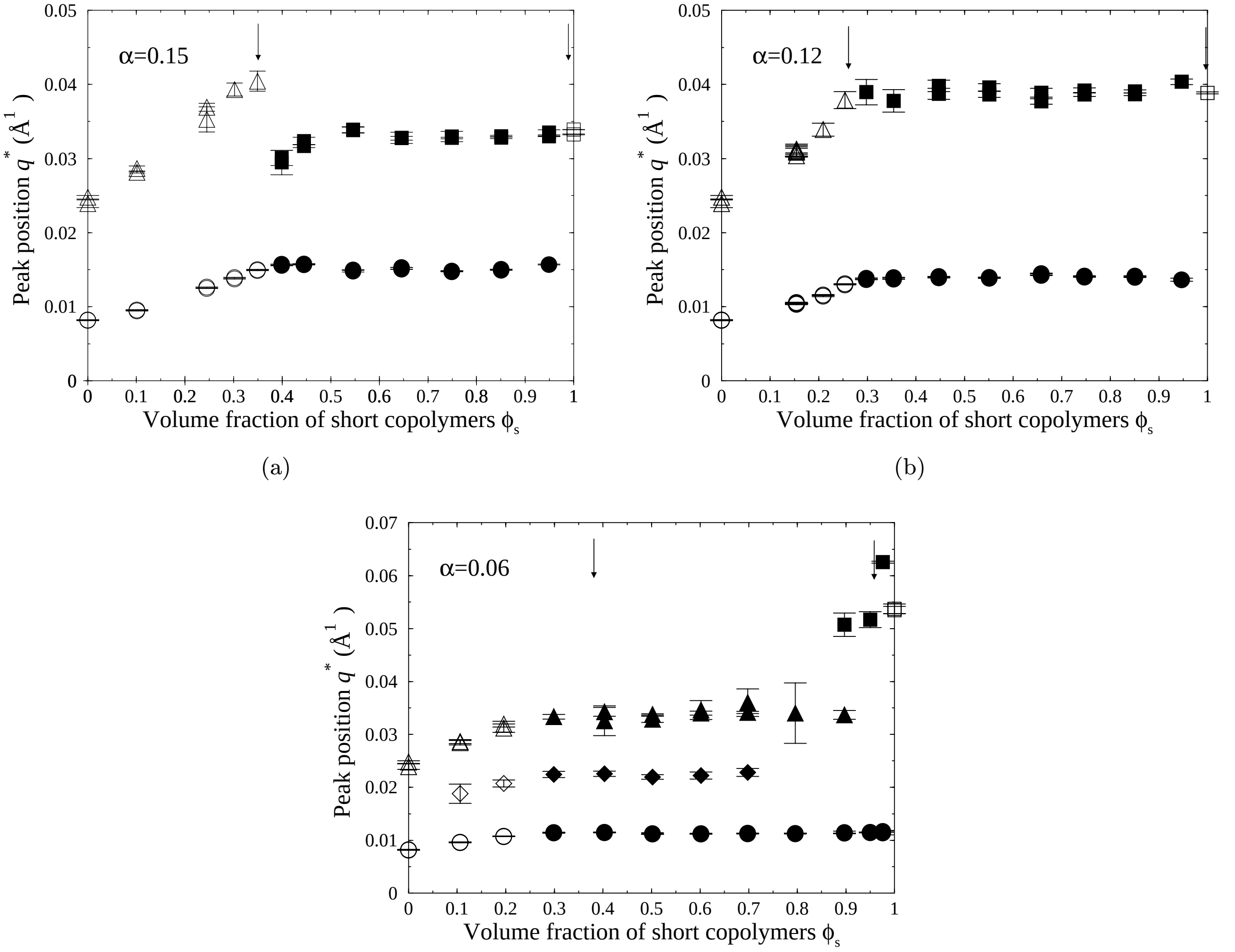
$\Delta\rho$ denotes the difference in scattering length density of the two parts of the lamellae. The Lorentz-factor for polycrystals, $1/(4\pi q^2)$, has here been taken into account. The scattered intensity has maxima at integer multiples of $2\pi/D$. At these q-values, the last term takes the value N^2. Then,

