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Interface Width of Poly(styrene-*b*-butyl methacrylate) Diblock Copolymers

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Introduction. The understanding of polymer blends and interfaces is quite important with respect to industrial applications. It is the purpose of many efforts to optimize polymer blends and to design materials with properties tailored to a specific use. To provide a particular mechanical behavior, the use of block copolymers opens a wide field of possibilities due to different available microstructures. For diblock copolymer melts, lamellar, bicontinuous double diamond, hexagonal, and body-centered cubic structures have been observed.[1] It has been recognized that the interface as the region connecting adjacent microphases is one of the determining factors for many bulk materials properties. However, only few experimental investigations are reported dealing with block copolymer interfaces. Anastasiadis et al.[2] have for instance determined the interface width in poly(styrene-*b*-methyl methacrylate) by neutron reflectometry, which turns out to be one of the most sensitive techniques to measure the narrow interfaces between incompatible polymers.[3]

Much work has been done to describe the behavior of block copolymers in theory or simulation (for a review see, e.g., refs 1, 4, and 5). It is the purpose of this work to demonstrate consistent experimental results obtained by neutron reflectometry (NR) and transmission electron microscopy (TEM) with respect to interfacial thickness and morphology. Our experimental data are compared to theoretical predictions by Semenov[6] utilizing the interaction parameter of the homopolymer blend.[7,8]

Results and Discussion. Poly(styrene-*b*-*n*-butyl methacrylate) block copolymers, P(S-*b*-nBMA), were prepared by anionic polymerization procedures, which yield well-defined block lengths and narrow molecular weight distributions. Samples were characterized by gel permeation chromatography with respect to molecular weight and distribution, and by NMR to determine the composition. For the NR experiments a symmetric diblock copolymer of PS(D) and PnBMA was used ($f = 0.5$, $M_w = 248\,300$, $M_w/M_n = 1.03$), where the polystyrene block has been deuterated for contrast reasons. A virtually identical but nondeuterated sample has been used for the TEM studies ($f = 0.5$, $M_w = 278\,000$, $M_w/M_n = 1.05$). It should, of course, be kept in mind that deuteration also changes thermodynamics slightly, which for strongly incompatible systems is usually negligible.[3]

To investigate the interface width by TEM, samples were prepared by solution casting of a ca. 1 mm thick films utilizing dilute solutions of the polymer in toluene. The solvent was slowly evaporated over 5−7 days at room temperature. Subsequently, the film was annealed under vacuum for 3 days at 150 °C. Thin slices of the film were cut at room temperature using a diamond knife. Sufficient contrast for the TEM investigation was achieved by staining the polystyrene block with ruthenium tetroxide (RuO_4) at 23 °C for 15 min. It was shown for other block copolymers that the interface thickness can be estimated from TEM images by using staining with RuO_4 for a short time of about 5 min[9] instead of 30−45 min, as described otherwise.[10,11] In Figures 1 and 2 the TEM images of the copolymer are shown after staining.

The PS lamellae appear to be dark with a thickness of 33 ± 2 nm. The thickness of the PS lamellae appears to be bigger than the PnBMA lamellae, which is due to a decomposition of the PnBMA component in the electron beam. From Figures 1 and 2 one obtains a long period of the lamellar structure of 60 ± 5 nm. It is, however, also observed that between adjacent domains the interface can be recognized as a dark line. Possible reasons for the preferential staining of the interface between the phases may be seen in a better accessibility of PS chains surrounded by PnBMA and an enhancement of the reactivity of those chains with respect to RuO_4 due to strain in the interfacial region.[9] From an analysis of the width of those dark lines we obtain an interface thickness of 8 ± 2 nm, which is relatively large compared to other block copolymer systems reported in the literature.[2,12] Other measurements of interface thickness have been either performed by NR or TEM investigations, while in this study the two techniques are compared for the first time.

A better resolution of up to 0.1 nm for long spacing and interface width is obtained by NR utilizing partially deuterated samples.[3] Experiments were performed at the neutron reflectometer TOREMA II at GKSS Research Centre, Geesthacht. The wavelength is fixed to 0.43 nm, and a position sensitive gas detector is used. Samples were prepared by spin coating[13] on 10 × 10 cm^2 float glass plates as a substrate and have been annealed at different temperatures for 2 weeks. They are quenched to room temperature for the NR experiments. The analysis of specular reflectivity curves (Figure 3) yields information on the neutron refractive index or composition profile perpendicular to the interface.[3] The lamellae are nicely oriented parallel to the substrate, and the profile perpendicular to the surface

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is obtained from NR, which is averaged laterally over the coherence length of the neutrons. The interfacial profile between microphase-separated regions is described by a hyperbolic tangent profile, which is the simplest profile assumed in theoretical approximations[5] and which similarly has been used at the interface between incompatible homopolymers.[3,7] Results of fits at different annealing temperatures on interface width a_I and long period L are summarized in Table 1.

