A diblock copolymer blend with closed-loop phase behavior

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Blends of block copolymers have recently attracted a lot of attention since interesting new phase behavior and consequently new material properties may be observed [e.g. 1,2]. In the present contribution, blends of two symmetric diblock copolymers of quite different molecular masses ($M_n$) are considered. The short chain diblock copolymer will be unable to assume an ordered state in contrast to the long chain one. Then the former can dwell within the ordered domains formed by the latter where it acts as filler, or it can stay at the interface between the two domains where it acts as surfactant [1,2]. These two cases are called solubilization and localization, respectively. Their relative fraction depends on interaction parameter, chain length and component volume fraction.

Two grades of polystyrene-$b$-poly(ferrocenyl dimethylsilane) (PS-$b$-PFS) diblock copolymers, both with mass fractions of PS 0.49, were synthesized by anionic polymerization [3]. They differed in $M_n$: grade “BL1” had a molecular mass ($M_n$) of 30.4 kg/mol and grade “BL2” had a $M_n$ of 16.4 kg/mol. Grade BL2 contained 1 wt. % PS with $M_n$ of 8.0 kg/mol. In PS-$b$-PFS, the PS is amorphous and the PFS is crystallizable. The order-disorder transition (ODT) temperature for BL1 is above the measurable temperature range (i.e. > 240°C), and that of BL2 is below room temperature (RT). BL1 remains therefore in any case disordered. Five samples were prepared by blending BL1 and BL2, with mass fractions ($f_1$) of BL1 as 0, 0.25, 0.50, 0.75 and 1, respectively. The samples were crystallized at 127°C for 60h, after cooling from the melt [3]. Small angle X-ray scattering (SAXS) experiments were carried out at HASYLAB/DESY at beamline A2. A two-dimensional (2D) CCD detector was used where the sample to detector distance was around 3.1 m [3]. The 2D SAXS data were circularly integrated, using the program Fit2D from ESRF. The resulting one-dimensional data were calibrated using a rat-tail tendon, then normalized and finally the background was subtracted [3].

Since the ratio 1.9 of the degrees of polymerization of the two diblock copolymers is well below 5, all blends are expected to be mixed down to the molecular level [1,2]. The samples with $f_1 \leq 0.5$ showed a well-ordered lamellar morphology with SAXS peaks up to the third order (the fourth order peak is beyond the setup limit). The variation of the lamellar long spacing $L$ at RT with equivalent molecular mass of the blend can be approximately described by a scaling law $L \sim M_n^{t}$ with $t = 0.58$. For strongly segregated block copolymers, the exponent $t$ was found to be 2/3 [4].

The blend with $f_1 = 0.25$ is fully disordered at RT. An interesting “closed-loop” phase behaviour [5,6] was found for this blend (Figure 1). Upon heating, the sample was still disordered at 100°C because the scattering peak remained broad, and there was no second order scattering peak. However, at 120°C, there is a step-like decrease in width of the peak, and the second order scattering peak appeared (Figure 1a). This indicates a disorder-to-order transition. Upon further heating (at 1°C/min) to 136°C, the first order scattering peak narrowed further. Surprisingly, the second order scattering peak disappeared at around 152°C although the first order peak remained narrow (Figure 1a). That peak broadened again at 168°C, indicating now structural reversal and consequently occurrence of an order-to-disorder transition. The full widths at half maximum (FWHM) for the first order peak vs. temperature are given in Figure 1b. That sample exhibits consequently a so-called closed-loop phase behaviour [5,6]. It was not observed for all other samples, including the neat low molecular mass diblock copolymer BL2.
Figure 1: (a) SAXS patterns of the amorphous blend with $f_1 = 0.25$ at different temperatures ($T$). The peak intensity and the intensity at low $q$ side decrease as the $T$ increases. The second order scattering peak can be seen for the $T$ between 120°C and 152°C. (b) Full width at half maximum (FWHM) of the first order SAXS peak as a function of the $T$. The indicated boundaries between the ordered and the disordered regions, respectively, were estimated from the appearance of a second order peak and considering the FWHM.

This closed-loop phase behavior is a result of the delicate balance between entropy and enthalpy. It is well known in blend systems with specific intermolecular interactions. Small molecules which form highly directional intermolecular interactions, e.g. H-bonding between unlike molecules, may serve as examples [5]. In weakly interacting (polymeric) systems, however, this closed-loop phase behaviour has only recently been observed for a diblock copolymer of polystyrene and polyl(n-pentylmethacrylate) [6]. The origin of this behavior in polymeric systems is still under discussion [5]. It was explained in a similar way as in case of the small molecules: the macromolecular character of the polymers shall magnify the very weak directional dispersive interactions [6] and result in the observed phenomenon.

The crystallization of the blend with $f_1 = 0.25$ differed from that of the other samples, too. It is known that, in partially crystallized similar samples, the amorphous and the crystalline lamellar peaks coexist [3]. For the blend with $f_1 = 0.25$, the ordered lamellar structure of the amorphous phase at the crystallization temperature can be frozen by the crystalline phase (for partially crystallized sample) upon further cooling to the room temperature, because the crystallization proceeded in the ordered region (Figure 1b).

References