Thermodynamically Controlled Morphological Disorder in a Microphase-Separated Cylindrical Block Copolymer

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Block copolymers formed from chemically different, immiscible polymer chains show the formation of microphases which arrange into highly ordered crystal-like mesophase structures. Besides the cubic, hexagonal, gyroid, and lamellar symmetries, which have been identified in AB and ABA block copolymers,[1] the more recent work on ABC triblock copolymers has demonstrated that much more complex microphase morphologies can be realized.[2−6] Consequently, theoretical models have been developed to describe the formation of these new morphologies.[7−9]

In contrast to binary diblock copolymers in the strong segregation limit, where the composition is the main variable which determines the equilibrium microphase morphology, the morphology of ternary block copolymers is governed not only by two independent composition variables (i.e. volume fractions ϕ_A, ϕ_B, $\phi_C = 1 - \phi_A - \phi_B$) but also by the balance of the three interaction parameters (χ_{AB}, χ_{BC}, χ_{AC}), and their respective interfacial tensions (γ_{AB}, γ_{BC}, γ_{AC}). The other major factor influencing the microphase morphology is the chain topology, i.e. the block sequence in linear ABC systems.

In our previous work poly(styrene-*block*-butadiene-*block*-methyl methacrylate) (SBM) block copolymers have been studied. In that system the two end blocks poly(styrene) (**S**) and poly(methyl methacrylate) (**M**) show a pronounced incompatibility toward the polybutadiene block (**B**), while they are only weakly incompatible with each other; i.e. they have a low interfacial tension. As a consequence morphologies are formed in which **S**/**M** interfaces are created despite the fact that these two components are not chemically connected.

In the present communication we report the morphology of a block copolymer where we have changed the monomer sequence, i.e. a poly(butadiene-*block*-styrene-*block*-methyl methacrylate) (BSM) triblock. In this system the poly(butadiene) block (**B**) which is strongly incompatible with the **S** block is located on one end and the **M** block which has a rather low interfacial tension toward **S** is located on the other end.

The synthesis of the poly(butadiene-*block*-styrene-*block*-methyl methacrylate) block copolymer was accomplished by sequential anionic polymerization of butadiene, styrene, and methyl methacrylate in tetrahydrofuran in the presence of lithium alkoxides using *s*-butyllithium as initiator.[10] The block copolymer has the following characteristics: **B** block $M_n = 38\,000$, 20 wt %; **S** block $M_n = 116\,000$, 60 wt %; **M** block $M_n = 38\,000$, 20 wt %; total molecular weight $M_n = 192\,000$; $M_w/M_n = 1.13$ (molecular weight by membrane osmometry; molecular weight distribution by size exclusion chromatography SEC). If simple volume additivity is assumed, the volume fractions are calculated on the basis of the room temperature densities: $\phi_B = 0.22$, $\phi_S = 0.6$, and $\phi_M = 0.18$. Transparent films of the triblock copolymer were slowly cast from chloroform. To avoid cross-linking of the 1,2-polybutadiene block, further drying and annealing of the block copolymer was performed at 100 °C for 2 days followed by heating at 170 °C in high vacuum for 6 h. SEC done after this annealing procedure yielded results comparable to the unannealed sample. As expected for the high molecular weight of the block copolymer, differential scanning calorimetry shows the occurrence of three glass transitions located at $T_{gB} = -9.5$ °C, $T_{gS} = 111$ °C, and $T_{gM} = 138$ °C (observed at a heating rate of 20 deg/min).

The morphology was studied by transmission electron microscopy using a Phillips transmission electron microscope operating at 80 kV. Ultrathin sections of the block copolymer were obtained using a Reichert ultramicrotome equipped with a diamond knife. The rigidity of the sample was high enough to prepare high-quality ultrathin sections at room temperature. The ultrathin sections were stained using ruthenium tetroxide and osmium tetroxide.

Polystyrene (**S**) is the major component in the block copolymer. The two end blocks with 20 wt % each are expected to form cylinders. In AB block copolymers, the cylinders usually form a hexagonal matrix. Mogi et al.[5] reported the morphology of a poly(isoprene-*block*-styrene-*block*-2-vinylpyridine) ($I_{14}S_{68}2VP_{18}$) block copolymer of similar composition ($\phi_I = 0.14$, $\phi_S = 0.68$, $\phi_{2VP} = 0.18$). The PI and P2VP blocks formed highly ordered cylinders on a tetragonal lattice. In the I−S−2VP system both end blocks are highly incompatible with the styrene center block.

