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Micro- *vs.* macro-phase separation in binary blends of poly(styrene)-poly(isoprene) and poly(isoprene)-poly(ethylene oxide) diblock copolymers

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Abstract. – In this paper we present an experimentally determined phase diagram of binary blends of the diblock copolymers poly(styrene)-poly(isoprene) and poly(isoprene)-poly(ethylene oxide). At high temperatures, the blends form an isotropic mixture. Upon lowering the temperature, the blend macro-phase separates before micro-phase separation occurs. The observed phase diagram is compared to theoretical predictions based on experimental parameters. In the low-temperature phase the crystallisation of the poly(ethylene oxide) block influences the spacing of the ordered phase.

Binary blends of polymers are immiscible at low temperatures in the case of upper critical solution temperature behaviour, leading to macro-phase separation below a binodal line. In contrast, phase separation in single-component block copolymers leads to micro-phase separation (below an order-disorder transition) because macro-phase separation is prevented by the connectivity of the polymer chains. In blends of a block copolymer with a homopolymer or in blends of block copolymers an interesting interplay occurs between micro- and macro-phase separation. Previous experimental and theoretical work on these systems has been reviewed [1]. Here, we probe phase-separated structures in binary blends of block copolymers with one common B-block, AB/BC. In contrast to binary blends of AB block copolymers, the phase behaviour of this AB/BC system is predicted to be much richer, because there are three independent Flory-Huggins interaction parameters.

Recent theoretical work highlights the possibility of intriguing critical phenomena, such as Lifshitz points, resulting from the competition between micro- and macro-phase separation in AB/BC block copolymer blends [2]. To date, there has been little experimental work on such systems. Kimishima *et al.* [3] have investigated the phase behaviour of 50:50 blends of a poly(styrene)-poly(ethylene-co-propylene) diblock copolymer with one of a series of poly(styrene)-hydrogenated poly(isoprene) copolymers. The degree of hydrogenation of the latter was varied (100% hydrogenation corresponds to PEP), and the phase separation process studied for solvent-cast structures using small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). The solvent-casting process led to initial micro-phase separation for all blends, the subsequent morphology depending on the incompatibility between the rubbery PEP and hPI blocks. Macro-phase separation was observed for sufficiently large incompatibility between these blocks. However, studies of equilibrium morphologies in these systems are hampered by the non-equilibrium nature of the solvent-casting process. Here, we perform SAXS and small-angle neutron scattering (SANS) experiments to determine the phase-separated structures in blends of a poly(styrene)-poly(isoprene) and a poly(isoprene)-poly(ethylene oxide) diblock copolymer. The phase diagram as a function of composition is obtained for the first time, and is compared to the predictions of mean-field theory, which is shown to provide a semi-quantitative description.

The phase behaviour of diblock copolymer blends was described by the random phase approximation [3], which is a mean-field theory. This theory includes architectural parameters, such as the chain length N_i and the block length ratio f_i (defined by volume fraction of the B-block) for the individual chain i. In addition, the composition Φ of the blend, and the interaction parameters χ_{ij} between the different segments of the chains must be specified. The temperature dependence of χ_{ij} can be determined experimentally, and thus the interaction parameters are reduced to only one variable, the temperature T.

One way of determining the interaction parameter between two different chain segments is to measure the phase diagram of either a diblock copolymer or a homopolymer blend. Within mean-field theory the interaction parameter at the order-disorder transition temperature is given by $\chi = 10.5/N$ for a symmetrical diblock copolymer, and at the critical demixing temperature by $\chi = 2/N$ for a symmetrical homopolymer blend. The values follow from the mean-field theories of Leibler [4], and Flory and Huggins [5], and assume that composition fluctuations can be neglected. Even though experiments have shown that fluctuations are important for homopolymer blends and diblock copolymers near the binodal line [6], we apply mean field using the random phase approximation because a theory allowing for composition fluctuations has yet to be developed for diblock copolymer blends.

For a comparison with experiments, we used the mean-field theory following ref. [3] to compute a phase diagram, shown in fig. 1. The experimental parameters were used in the theory. The figure shows the state of the system as a function of composition. With the given parameters the blend forms one homogeneous phase at high temperatures. At lower temperatures the blend can either macro- or micro-phase separate. The theory describes the phase behaviour with a macro-phase and a micro-phase mode, which become critical at the corresponding spinodals. The blend at low temperatures is controlled by macro-phase separation. The predicted order-disorder transition temperatures principally depend on the composition, but become horizontal lines in the macro-phase–separated region, since the two separated phases are defined by the binodal composition.

