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Phase Behavior of Binary Blends of Chemically Different, Symmetric Diblock Copolymers

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Introduction

Diblock copolymers A−B microphase separate, forming an ordered morphology on length scales of typically 10−100 nm.[1] Generally, an upper critical ordering temperature (UCOT) is encountered; i.e., above this temperature a disordered phase is formed. This behavior, known from polystyrene−polybutadiene (S−B),[2,3] for instance, is related to the decrease of the Flory−Huggins segment-segment interaction parameter, χ, with increasing temperature. In a few diblock copolymer melts, microphase separation is observed upon heating above a lower critical ordering temperature (LCOT), for instance in poly(styrene-d_8)−poly(n-butyl methacrylate), dS−BMA, and was attributed to entropic factors.[4,5] Here, we present the phase behavior of binary blends of compositionally symmetric S−B and dS−BMA representing an A−B/A−C diblock copolymer blend type (the interaction parameter between S and dS is negligible).

In blends of polystyrene−polyisoprene (PS−PI) with polystyrene−poly(2-vinylpyridine) diblock copolymers, the resulting structure depends strongly on the preparation conditions.[6] Blends of polystyrene−poly(ethylene propylene) (PS−PEP) with different PS−HPI diblock copolymers (HPI denotes partially hydrogenated PI) showed macrophase separated states with coexisting lamellar domains and different lamellar one-phase states, depending on the degree of hydrogenation of the HPI block.[7] For blends of weakly segregated diblock copolymers A−B and A−C (both being symmetric), both micro- and macrophase separated states were predicted as a function of the mixing ratio, the ratio of the overall degrees of polymerization, and the three interaction parameters $\chi_{\mathrm{A-B}}$, $\chi_{\mathrm{A-C}}$, and $\chi_{\mathrm{B-C}}$.[8] These predictions could be verified for blends of PS−PI and polyisoprene−poly(ethylene oxide):[9] Isotropic mixtures formed at high temperatures macrophase separated upon lowering the temperature.

Table 1. Characteristics of the Parent Diblock Copolymers

sample	$\bar{M}_{\mathrm{n}}$ (kg/mol)	N	ϕ_{PS}	D_{lam} (nm)	T_{LCOT}, T_{UCOT} (°C)
dS−BMA	68.0	640	0.46	28.6−30.9[a]	LCOT: 173
S−B02	54.5	524	0.52	42.3−38.9[a]	UCOT: ≫200
S−B11	18.3	176	0.52	16.8−15.0[b]	UCOT: 125

[a] Given are the overall molar mass, $\bar{M}_n$, the overall degree of polymerization, N, based on the monomer volume of polystyrene, the volume fraction of the polystyrene block, ϕ_{PS}, the lamellar thickness, D_{lam}, and the phase transition temperatures, T_{LCOT} and T_{UCOT}. [b] Values for D_{lam}, T_{LCOT}, and T_{UCOT} are obtained in the present study. D_{lam} values are given at 110 and 200 °C (a) and at 110 and 180 °C (b).

We have studied two series of binary blends of dS−BMA with S−B diblock copolymers. The dS−BMA copolymers were blended in different proportions with S−B copolymers having a larger respectively a smaller lamellar thickness in the pure state than dS−BMA (ratios of lamellar thicknesses 1.3−1.5 and 0.48−0.59). S−B and dS−BMA show opposite temperature behavior for ordering and formation of the lamellar structure and for the interface width of the two blocks.[3,10] The phase behavior of diblock copolymer blends is to a great extent governed by chain stretching at the lamellar interface.[11] We therefore expected that this opposite temperature behavior would have an influence on the temperature-dependent phase behavior of S−B/dS−BMA blends, causing a mixing behavior different from blends where both diblock copolymers have the same temperature behavior.

Experimental Section

The parent copolymers (Table 1) have been characterized previously.[2,3,5] The Flory−Huggins segment−segment interaction parameters are $\chi_{\mathrm{S-B}} = 38\ \mathrm{K}/T - 0.034$ and $\chi_{\mathrm{dS-BMA}} = -4.56\ \mathrm{K}/T + 0.024$. The blends were prepared by codissolution in toluene together with 0.5 wt % Irganox 1010 (relative to the mass of S−B). After being dried at room temperature and subsequent heat treatment at 150 °C, pills were pressed at 120 °C under vacuum. They were mounted in a nitrogen atmosphere in cells made of a brass ring of 1 mm thickness having a hole of 9 mm diameter onto which quartz glass plates (Hellma) of 1.25 mm thickness were glued.