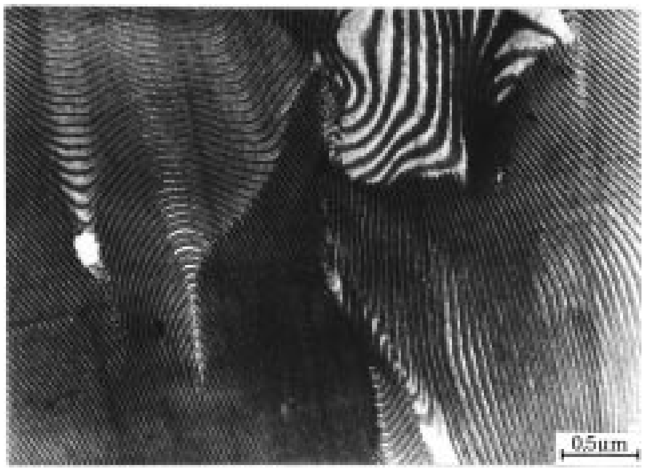

Figure 1. TEM picture of a symmetric P(S-*b*-nBMA) diblock copolymer stained with RuO_4.

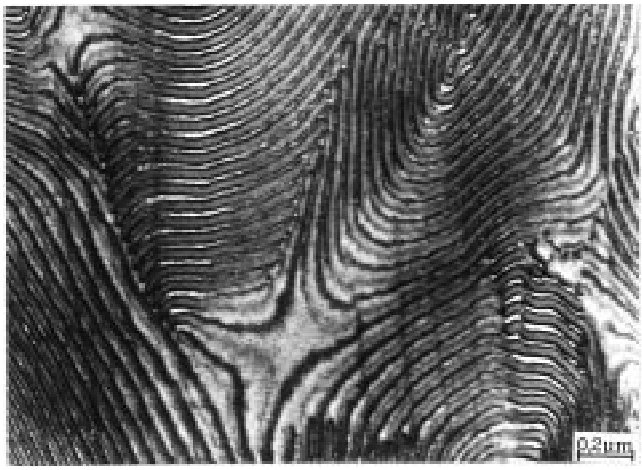

Figure 2. Higher magnification of lamellar morphology. The dark lines between the PS (dark) and PnBMA (light) domains correspond to the interface.

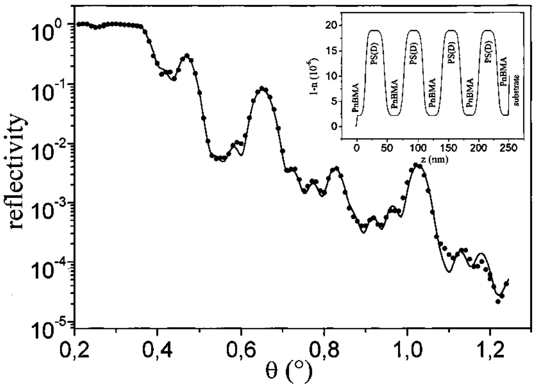

Figure 3. Neutron reflectivity data (●) and calculated fit curve from a thin film of P(S-*b*-nBMA). The inset shows the corresponding refractive index profile normal to the film surface that was used to calculate the reflectivity.

Table 1. Results of NR Experiments on P(S(D)-*b*-nBMA) Samples at Different Temperatures[a]

T (C°)	L (nm)	a_I (nm)
140	62.06 ± 0.05	7.7 ± 0.2
151	60.14 ± 0.05	8.4 ± 0.2
163	61.74 ± 0.05	7.7 ± 0.2

[a] L represents the long period of the lamellar structure and a_I the interface width between microphases.