$$\Phi = \frac{\arccos(2\sqrt{I_2/I_1})}{\pi} \qquad (2)$$

where $I_1 = I(2\pi/D)$ and $I_2 = I(4\pi/D)$. For the blends having $\alpha = 0.06$ and $\phi_s = 0.11 - 0.50$, we obtain $\Phi = 0.47 - 0.49$ with errors below 0.005, *i.e.* values slightly different from the stoichiometric value 0.49 ± 0.01. (Also for $\phi_s = 0.60$ and 0.70, weak second-order peaks are observed, but the values of Φ are very uncertain and are therefore not given here.) Note that these values for Φ are not very precise, because we asssumed a rectangular profile, which is not necessarily the case, and because of limited experimental precision.

Several explanations are possible for the asymmetry observed, which seems to be most pronounced for small α, *i.e.* when the chain lengths of the long and the short chains are very much different. The preferential dissolution of the short copolymers might be driven by the conformational asymmetry of the long copolymers, *i.e.* the difference in volumes and lengths of the polystyrene and the polybutadiene segments. The experimentally determined phase diagrams of polystyrene/polybutadiene homopolymer blends are asymmetric in blend composition [21], which might influence the block copolymer miscibility. Asymmetric solubility in copolymer systems has previously been observed with a polystyrene-poly(methyl methacrylate) (PS-PMMA) random copolymer at the interface of PS and PMMA bulk homopolymers [22,23]. The interface of the random copolymer with PMMA was found to be much wider than the one with PS. It was proposed that PMMA cannot pack with itself as good as PS with itself and that therefore a certain amount of PS-segments is dissolved in the PMMA melt in order to achieve better packing, in spite of the increase in enthalpy. The same might hold for the polystyrene-polybutadiene system studied here.

Another explanation could be the following: for small α, the short copolymers have been predicted not only to



(a)

(b)

(c)

Fig. 5. Peak positions, q^*, as a function of the volume fraction of short chains, ϕ_s for the three chain length ratios studied. Given are the positions of the first-order (○, ●), second-order (◊, ⧫) and third-order Bragg-peaks (△, ▲) of the domains rich in long copolymers, as well as those of the first-order Bragg-peaks of the domains rich in short copolymers (☐, ■). The values have been obtained by fitting Lorentz-functions (convoluted with instrumental resolution) to the azimuthally averaged SANS spectra measured with different settings. Open symbols represent samples in the one-phase state and filled symbols those in the macrophase-separated state. The arrows denote the locations of the theoretically determined phase boundaries as read off from Figure 1.

reside at the interfaces, but the entropy of mixing tends to distribute them throughout the lamellar matrix [13]. It might be that, at 150 °C, the temperature chosen for preparation and measurements, the polystyrene domains are mechanically "harder" than the polybutadiene domains, because polystyrene is much closer to its glass transition temperature ($T_g \simeq 100$ °C) than polybutadiene is ($T_g \simeq -80$ °C). The dissolution of the short copolymers in the polystyrene lamellae might therefore be hindered. However, this would imply that the blends are in a non-equilibrium state. Our blends were left to equilibrate at the measuring temperature of 150 °C for one day and, in addition, for at least 10 min right before the measurements. It might be that this time is too short. On the other hand, keeping the samples at high temperature for longer times might lead to substantial crosslinking of the polybutadiene blocks, which is why we did not choose longer equilibration times.

A third reason might be that the polybutadiene blocks of the long copolymers are slightly cross-linked, which might hinder the diffusion of short copolymers into the polybutadiene domains.