Parts a and b of Figure 1 show electron micrographs of the BSM block copolymer stained with OsO_4, at two different magnifications. OsO_4 predominantly reacts with the **B** block.

While the micrograph clearly shows the formation of a cylindrical microphase morphology for the polybutadiene microphase, there are obvious differences when compared to the ordered cylindrical microphases in AB diblocks or to the I−S−2VP reported by Mogi et al. The most prominent difference is the observation of bent "banana-like" cylinders which result in a lack of long range positional order of the cylinders. In areas where a short range order of perpendicularly cut cylinders is observed, the cylinders are more likely to be packed tetragonal and not hexagonal, which is expected for an ABC system.[7]

Figure 2 shows the electron micrograph of the same BSM block copolymer stained with RuO_4, which attacks both **S** and **B**. As has been demonstrated earlier, however, a careful treatment with RuO_4 allows one to stain preferably the **S**/**M** interface.[11] Treating the sample too long with the staining agent results in a loss of contrast. Thus, the boundary of the **M** microphase within the PS matrix can be clearly recognized. As for poly(butadiene), the poly(methyl methacrylate) also forms bent cylinders which show tetragonal packing on a local scale.

The dimensions of the cylinders can be estimated directly from the electron micrograph. The diameter of the **B** cylinders is $D_B = 14$ nm, and the distance between two **B** cylinders is $L_{BB} = 27$ nm. The length of the **B** cylinders h_B is between 200 and 300 nm. The corresponding values for the **M** cylinders are $D_M = 11$ nm, $L_{MM} = 30$ nm, and $h_M = 200-500$ nm. Using the average value of the long period ($D_{av} = 28.5$ nm), the

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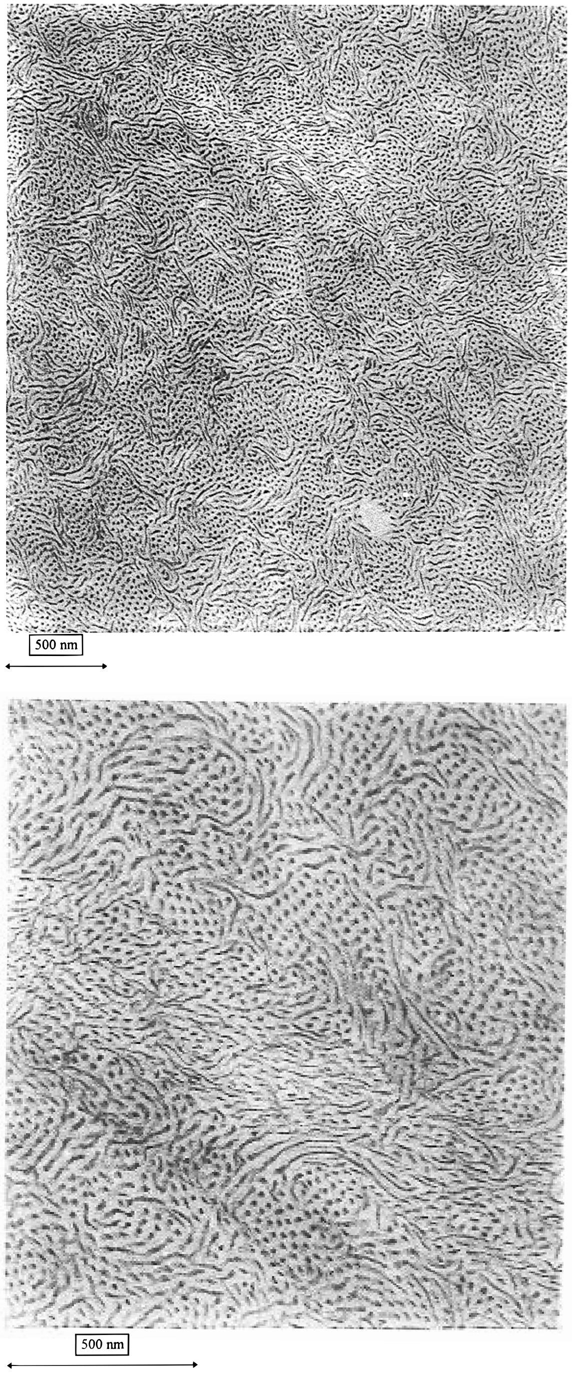

Figure 1. a, b) $B_{20}S_{60}M_{20}{}^{192}$ stained with OsO_4 at two different magnifications.

diameters of the **B** and **M** cylinders can be calculated by assuming the cylinders (of the mentioned volume fractions) are tetragonally packed. The calculated diameters are $D_{B(calc)} = 15$ nm and $D_{M(calc)} = 13$ nm, respectively. These values are in reasonable agreement with those estimated from the micrographs.

