Macrophase-separation in binary blends of symmetric polystyrene-polybutadiene diblock copolymers

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SUMMARY: Binary blends of compositionally symmetric polystyrene-polybutadiene diblock copolymers are investigated as a function of chain length ratio and blend composition using small-angle neutron scattering. Three different low molar mass copolymers were blended with a high molar mass copolymer. The results are related to the theoretical phase diagram put forward by M. W. Matsen (J. Chem. Phys. **103**, 3268 (1995)). The conditions for macrophase-separation are established, an observed asymmetry of the lamellae rich in long copolymers is discussed and the variation of the lamellar thickness with the volume fraction of short chains in the one-phase state is compared with theoretical predictions.

Introduction

Diblock copolymers consist of two chemically distinct polymer blocks joined by a covalent bond. In the melt diblock copolymers may form a variety of morphologies, such as lamellar, hexagonal and body-centered cubic structures. The given topology depends on the volume fraction of one block, f, and the product of the segment-segment interaction parameter, χ, and the overall chain length, N. For a number of applications, diblock copolymers serve as templates (e.g Ref. 1), taking advantage of the ability to form matrices with well defined structures. Naturally, a diblock copolymer sample can be synthesized for the actual purpose, but the same structure may also be obtained by blending diblock copolymers differing in chain length and composition. However, even blends consisting of chemically equal diblock copolymers can under certain conditions undergo macroscopic phase separation, which is the topic of the present publication.

In binary blends of diblock copolymers, most block joints are localized at the interfaces, and thus the free energy related to chain stretching is a key factor in diblock copolymer blends. In the case of few short copolymers on the interface of the lamellar structure formed by the long copolymers, the short diblock copolymers are less stretched than if no long diblock copolymers were present, which gives rise to an increase of their conformational entropy. The long diblock copolymers, on the other hand, loose conformational entropy because they must stretch through the brush of short chains at the interface into the middle of the lamellae, which makes them assume a mushroom conformation and thus loose conformational entropy. In the case of few long copolymers being added to a lamellar matrix of short diblock copolymers, the long copolymers loose a significant amount of entropy due to the confinement in a narrow lamellar domain. These effects may lead to macroscopic phase separation. In experimental studies of binary blends of chemically identical, symmetric diblock copolymers having different chain lengths, the macrophase-separated state has been observed for chain length ratios $\alpha = N_s/N_l < 0.2$ (N_s and N_l denote the overall degrees of polymerization of the short and

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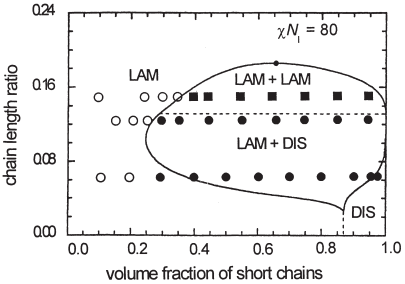

Fig. 1: Theoretical phase diagram for binary blends of symmetric diblock copolymers for χN_l = 80, as calculated by M.W. Matsen. Reproduced from Ref. 8. The lines denote the phase boundaries. The symbols indicate the blends studied in the present work.⁶⁾ (○) Blends in the lamellar one-phase state, (●) macrophase-separated blends consisting of lamellar and disordered domains, and (■) macrophase-separated blends with coexisting lamellar domains.

long copolymers, resp.) and for volume fractions of short copolymers $\phi_s > 0.2$-0.3.$^{2-6)}$ The phase diagram in Fig. 1 is asymmetric in the sense that the solubility of short copolymers in a matrix of long copolymers is much larger than vice versa.

Various mean-field theories have been put forward to describe the phase behavior of binary blends of diblock copolymers.$^{7,8)}$ The entropy losses described above are included in all the approaches cited above; however, all of them, except the one described in Ref. 8, fail in predicting macrophase-separation. The latter approach 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.$^{8)}$ The phases 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 $\chi N_l = 80$, 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 $\phi_s \cong 0.87$.