4 Summary

We have studied three series of binary blends of symmetric polystyrene-polybutadiene diblock copolymers with different chain length ratios, the high molar mass parent copolymer being the same in all three series. Using small-angle neutron scattering, we have identified the conditions for macrophase-separation (Fig. 1). The agreement with theory [13] is very good for chain length ratios $\alpha = 0.15$ and 0.12. A slight discrepancy is observed for $\alpha = 0.06$; here, theory predicts that a larger amount of short copolymers can be dissolved in the lamellar matrix of long copolymers, and *vice versa*. For $\alpha = 0.06$, the second-order Bragg-peaks are non-vanishing, *i.e.* the thick lamellae are slightly asymmetric, in contrast to the pure systems. This indicates asymmetric solubility of the short copolymers in the matrix of long copolymers. By means of a simple model we relate the asymmetry of the lamellae to the ratios of peak heights of the second- and the first-order Bragg-peaks and find values of $0.47-0.49$ for the relative thickness of one part of the lamellae. Possible reasons for this asymmetry might be that the packing of one type of segments is improved when a certain amount of the other type of segments is present, the difference in mechanical stiffness of the polystyrene and the polybutadiene domains, or cross-linking of the polybutadiene blocks.

We thank Lotte Nielsen and Walther Batsberg Pedersen for their help with chromatography and Mark W. Matsen for stimulating discussions.

References

1. F.S. Bates, G.H. Fredrickson, Annu. Rev. Phys. Chem. **41**, 525 (1990).
2. L. Leibler, Macromol. **13**, 1602 (1980).
3. G.H. Fredrickson, E. Helfand, J. Chem. Phys. **87**, 697 (1987).
4. H. Hasegawa, M. Shibayama, T. Hashimoto, H. Kawai, Polym. Prepr. Jpn **30**, 2110 (1981).
5. T. Hashimoto, K. Yamasaki, S. Koizumi, H. Hasegawa, Macromol. **26**, 2895 (1993).
6. T. Hashimoto, S. Koizumi, H. Hasegawa, Macromol. **27**, 1562 (1994).
7. L. Kane, M.M. Satkowski, S.D. Smith, R.J. Spontak, Macromol. **29**, 8862 (1996).
8. A.M. Mayes, T.P. Russell, V.R. Deline, S.K. Satija, C.F. Majkrzak, Macromol. **27**, 7447 (1994).
9. T.M. Birshtein, Y.V. Liatskaya, E.B. Zhulina, Polymer **31**, 2185 (1990).
10. E.B. Zhulina, T.M. Birshtein, Polymer **32**, 1299 (1991).
11. A.-C. Shi, J. Noolandi, Macromol. **27**, 2936 (1994).
12. R.J. Spontak, Macromol. **27**, 6363 (1994).
13. M.W. Matsen, J. Chem. Phys. **103**, 3268 (1995).
14. C.M. Papadakis, K. Almdal, K. Mortensen, D. Posselt, Europhys. Lett. **36**, 289 (1996).
15. C.M. Papadakis, Ph.D. thesis, Roskilde University, Denmark, April 1996.
16. C.M. Papadakis, K. Almdal, K. Mortensen, D. Posselt, J. Phys. II France **7**, 1829 (1997).
17. S. Ndoni, C.M. Papadakis, F.S. Bates, K. Almdal, Rev. Sci. Instrum. **66**, 1090 (1995).
18. J.S. Pedersen, D. Posselt, K. Mortensen, J. Appl. Cryst. **23**, 321 (1990).
19. E. Helfand, Z.R. Wasserman, Macromol. **9**, 879 (1976).
20. R. Hosemann, S.N. Bagchi, *Direct analysis of diffraction by matter* (North-Holland Publishing Company, 1962).
21. R.-J. Roe, W.-C. Zin, Macromol. **13**, 1221 (1980).
22. R. Kulasekere, H. Kaiser, J.F. Ankner, G.D. Smith, T.P. Russell, H.R. Brown, C.J. Hawker, A.M. Mayes, Bull. Am. Phys. Soc. **41**, 318 (1996).
23. M. Sikka, N.N. Pellegrini, E.A. Schmitt, K.I. Winey, Macromol. **30**, 445 (1997).