Chiral Assembly in Amorphous ABC Triblock Copolymers. Formation of a Helical Morphology in Polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) Block Copolymers

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ABSTRACT: The microphase separation in a linear ternary block copolymer consisting of three immiscible components, namely, polystyrene, polybutadiene, and poly(methyl methacrylate), gives rise to the formation of a chiral supramolecular assembly in which the chirality is not defined on a molecular (or macromolecular) level but only by the assembly of the linear triblock copolymer molecules. The polybutadiene midblock (7 and 12 wt %) forms helical strands surrounding the polystyrene cylinders (25 and 26 wt %) which are embedded in a poly(methyl methacrylate) matrix. This chiral mesoscopic assembly can be recognized by transmission electron microscopy. The formation of this structure is controlled by the relative incompatibilities of the three polymeric components in the block copolymer.

Introduction

Amorphous polymers consisting of blocks of different chemical nature show the formation of ordered spherical, cylindrical, lamellar, or bicontinuous double-diamond "mesophases". This has been demonstrated for poly(A)-*block*-poly(B) (AB) diblock for poly(A)-*block*-poly(B)-*block*-poly(A) (ABA) triblock as well as for corresponding star block copolymers which consist of two chemically different components.[1] Owing to the synthetic difficulties, rather little attention has been given to block copolymers consisting of three chemically different components. As a result, the various principles of assembling ABC block copolymers into ordered microphase morphologies are far from being understood in spite of some early[2–4] and more recent experimental[5–7] and theoretical[8] work. In binary diblock copolymers the composition determines the equilibrium microphase morphology. In ternary block copolymers two independent composition variables have to be taken into account. In addition, as we have demonstrated recently,[9] the mesoscopic assembly of ABC triblock copolymers not only is governed by the composition but is strongly influenced by the balance of the three binary interaction parameters (more exactly, the product of the degree of polymerization and the segment interaction parameter) or interfacial energies between the different polymer pairs as represented by the surface tensions γ_{AB}, γ_{BC}, and γ_{AC}, respectively. An example for linear ABC block copolymers in which the morphologies are determined by the balance of the surface tensions is high molecular weight polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (SBM) triblock copolymers. In this system both PS and PMMA show a pronounced incompatibility toward PB as is manifested by the large surface tensions.[10] PS and PMMA, on the contrary, are only weakly incompatible. As a consequence of this "thermodynamic imbalance", new types of ordered microphase morphologies result. In a symmetric block copolymer with nearly equal amounts of the three components ($\phi_A \approx \phi_B \approx \phi_C$), a lamellar morphology is formed. If the fraction of the center block ϕ_B is reduced below a critical volume fraction ϕ_B^{crit}, the minimization the free energy results in the formation of curved PS/PB (A/B) and PB/PMMA (B/C) interfaces and in the creation of an additional PS/PMMA (A/C) interface despite the fact that A and C are not directly linked. Substitution of the enthalpically unfavored AB and BC contacts by AC contacts is the main driving force of the morphological transition. For a polymer with $\phi_A = \phi_C \approx 0.4$, $\phi_B \approx 0.2$, the major components A and C form a lamellar structure with B cylinders located at the lamellar A/C interface.[9,11] This transition is shown schematically in Figure 1 as a two-dimensional sketch. This transition depends on the ratio of the surface tensions $f = \gamma_{AC}/(\gamma_{AB} + \gamma_{BC})$. If the important elastic contributions are *not* taken into account, the critical volume fraction of the transition is

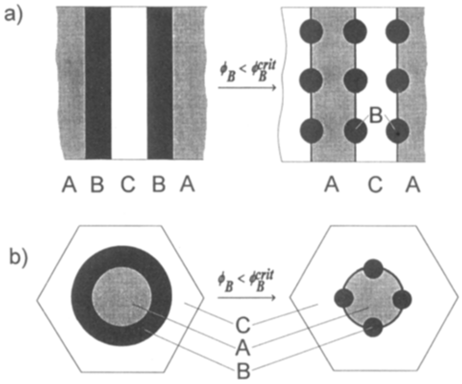

Figure 1.

$$\phi_B^{crit} = \pi\frac{(1-f)^2}{(2\pi - f)^2}$$

If the total free energy including the elastic potential is considered, ϕ_B^{crit} will be shifted to lower values.[11]

So far all lattices of regular microdomain structures based on binary AB, ABA, or ternary ABC block