As emphasized already, the cylinders do not possess long range order or distinctive grain boundaries. The grains of locally ordered cylinders have dimensions of only about 200 nm in diameter.

In those areas where the cylinders are cut perpendicular to their cross-section, i.e. where the curvature of the cylinders can be clearly identified, it can be observed that a couple of cylinders form a bundle over a short distance. Afterward they split apart to merge with other cylinders. To check if this disordered structure results from sample preparation, the casted sample was annealed additionally at 180 °C for 6 h. No changes in the morphology were observed.

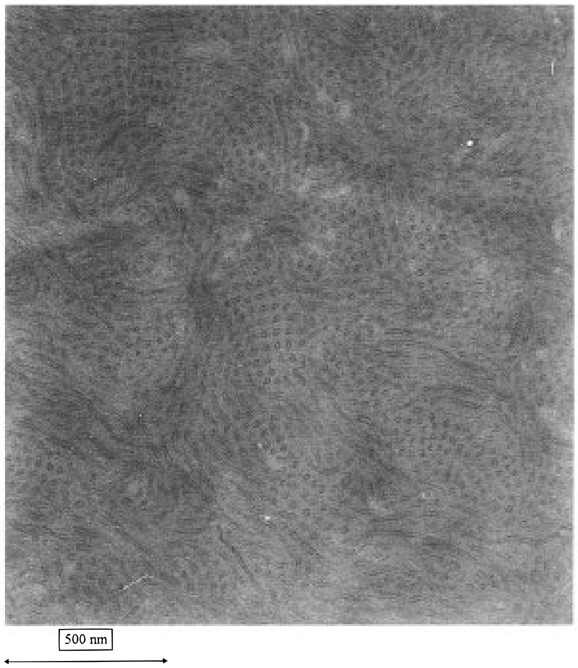

Figure 2. $B_{20}S_{60}M_{20}{}^{192}$ stained with RuO_4.

A straightforward explanation of the formation of this bent cylinder morphology can be given on the basis of the balance of interfacial tensions.

The surface tension between **S** and **M**, γ_{SM}, is considerably smaller than that between **S** and **B**, γ_{SB}.[12] This smaller γ_{SM} increases the contact area per **S**–**M** junction Σ_{SM} (compared to S–B) and reduces the stretching of **M** chains. Likewise, the high γ_{SB} reduces Σ_{SB} and accepts a stronger stretching of the **B** chains. Consequently, the **M** cylinders will tend to become thinner than **B** cylinders at the same volume fraction.

Based on Semenov's[13] work on AB diblock cylinders, the radius of a cylinder scales with $\gamma^{1/3}$. If we assume that the chain characteristics (Kuhn length, segmental volume) of A and C are comparable, the ratio of the different cylinder diameters will be given by

$$\frac{R_B}{R_M} \approx \left(\frac{\gamma_{SB}}{\gamma_{SM}}\right)^{1/3} \approx 1.24$$

The relative length ratio of the cylinders h_M/h_B is given by

$$\frac{h_M}{h_B} = \frac{\phi_M}{\phi_B}\left(\frac{\gamma_{SM}}{\gamma_{SB}}\right)^{2/3}$$

which is about 1.5 for $\phi_M \cong \phi_B$. This corresponds to a severe mismatch between cylinder dimensions. As a consequence, there will be an additional elastic contribution in the direction parallel to the cylinder which is not present in an AB diblock or an ABC triblock where the cylinders are of equal diameter.[14]

This chain frustration gives rise to the bending of the cylinders and makes long range order impossible.

We thus conclude that the observed disorder is an inherent property of this block copolymer system. This disordered structure may be described as a colloidal glass of nonspherical particles.[15]

There are a couple of interesting properties of this block copolymer which are associated with this structural disorder. The lack of long range order (i.e. the formation of a structural glass without long grains) causes the material to be highly transparent. In addition, the disappearance of these grain boundaries should also influence the block copolymers' mechanical properties. Furthermore, it should be possible to follow the transition from disordered to ordered cylinders by variation of the block copolymers' composition. Studies along these directions are currently in progress.

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(14) A detailed thermodynamic analysis will have to take into account the additional elastic as well the additional surface energy contributions from the cylinder ends: V. Abetz, K. Jung, R. Stadler, work in progress.

(15) R.S. is indebted to Prof. K. Binder, Mainz, who drew our attention to the analogy of the disordered cylinders to structural glasses (like colloid glasses).

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