In the present study, we investigate systematically the conditions for macrophase-separation in binary mixtures of symmetric polystyrene-polybutadiene (PS-PB) diblock copolymers, which only differ in their overall chain length.$^{6)}$ As we have determined the χ-parameter of the PS-PB pair,$^{9)}$ we are able to compare our results quantitatively with the phase diagram given in Fig. 1. For this purpose, we have prepared three series of blends: three low molar mass copolymers (N_s = 374, 310, and 156) were blended with the same high molar mass copolymer (N_l = 2511), the latter having $\chi N_l \cong 81$ at the measuring temperature chosen.$^{9)}$ The three series have the chain length ratios α = 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 be macrophase-separated. The sample structures were studied using small-angle neutron scattering (SANS).

Experimental

The blends were prepared from compositionally symmetric polystyrene-polybutadiene diblock copolymers, which were polymerized anionically under inert atmosphere[10)] and have narrow molar-mass distributions (Ref. 9 and Table I). The χ-parameter at 150 °C (the temperature chosen for all preparations and measurements) is 0.033 ± 0.007.[9)]

Table I: Characteristics of the parent diblock copolymers. N denotes the overall degree of polymerization based on the polybutadiene monomer and f_{PB} the volume fraction of the polybutadiene block as determined using ^{1}H NMR.[9)] (a) Outside the experimentally accessible temperature range.

N	T_{ODT} (°C)	χN at 150 °C	f_{PB} (NMR)
$N_{\mathrm{l}} = 2511$	(a)	81	0.50
$N_{\mathrm{s}} = 374$	181±1	12	0.52
310	130±1	10	0.48
156	(a)	5	0.49

The blends were prepared by dissolving the copolymers in toluene at concentrations of 25 – 30 mg/ml together with 1 wt-% (relative to the polymer mass) of the antioxidant Irganox 1010. The solutions were left to dry at room temperature and at 140 – 160 °C (under vacuum). The blends containing short copolymers with $N = 374$ were heated to 200 °C for 10 min right before the measurements. SANS measurements were carried out at Risø National Laboratory. The two-dimensional spectra – all measured at 150 °C – show Debye-Scherrer rings from the lamellar domains and, in some cases, broad rings corresponding to correlation peaks from disordered domains. Data analysis was made using standard Risø software. The spectra were azimuthally averaged and the background was subtracted. In order to determine the peak positions, q^*, one or two Lorentz-functions were convoluted with the instrumental resolution and fitted to the peaks[11)] both in the ordered and the disordered state, for reasons of consistency.[6)]

Results and discussion

The azimuthally averaged SANS spectra of the three series of blends display Bragg-peaks from the lamellar domains and/or correlation peaks from the disordered domains (Fig. 2). The peaks at low q are the first-order Bragg-peaks from the lamellar phase rich in long copolymers. Also third-order Bragg-peaks are present in some of the spectra, indicating narrow interfaces between the blocks, as expected for samples in the strong-segregation regime.[12)] The positions of the Bragg-peaks increase with ϕ_s, as expected. The peak positions remain constant for values of $\phi_s = 0.40 - 0.95$ for $\alpha = 0.15$, $\phi_s = 0.30 - 0.95$ for $\alpha = 0.12$ and $\phi_s = 0.30 - 0.98$ for $\alpha = 0.06$. 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. Note that – in contrast to homopolymer blends – no forward scattering is observed in the macrophase-separated state because there is no contrast between the domains.

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 $\phi_s \geq 0.40$, 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).[8)] The intensity of the latter peaks relative to those from the do-