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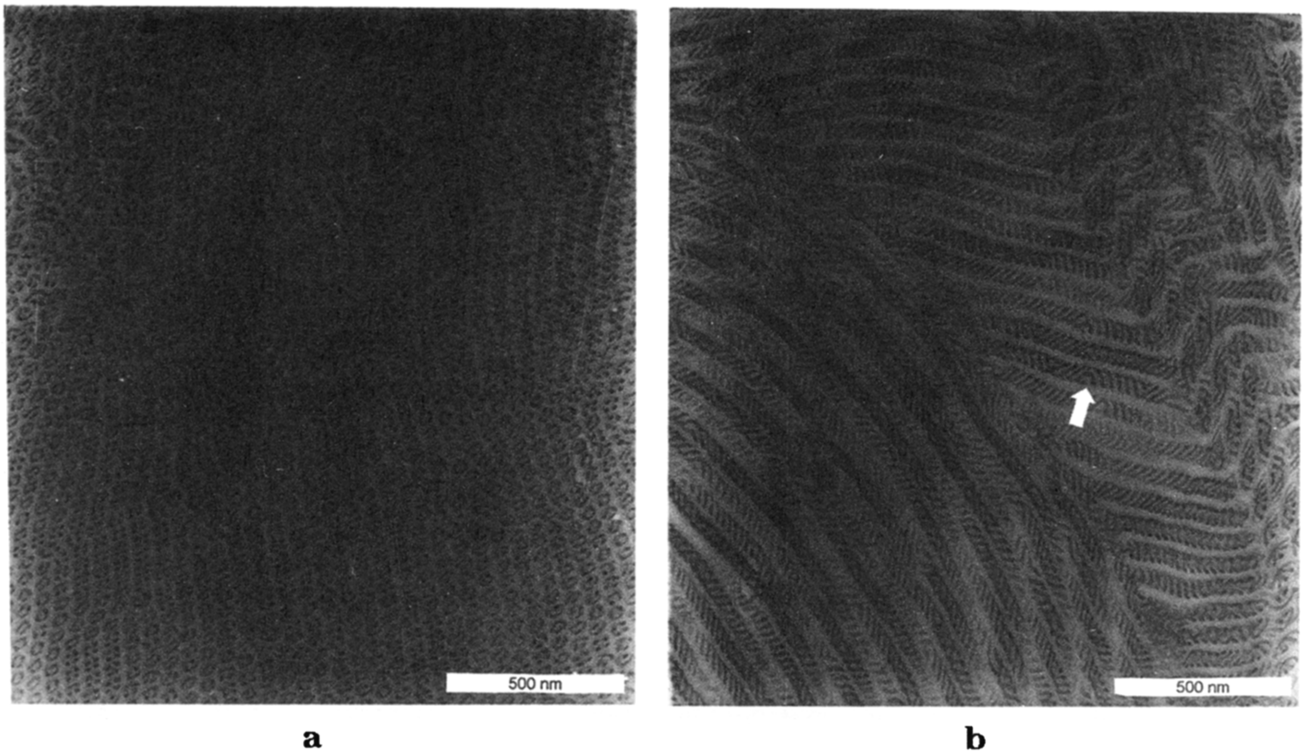

Figure 2.

copolymers can be described using simple symmetry elements like mirror planes, symmetry centers, and a rotation axis. In the ordered bicontinuous double-diamond structure (OBDD) and the ordered tricontinuous double-diamond structure (OTDD) also screw axes (4_2 and 2_1) are known, but in none of these structures do these symmetry elements lead to chirality.

In the present contribution we report the first example of a "chiral" mesoscopic structure based on linear amorphous triblock systems.

Results and Discussion

The synthesis of the polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) block copolymers was accomplished by sequential anionic polymerization of styrene, butadiene, and methyl methacrylate in tetrahydrofuran (THF) in the presence of lithium alkoxides using *sec*-butyllithium as initiator.[12] The block copolymers have the following characteristics. *SBM55*: PS block, $M_n = 55000$, 26 wt %; PB block, $M_n = 26000$ 12 wt % (microstructure, 90 mol % 1,2-units, 10 mol % 1,4-units); PMMA block $M_n = 137000$, 62 wt %; total molecular weight $M_n^{tot} = 218000$, $M_w/M_n = 1.09$. *SBM40*: PS block, $M_n = 49000$, 23.8 wt %; PB block, $M_n = 15000$, 7.2 wt % (microstructure, 90 mol % 1,2-units, 10 mol % 1,4-units); PMMA block, 142000, 69 wt %; total molecular weight $M_n^{tot} = 206000$, $M_w/M_n = 1.16$.