Small-angle neutron scattering (SANS) measurements were carried out at the SANS-2 instrument at the Geesthacht Neutron Facility. The samples were mounted in a helium-filled oven. Heating and cooling runs were performed between 105 and 200 °C in steps of 5 or 10 K with a stability of 0.5 K. A pinhole of 6 mm diameter was placed right in front of the sample. A wavelength $\lambda = 0.57$ nm ($\Delta\lambda/\lambda = 0.2$) was used for all measurements. The sample−detector distance was 5.05 m. A gas-filled ^{3}He area detector was used. By use of the program SANDRA,[12] the two-dimensional spectra were corrected for the detector sensitivity, they were azimuthally averaged, and the background from the cell, the aluminum windows, and air was subtracted. The transmission of the samples and the cells were determined at a sample−detector distance of 21.05 m. One or two Lorentz functions were fitted to the peaks in order to determine the peak positions q^* ($q = 4\pi \sin(\theta/2)/\lambda$ with θ being the scattering angle) and full widths at half-maximum (fwhm). Smearing was not taken into account. The differences of scattering length densities are 1.0×10^{10} and 5.9×10^{10} cm^{-2} for S−B and for dS−BMA, respectively; i.e., the contrast of S−B is a factor of 35 lower than the one of dS−BMA.[13]

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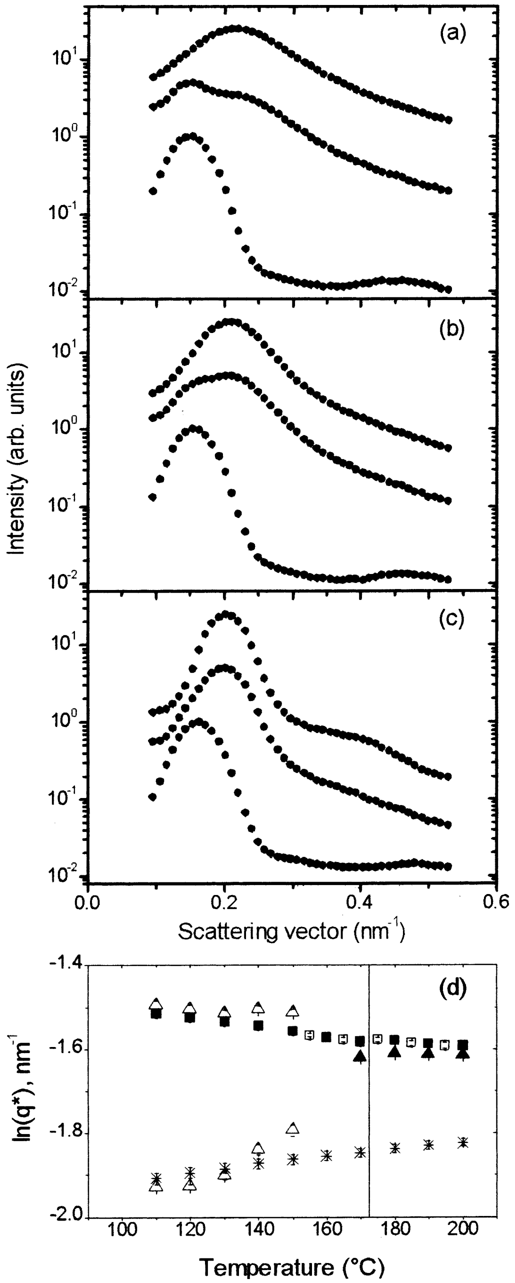

Figure 1. (a−c) Spectra from the blends of dS−BMA and S−B02 at 110 (a), 150 (b), and 200 °C (c). From top to bottom: dS−BMA, blend with ϕ_{S-B02} = 0.50, and S−B02. The curves were normalized such that the height of the first peak is unity and were shifted by a factor of 5. (d) Positions of the first-order Bragg peaks in a semilogarithmic representation. Results from fits of a single Lorentz function to the spectra of dS−BMA (heat (■), cool (□)), and to the heating run of S−B02 (∗). Results from fits of a single (▲) and of two (△) Lorentz functions to the blend spectra. Vertical line: LCOT of dS−BMA, determined from the discontinuous change of the fwhm (Figure 3b).