The macro-phase separation binodal and spinodal are calculated by the effective macro-phase interaction parameter, which reads

$$\chi_{\mathrm{macro}} = \chi_{\mathrm{AC}}(1-f_1)(1-f_2) + \chi_{\mathrm{AB}}(1-f_1)(f_2-f_1) + \chi_{\mathrm{BC}}(f_1-f_2)(1-f_2).$$

This parameter combines the individual segmental interaction parameters as in the theory for random copolymers. For the symmetrical case ($f_2 = f_1 = f$) the effective interaction parameter depends only on the interaction between the distinct blocks A and C, and miscibility is increased by an increasing block length ratio f.

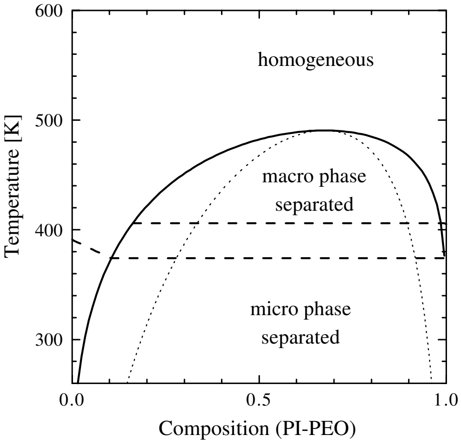

Fig. 1 – The phase diagram predicted by the random phase approximation for the PS-PI/PI-PEO blend. The binodal (solid line) separates the macro-phase–separated region from the one-phase region. The binodal and the according spinodal (dotted line) are calculated within the random phase approximation, and therefore meet at the critical point. The spinodal of the micro-phase separation (dashed line) depends weakly on the composition, and appears to be horizontal within the two-phase region, because the compositions of the phases are determined by the macro-phase binodal. The coexisting phases order independently.

The diblock copolymers were synthesised by anionic polymerisation, using already known methods [7]. The poly(styrene)-block-poly(isoprene) (PS-PI) diblock copolymer was synthesised in cyclohexane with sec-butyllithium as initiator, where the monomers styrene and isoprene were added sequentially. In contrast, the poly(isoprene)-block-poly(ethylene oxide) (PI-PEO) was synthesised by a two-step synthesis. The poly(isoprene)-block was first synthesised in cyclohexane with sec-butyllithium as initiator. After full conversion ($\geq$ 99.9%) the poly(isoprene) was end-capped with ethylene oxide. The in-methanol precipitated and dried polymeric alcohol was dissolved in dry tetrahydrofuran, where it was titrated with potassium naphthalenide to yield the analogous potassium alkoxide. This macroinitiator was used for the polymerisation of the ethylene oxide block.

The number average molar masses were determined from the synthesis stoichiometry. The block length ratio was confirmed by ^{1}H NMR measurements. Size exclusion chromatography was used to confirm the molar mass, and to characterise the molar mass distribution. For all polymers the molar mass distribution was narrow ($M_W/M_N < 1.1$). The order-disorder transition temperatures T_{ODT} were measured by rheology. The PS-PI and PI-PEO diblock copolymers are characterised by molecular weights of 17 kg/mol and 4 kg/mol, both PI volume fractions of 0.46, and order-disorder transition temperatures of 390 K and 405 K, respectively.

Blends of PS-PI and PEO-PI were dissolved in chloroform, stirred, and dried under high vacuum. The volume compositions were determined by weight. We used 9 compositions in between the pure components. SANS experiments were performed at the DR3 reactor at the Risø National Laboratory in Denmark, using neutrons of 6.5 Å wavelength, with a wavelength distribution of $\Delta\lambda/\lambda = 9\%$. The samples were filled into quartz cuvettes, which were sealed under high vacuum. These cuvettes were mounted in a SANS-oven, with a temperature stability of better than 0.05 K. The scattering data were radially averaged, corrected for background scattering, and detector efficiency. SAXS experiments were performed on station 8.2 at the Synchrotron Radiation Source, Daresbury Laboratory, Warrington, UK. The X-ray wavelength was $\lambda = 1.5$ Å. The samples were filled into DSC pans with Mica windows.

Table I – *Experimental* χ *parameters. The uncertainty of* χ *is* ±10% *within the experimental temperature range of* 390 K *and* 555 K.