The results obtained by NR demonstrate that both methods NR and TEM provide comparable values for the long period of the lamellae structure and for the interface width between lamellar domains. Whereas TEM gives an optical impression of the morphology, its fluctuations, and its long range order on cut and stained "bulk" samples, NR yields more quantitative and accurate values (no sample degradation by electron beam or swelling by contrast agent), which are obtained with thin films (different preparation) and which are averaged laterally. The long period is of course also obtained by small-angle X-ray and other techniques, which, however, hardly can provide accurate values of the interface width.[14]

The temperature dependence of the long period and interfacial width obtained in NR experiments can be understood by utilizing a temperature-dependent interaction parameter χ determined for the respective homopolymers. The temperature-dependent interaction parameter χ and the mean segment length b of PS and PnBMA are well-known in the range 120−156 °C.[7,8] Thus we use $b = 0.78$ nm and $\chi = 0.0098$ and 0.0081 for the homopolymers at 140 and 151 °C, respectively. The theory by Semenov[6] predicts for the lamellar morphology of symmetric diblock copolymers the period L and interfacial width a_I in the strong segregation limit.

$$L = 4\left(\frac{3}{\pi^2}\right)^{1/3} \frac{b}{\sqrt{6}} N^{2/3}\chi^{1/6} \tag{1}$$

$$a_I = \frac{2b}{\sqrt{6\chi}}\left[1 + \frac{1.34}{(\chi N)^{1/3}}\right] + \text{fluctuation corrections} \tag{2}$$

Calculating the period L from eq 1 based on the homopolymer χ values, one finds excellent agreement with the NR results for L as given in Table 1. Calculated values of L are 62 and 60 nm at 140 and 151 °C, respectively. Regarding the interfacial width a_I, the experimentally determined values are slightly smaller than the theoretical ones from eq 2. The deviation might be due to the fact that eq 2 was derived in the strong segregation limit[15] and for the present case χN is approximately 20. For a more detailed analysis of interface width and lamellar spacing in the present regime, further experimental studies are required, varying the molecular weight. Nevertheless, the experimental a_I values fulfill the relation

$$\frac{a_I(151\ °\mathrm{C})}{a_I(140\ °\mathrm{C})} = \sqrt{\frac{\chi(140\ °\mathrm{C})}{\chi(151\ °\mathrm{C})}} \tag{3}$$

derived by utilizing eq 2 where the small differences in $1.34/(\chi N)^{1/3}$ are neglected.

From eq 2 one obtains for a_I 9.7 and 10.8 nm at 140 and 151 °C, respectively, while the influence of fluctuations was not taken into account. Estimating the contribution of such corrections a still much bigger interfacial width would be calculated. Consequently, fluctuations such as capillary waves should not play an important role for the investigated system, which might be a consequence of the thin film preparation. Also, the TEM investigation on much thicker samples yields comparable values for the interfacial width. Fluctuations could be quenched by the influence of the smooth substrate and surface. In addition, large fluctuations are damped out due to the finite film dimensions, and only those fluctuations are recorded in NR experiments, which can be seen within the lateral coherence length of the incident neutrons (typically some micrometers depending on the angle of incidence).

The results are in accordance with small-angle X-ray scattering studies performed by Russell and co-workers[16] for this system, indicating the existence of both an upper and lower critical ordering transition. We observe an increase of the long period correlated with a decrease of the interfacial width (Table 1), which occurs for both decreasing and increasing temperatures starting at 151 °C. The investigated temperature range in this work is limited by two effects. At temperatures below 140 °C, problems arise with respect to kinetics and sufficient annealing times in order to reach equilibrium. On the other hand at high temperatures (above 160 °C) a degradation of acrylic polymers may occur.[17] However, the experimental errors of the NR results are sufficiently small and thus also provide evidence for the existence of two transitions, as predicted by Russell.[16] It should be noted that the lower critical ordering transition can be explained when the compressibility of the blocks is taken into account in a phenomenological interaction parameter while the theory of Semenov[6] employs the incompressibility argument and thus a lower critical ordering transition cannot occur. The concept using the incompressibility argument together with a phenomenological interaction parameter is the usual way to understand the experimental results.

In conclusion we have shown for the investigated P(S-*b*-nBMA) diblock copolymers that both neutron reflectivity and transmission electron microscopy provide accurate data on the long period and interface width in the ordered regime. The temperature dependence and absolute values obtained are consistent within mean field theory with the already known segment interaction parameters and the mean segment length measured for the homopolymers. It is thus shown that the phase and morphological behavior of the copolymer can be understood on the basis of the knowledge of the homopolymers and that in this particular case TEM can be used in a quantitative way to determine also the interfacial width between phases. The reason for this particular sensivity of TEM for the interfacial region is not yet fully understood, and further investigations also with respect to the unusual mechanical properties of this interesting copolymer[18] system are under way.

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