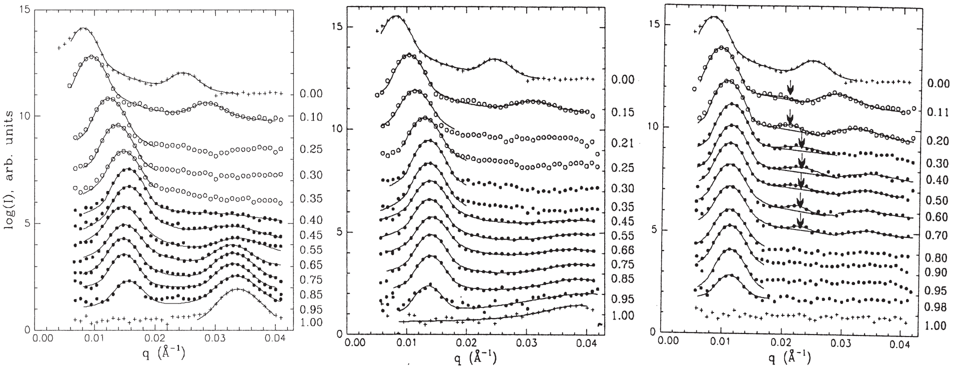

Fig. 2: Semi-logarithmic representation of azimuthally averaged SANS spectra of the blends with different chain length ratios. Left figure: $\alpha = 0.15$, middle: $\alpha = 0.12$, right: $\alpha = 0.06$. (+) Parent copolymers, (○) blends in the one-phase state, (●) macrophase-separated blends. The curves are shifted. The lines are fits of Lorentz-functions, convoluted with instrumental resolution. On the right of each plot, ϕ_s is given. The arrows and straight lines in the right figure indicate the second-order Bragg-peaks.

main in long copolymers increases with ϕ_s, indicating that the domain rich in short copolymers grows upon addition of short copolymers, which is reasonable. For $\alpha = 0.12$, broad correlation peaks close to the one of the parent short copolymer (which at, 150 °C, is disordered, but close to the ODT) are observed for $\phi_s \geq 0.45$, indicating coexistence of a lamellar domain rich in long copolymers and a disordered domain rich in short copolymers, as expected. This correlation peak cannot be distinguished from the background for $\phi_s = 0.30$ and 0.35, because it is relatively broad and because the domain rich in short copolymers is still small. The same general behavior as for $\alpha = 0.12$ is observed with the blends having $\alpha = 0.06$, where the short copolymer is deep in the disordered state. In contrast to theory, which predicts the disordered one-phase state for $\phi_s > 0.96$ (Fig. 1), we observe first-order Bragg-peaks from the lamellar structure rich in long copolymers, i.e. macrophase-separation, up to $\phi_s = 0.98$.

The theoretical predictions for the phase behavior8) coincide very well with our experimental findings for $\alpha = 0.15$ and 0.12 (Fig. 1), which is amazing, since no molecular details are incorporated into this theory. However, 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 and vice versa. The discrepancies may be due to inaccuracies in the mean field theory as well as to experimental errors in determining ϕ_s, α, and χ, the polydispersity of the parent copolymers and to the conformational asymmetry of the polystyrene-polybutadiene pair, the latter two parameters not being included in the theory.8)

Based on the appearance of second-order Bragg-peaks from the domains rich in long copolymers for the $\alpha = 0.06$ series, we conclude that the short copolymers are preferentially dissolved in one of the two blocks, thus giving rise to an asymmetry in the thickness of the two halves of a lamella. (Very weak second-order peaks are also observed in the spectra of blends having $\alpha = 0.15$ and $\phi_s = 0.10$ and 0.95, and with $\alpha = 0.12$ and $\phi_s = 0.15$). The asymmetry can be quantified by the following relationship6) between the ratio of thicknesses of the PS or PB part of the lamella and the overall lamellar thickness, Φ, and the ratio of peak heights of the second- and the first-order Bragg peak, I_2/I_1, assuming that the lamellar profile is rectangular and that the sample is polycrystalline:13)

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

For the blends having $\alpha = 0.06$ and $\phi_s = 0.11 - 0.50$, we obtain $\Phi = 0.51 - 0.53$ with uncertainties below 0.005. Note that the values for the deviations represent a lower limit, because we assumed a rectangular profile. The asymmetry is most pronounced for the series containing the lowest molar mass short copolymers. The preferential dissolution of the short copolymers may 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. Asymmetric solubility in copolymer systems has previously been observed in the polystyrene/poly(methyl methacrylate) system and was attributed to an improvement of packing of PMMA segments upon dissolving a few PS-segments, in spite of the increase in enthalpy,14) which might also hold for the system studied here. Another explanation could be that, especially for small α, the short copolymers have been predicted also to be present in the lamellae.8) At 150 °C, the polystyrene domains are mechanically 'harder' than the polybutadiene domains, because polystyrene is much closer to its glass transition temperature ($T_g \cong 100$°C) than polybutadiene ($T_g \cong -80$ °C), which may hinder the dissolution of the short copolymers in the polystyrene lamellae. This would imply that the asymmetry would disappear upon longer annealing, which we did not attempt. 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.