Results

The LCOT behavior of dS−BMA[5] is evidenced by the discontinuous decrease of the fwhm of the peak at 0.20−0.22 nm^{-1} in the azimuthally averaged SANS spectra at ∼173 °C (Figures 1a−c and 3b). The peak position decreases with increasing temperature over the whole temperature range investigated (Figure 1d). Above the LCOT temperature, second-order Bragg peaks are present as well (Figure 1c); i.e., the structure is lamellar. The azimuthally averaged spectra of S−B02 and S−B11 show peaks at 0.14−0.16 and 0.37−0.42 nm^{-1}, respectively (Figures 1 and 2).[3] SB-02 is lamellar in the temperature range studied (Figure 1). S−B11 displays UCOT behavior: The peak observed is much broader above ∼125 °C, the UCOT temperature, than below (Figures 2 and 3c).

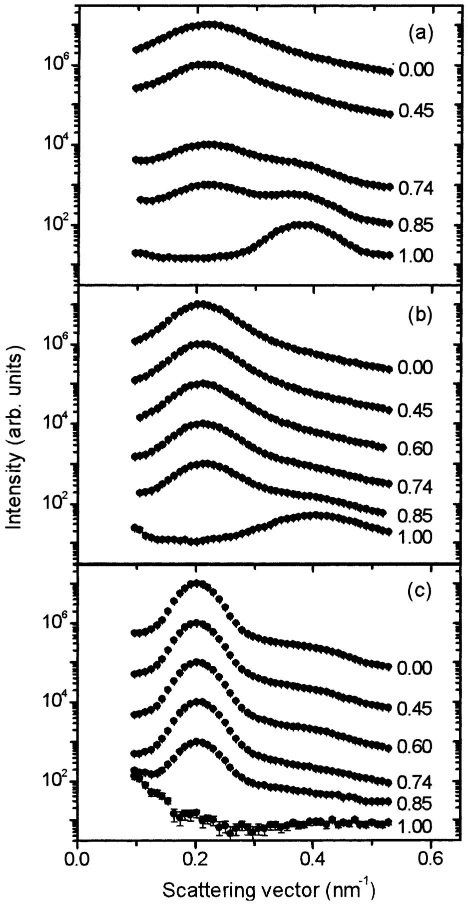

Figure 2. Spectra from the blends of dS−BMA and S−B11 at 110 (a), 150 (b), and 200 °C (c). The numbers indicate the volume fraction of S−B11 in the blends. The curves were normalized such that the height of the peak at ∼0.20−0.22 nm^{-1} is unity (the curves of S−B11 were normalized such that the height of the peak at ∼0.38−0.40 nm^{-1} is unity). The curves were shifted by one decade.

The spectra of the blend of S−B02/dS−BMA (lamellar thickness of S−B is 1.3−1.5 times that of dS−BMA) consisting of equal volume fractions of both copolymers show peaks at positions similar to the first-order Bragg peaks from the parent components (Figure 1); i.e., the blends are macrophase separated into dS−BMA-rich and S−B02-rich domains. (In the one-phase state, a single peak would be expected between the peaks from the pure copolymers.) Above 150 °C, the two first-order peaks are difficult to separate in the blend spectra, because the relative height of the S−B02 peak decreases with increasing temperature. The positions of the peaks related to the dS−BMA-rich and to the S−B02-rich domains in the blend are very similar to those from the pure copolymers (Figure 1d); i.e., the correlation lengths/lamellar thicknesses remain nearly unchanged upon mixing. (“Correlation length” designates the value of $2\pi/q^*$ in the disordered state.)