Sample	χ
PS-PI	$26.4/T - 0.0288$
PI-PEO	$90.7/T - 0.0579$
PS-PEO	$29.8/T - 0.0229$
PS/PEO	$72.9/T - 0.0810$

The pans were placed in a spring-loaded holder in a Linkam TMH600 hot stage mounted on an optical bench. The design and operation of the X-ray DSC have been described in detail elsewhere [8]. The experimental data were corrected for background scattering, sample absorption, and the positional alinearity of the detectors. Small-angle scattering data are presented as a function of wave number $Q = 4\pi \sin\theta/\lambda$, where 2θ is the scattering angle.

The Flory-Huggins parameters, χ, of the pure diblock copolymers and the homopolymer blends determined experimentally are listed in table I. These parameters were obtained using the mean-field theory for either a binary homopolymer blend or a diblock copolymer. The degree of polymerisation N was defined on the basis of a common segment volume $70.5\,\mathrm{cm}^3/\mathrm{mol}$ [9]. The temperature dependence of χ is determined by measuring the phase diagram for different degrees of polymerisation. The Flory-Huggins parameter has an enthalpic and an entropic contribution, according to $\chi = \chi_h/T - \chi_\sigma$. The phase boundary measurements and the resulting interaction parameter agree well with literature [10]. The interaction parameter of scattering experiments [10, 11] is found to be different from phase boundary measurements, as discussed elsewhere [12]. However, the phase-boundaries–determined interaction parameter χ seems to be suitable for the purpose of predicting phase boundaries. The Flory-Huggins parameter of the corresponding PS/PEO homopolymer blend and diblock copolymer was found to differ considerably [13], in agreement with other experiments [6, 12]. In the application of the random phase approximation for a PS-PI/PI-PEO blend, χ of the

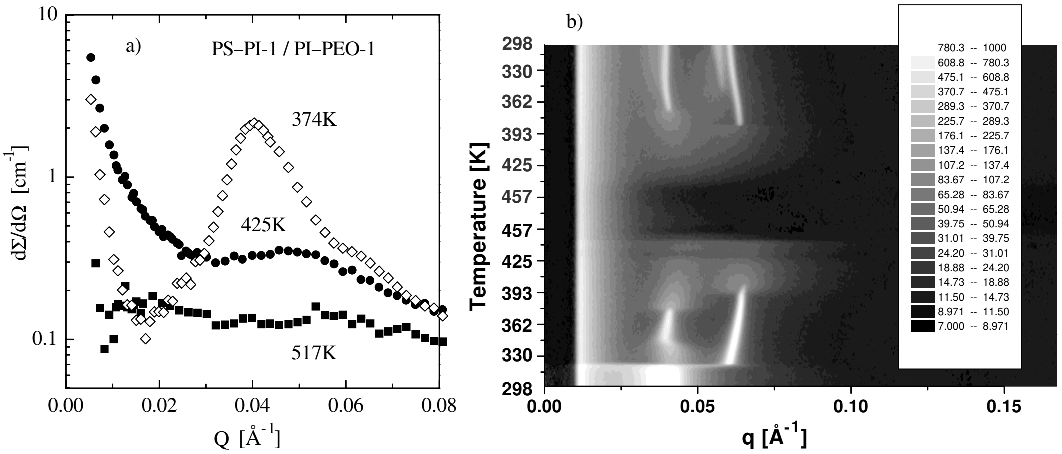

Fig. 2 – (a) The SANS spectra for the PS-PI/PI-PEO blend with a composition $\Phi = 0.5$ at different temperatures 517 K (■), 425 K (◊), and 374 K (•). At 517 K no particular structure is observed. At 425 K the small-angle intensity increases and a peak at $0.05\,\text{Å}^{-1}$ develops. At 374 K the intensity at small angles decreases, and two peaks at $0.04\,\text{Å}^{-1}$ and $0.065\,\text{Å}^{-1}$ develop. (b) The SAXS spectra for the PS-PI/PI-PEO blend with a composition $\Phi = 0.5$ on a heating and cooling run. The intensity is depicted by grey-scaled brightness. Up to 322 K the PEO portion is crystalline, then two correlation peaks develop, which broaden suddenly up, independently.

homopolymer blends was used as the PS and PEO blocks are on different chains.