Various predictions have been made for the variation of the lamellar thickness D with ϕ_s in the one-phase state.3,5,15) Hashimoto assumed that the segment density in the two halves of the lamella are the same as in the corresponding homopolymers, i.e. that space filling is uniform.15) Assuming furthermore that long and short copolymers are interdispersed on the lamellar interfaces with the probability of many short copolymers (or many long copolymers) opposing each other on the opposite interfaces being small, he concluded that, in the one-phase state, the lamellar volume in the blend, V, is equal to the sum of the lamellar volumes V_A and V_B in the two parent copolymer systems A and B, respectively.15) In this way, he obtained the same scaling law $D \propto \overline{N}^{2/3}$ as predicted for the strong-segregation limit of a pure copolymer system.16) $\overline{N}$ is the average degree of polymerization of the blend: $\overline{N} = x_l N_l + (1-x_l)N_s$ with x_l being the mole fraction of long chains ($x_l = [1+\alpha^{-1}\phi_s(1-\phi_s)^{-1}]^{-1}$. Thus,

$$\frac{D}{D_l} = [1+(\alpha^{-1}-1)\phi_s]^{-2/3} \tag{1}$$

with D_l being the lamellar thickness of the long parent copolymer. Kane et al., on the other hand, propose the following expression for the case of both copolymers being in the strong-segregation regime:5)

$$\frac{D}{D_l} = \left[\alpha + (1-\alpha)\left(1+\frac{\phi_s}{\alpha(1-\phi_s)}\right)^{-1}\right] \times \left[\alpha + (1-\alpha)\left(1+\frac{\phi_s}{\alpha(1-\phi_s)}\right)^{-3}\right]^{-1/3} \tag{2}$$

In order to calculate the different contributions to the free energy, each half of the lamella was divided into layers containing the short blocks and a certain fraction of the long blocks and layers where only the unmixed fraction of long blocks (i.e. the chain ends) is placed.5) In Fig. 3, our experimental data from the one-phase state are shown together with both theoretical expressions (1) and (2). For $\alpha = 0.15$, the experimental data lie inbetween the two curves. The reason might be the uncertainty in determining α, resulting from the uncertainties in determining N_l and N_s. For $\alpha = 0.12$ and 0.06, the expression given by Kane et al.5) fits the data much

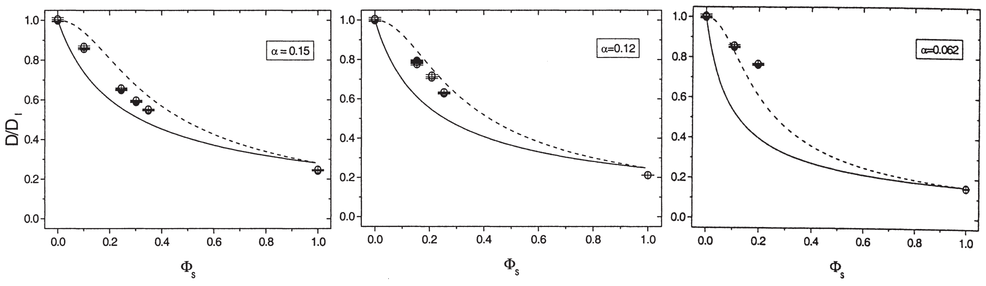

Fig. 3: D/D_l for the three series. Circles: experimental data for the one-phase state, lines: fits according to the expression given by Hashimoto et al. (full line)3,15) and by Kane et al. (dashed line)5)

copolymers in these two series are not strongly segregated as assumed in Kane's theory.5)

Conclusion

By means of three series of binary blends of symmetric polystyrene-polybutadiene diblock copolymers with different chain length ratios, we have identified the conditions for macrophase-separation. We found good agreement with theory,8) apart from a slight discrepancy for $\alpha = 0.06$. With this series, the thick lamellae are found to be slightly asymmetric, in contrast to the pure systems, indicating asymmetric solubility of the short copolymers in the matrix of long copolymers. The variation of the lamellar thickness with the volume fraction of short chains compare favorably with the theoretical predictions by Kane et al.5)

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