In the blend spectra, neither the third-order peak from the S−B02-rich domains nor the second-order peak from the dS−BMA-rich domains above the LCOT temperature can be discerned from the background. The

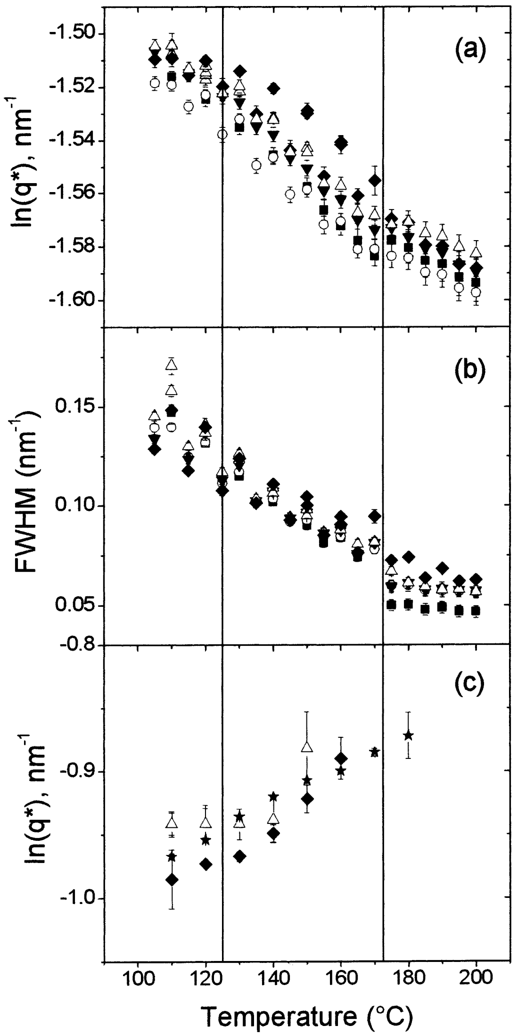

Figure 3. Semilogarithmic representation of the positions (a) and the fwhm (b) of the first peak and (c) of the positions of the second peaks of the spectra from the blends of dS−BMA and S−B11. ϕ_{S-B11} = 0 (■), 0.45 (○), 0.60 (▼), 0.74 (△), 0.85 (◆), 1.00 (★). (c) Heating runs. Results from fits of one or two Lorentz functions. Vertical lines: UCOT of S−B11 and LCOT of dS−BMA.

presence of higher order peaks is related to the shape of the concentration profile across the lamellae and indicates deviations from a sinusoidal profile. One possible reason for the absence of the higher order peaks in the blend spectra is that the interfaces in the blend are broader than in the parent copolymers, which could be caused by mixing. However, a decrease of the size of the ordered domains upon mixing or fluctuations of the lamellar thickness may cause similar effects.

The spectra of all blends of dS−BMA with S−B11 (Figure 2) show a peak close to that of pure dS−BMA. Below 170°C, the blends having ϕ_{S-B11} = 0.74 and 0.85 additionally display a peak close to that of S−B11. Contrary to expectations, no common disordered phase is manifest between the UCOT of S−B11 and the LCOT of dS−BMA—but the blends are macrophase separated into domains rich in dS−BMA and domains rich in S−B11.

The positions of the first peak are very similar to those of pure dS−BMA (Figure 3a). Also the LCOT temperature remains unchanged upon addition of S−B11, as evidenced by the discontinuity of the fwhm of this peak which remains at the same temperature (Figure 3b). In the spectra from blends having ϕ_{S-B11} = 0.74 and 0.85, the position of the second peak is very close to that of pure S−B11 (Figure 3c); i.e., only very little dS−BMA is present in the S−B-11-rich domains. This may be due to the entropic losses upon confinement of the long dS−BMA copolymers into the thin S−B11-lamellae, as is the case for A−B/A−B blends.

Conclusions

The two series of binary blends of dS−BMA and S−B are macrophase separated. In the blend where the repeat distance of S−B is larger than that of dS−BMA (ratio of lamellar thicknesses 1.3−1.5), the higher order Bragg peaks in the blend spectra are absent, which may be due to a certain degree of mixing. The series of blends where the lamellar thickness of S−B is smaller than that of dS−BMA (ratio of lamellar thicknesses 0.48−0.59), and where the UCOT temperature of S−B is 48 °C lower than the LCOT temperature of dS−BMA, the degree of mixing in the macrophase separated domains is very small, as evident from the nearly unchanged peak positions of the two domains. No common disordered phase is formed between the UCOT and the LCOT temperature. We conclude that the phase behavior of the two copolymers is not influenced significantly by the LCOT/UCOT behavior, but is dominated by other effects, such as the repulsion between the B and BMA blocks and the entropic losses upon mixing copolymer samples having different radii of gyration.

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