We consider first a blend with $\Phi = 0.5$. SANS measurements were performed for distinct temperatures (see fig. 2(a)), which typically took 1.5 hours for each spectrum. Upon lowering the temperature from 517 K to 425 K, the intensity at low scattering angles is strongly increased, signifying macro-phase composition fluctuations. At 425 K a correlation peak at $0.05\,\text{Å}^{-1}$ becomes visible. At 374 K the much more intense correlation peak is shifted to $0.04\,\text{Å}^{-1}$, and a second peak is observed, which could indicate an ordered phase. The intensity at low scattering angles is decreased, but still indicates macro-phase separation. The phase separation likely reached higher length scales, and, therefore, the small-angle intensity of our experimental set-up is less pronounced.

In the SAXS experiment the scattering intensity profile was measured during continuous heating and cooling ramps (with a ±10 K/min rate, and a 1 minute waiting period at 473 K). Figure 2(b) shows contour plots of the intensity profiles (as a function of Q) recorded at the temperatures indicated. Before reaching a temperature of 322 K a single diffraction peak at $Q = 0.040\,\text{Å}^{-1}$ was observed. Wide-angle X-ray scattering data obtained concurrently confirmed that the PEO portion of the sample was crystalline. Upon further heating the spectra showed two diffraction peaks at $0.040\,\text{Å}^{-1}$ and $0.062\,\text{Å}^{-1}$, which suddenly became broader at 379 K and 392 K, respectively. The two T_{ODT}'s are most likely due to the independent disordering of two diblock-copolymer–like phases. Upon further heating at approximately 430 K the two broad peaks merged. At approximately the same temperature of 440 K the scattered intensity at low scattering angles is suddenly lowered. Thus, the merging of the peaks seems to be correlated to homogenous mixing. The decrease of the low-angle scattering is less clear compared to the SANS data, because the X-ray scattering contrast is much more sensitive to micro-phase separation. This becomes obvious when comparing the scattering length densities of PS/PI/PEO for neutrons ($0.022/0.004/0.010 \times 10^{-12}\,\text{mol/cm}^2$) and for

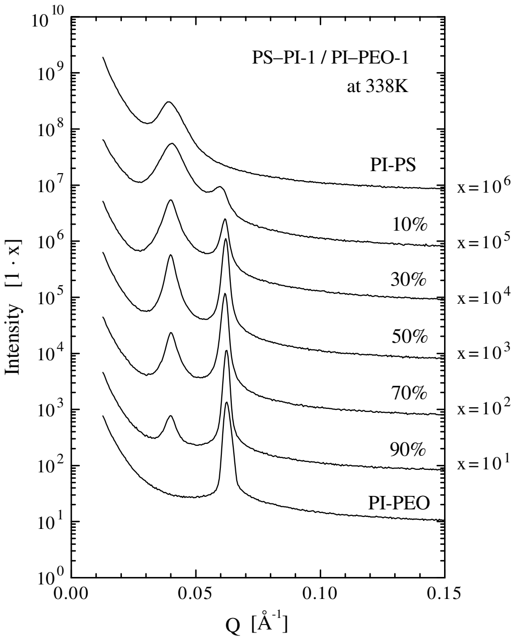

Fig. 3 – The SAXS spectra at constant temperature of 338 K for the PS-PI/PI-PEO blend for different compositions, including the pure diblock copolymer blends. The ratio of the peak integral intensity behaves like phase-separated pure diblock copolymers.

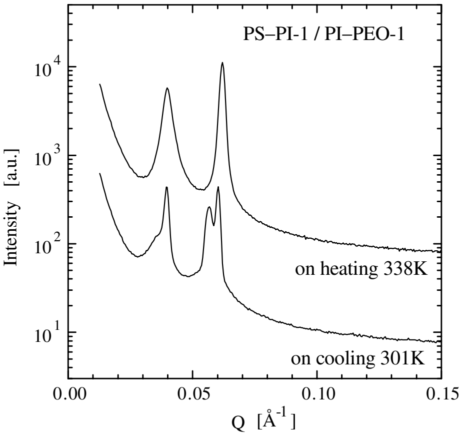

Fig. 4

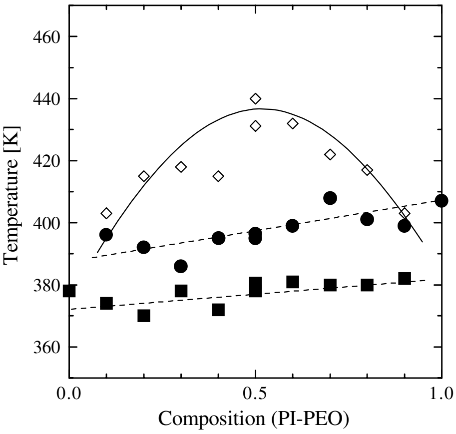

Fig. 5

Fig. 4 – The SAXS spectra for the PS-PI/PI-PEO blend with a composition $\Phi = 0.5$ on the heating run (338 K) and after cooling (301 K). After cooling, the two higher intensity peaks correspond to the melt structures, and the shoulders on the low-Q side are due to crystallisation of the PEO portion.

Fig. 5 – The phase diagram measured using SAXS for the PS-PI/PI-PEO blend. The order-disorder temperatures of the PS-PI rich phase (■) and the PI-PEO rich phase (•) are clearly defined by the broadening of the correlation peaks. The macro-phase binodal (◊) can either be determined by the scattering intensity at small angles, or by the merging of the correlation peaks.

X-rays ($0.118/0.101/0.126 \times 10^{-12}\,\mathrm{mol/cm^2}$). Upon cooling, micro-phase separation was signalled by the appearance of Bragg peaks, which become sharp at different temperatures. The observation of four peaks is distinct to the heating run, and this feature is discussed below.

We now discuss the SAXS intensity profiles (fig. 3) obtained on heating for different compositions at a constant temperature of 338 K, right above the crystallisation temperature of PEO. The ordered phase does not show a very sharp peak. One might speculate that the slowing down due to the neighbourhood of the glass transition temperature (339 K) [14] prevents the observation of fully relaxed PS-PI chains. We therefore discuss integral peak intensities. With increasing PI-PEO content the ratio of the peaks at $0.040\,\text{Å}^{-1}$ to $0.062\,\text{Å}^{-1}$ decreases. This change points to a macro-phase–separated system, where the relative amount of the phases is changed. Although higher-order reflections are absent, the coexisting phases can be expected both to be lamellar, since the diblock copolymers are symmetric [12].

The structure formed on cooling below the crystallisation temperature of the PEO is more complex, as shown in fig. 4, where the solidified structure is compared to the melt. The two higher-intensity peaks correspond to the melt structures. The two peaks at highest Q are associated with the PEO-PI structure. Such polymer are well known to stretch on crystallisation due to the formation of crystalline stems [15] and the peak at $Q = 0.056\,\text{Å}^{-1}$ is associated with crystalline PEO-PI regions, whereas the peak at $Q = 0.060\,\text{Å}^{-1}$ is associated with PI-PEO melt. The crystallisation was confirmed by the appearance of characteristic diffraction in the wide-angle region. Complex crystallisation of PEO into the expanded crystalline lamellae is prevented due to constrain by the glassy PS phase. The peak at $Q = 0.039\,\text{Å}^{-1}$ is diffraction from PS-PI and, on cooling, develops a low-Q shoulder. The weak shoulder on the PS-PI peak could be due to strain from crystallisation or inclusion of PS-PI in PI-PEO domains.

The phase diagram (fig. 5) was determined by structure identification from SAXS experiments upon heating. The order-disorder transition temperatures do slightly depend on the composition. The experimental binodal line was determined from the SAXS data, where the two correlation peaks merged. This binodal line shows the typical parabolic shape, which cuts the order-disorder transition lines at approximately 10% and 90% composition.

The diblock copolymer blends are found to be macro-phase–separated at low temperatures. This phase behaviour is confirmed by both scattering methods, SANS and SAXS, where an increase of the intensity at low scattering angles is found. It is an experimental result that the two scattering peaks merge at the macro-phase binodal. In the two-phase state, two independent order-disorder transition temperatures are observed upon heating. The two T_{ODT}'s depend only slightly on the composition, and do not differ significantly from the pure diblock copolymers. The two coexisting phases therefore consist of almost pure diblock copolymers. This interpretation is in agreement with the observed binodal line, which cuts the T_{ODT} lines at about 10% and 90%. Remarkably, given the simplicity of the random phase approximation mean-filed theory, the predicted phase diagram (fig. 1) is in semi-quantitative agreement with the experimentally observed phase diagram. In comparison to ref. [3] our system has a relatively large interaction parameter between the A and C blocks, and therefore the governing macro-phase separation is not a surprise.

In summary we investigated the phase behaviour of a binary diblock copolymer blend of poly(styrene)-poly(isoprene) and poly(isoprene)-poly(ethylene oxide). Micro- and macro-phase separation lines were obtained from small-angle scattering experiments. The diblock copolymers exhibit independent order-disorder transition lines in the two-phase region. The crystallisation of PEO changes the length scale of the lamellar ordered structure, but is inhibited by the glassy polystyrene. Mean-field theory provides a good description of the observed phase behaviour.

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