Transparent films of the triblock copolymer were cast over a period of 2 weeks from $CHCl_3$, tetrahydrofuran, dioxane, or methyl isobutyl ketone at room temperature. 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 2, 4, and 6 h. GPC analysis proved that no thermal degradation/cross-linking takes place under these annealing conditions. The morphology was studied by transmission electron microscopy (TEM) using a Philips transmission electron microscope operating at 80 kV. Ultrathin sections of the block copolymers 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. These sections were stained using gaseous ruthenium tetraoxide or osmium tetraoxide.

Poly(methyl methacrylate) (PMMA) is the major component in the block copolymers. From the overall composition ($\phi_{PS} + \phi_{PB}$):ϕ_{PMMA}, a cylindrical (hexagonal) microphase morphology can be expected, in which PS cylinders are embedded in the PMMA matrix. This is confirmed by electron microscopy of ultrathin sections stained with RuO_4, which predominantly reacts with PS. The distance between the centers of the hexagonally packed cylinders (in the following called lattice spacing) was about 40 nm in both triblock copolymers.

In the case of ABC triblock copolymers, a cylindrical core–shell morphology in which A cylinders surrounded by B cylindrical shells are arranged hexagonally in a C matrix is expected to be the most preferred structure if $\phi_A < \phi_B < \phi_C$ (preferred composition: A:B:C $\approx$ 1:4:9) and if $\gamma_{AB} \approx \gamma_{BC}$. Typical examples of such core–shell morphologies were given by Matsushita et al.[13] and Gido et al.[14]

In the triblock copolymers discussed in this work, the volume fraction of the B component ϕ_B is considerably smaller than ϕ_A. Similar to the transition from an ABC lamellar structure to a morphology where B cylinders are located at the A/C interface (Figure 1a), a transition of a cylindrical core–shell morphology to a structure in which the B component forms cylinders at the A/C interface could occur (Figure 1b).

Figure 2a shows the electron micrograph of the block copolymer *SBM55* stained with OsO_4, which predominantly reacts with the polybutadiene block and thus gives rise to the contrast in electron microscopy. A sample has been selected in which the ultrathin section is perpendicular to the main axis of the PS cylinders.

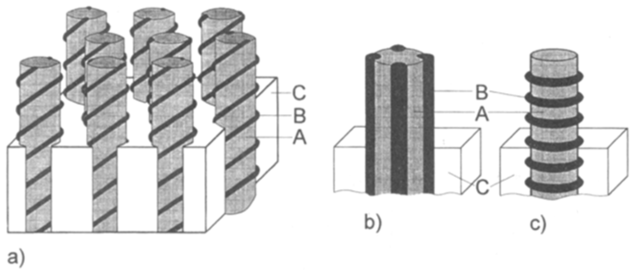

Figure 3.

The PB phase can be recognized as well-defined circular objects located at the weakly stained PS cylinders and the PMMA matrix.

Figure 2b shows a micrograph of an OsO_4-stained ultrathin section of *SBM55* in which the cutting direction is parallel to the main axis of the PS cylinders. It is evident from this micrograph that the polybutadiene phase forms cylinders which surround the PS cylinders as helices. Extensive tilting experiments were performed and verified the helical morphology which is shown schematically in Figure 3a.

From the height of the helix pitch, it must be concluded that either a double helix or a double double helix (i.e, 4-stranded helix) is formed in *SBM55*. In Figure 2a are 4 spots visible surrounding the cross section of the PS cylinder. Furthermore, in some regions in Figure 2b a single helix strand can be followed at the front and the rear side of a single PS cylinder. This observation clearly favors a 4-stranded helix.

The pitch height is 75 nm in the case of the double double helix in *SBM55*. From the pitch height and the PS cylinder lattice period (52 nm), the diameter of the PS cylinders ($D_{\text{cal PS}} = 23$ nm) and of the polybutadiene helix ($D_{\text{cal PB}} = 12$ nm) can be calculated from the known volume fractions. These values compare very well to the dimensions which can be directly estimated from the electron micrograph ($D_{\text{PB}} = 10$ nm, $D_{\text{PS}} = 26$ nm).

As can be seen from Figure 2b, both left- and right-handed helical structures are formed, either on different cylinders or along the same cylinder. In the latter case, helix reversals are observed (see arrow in Figure 2b). It is difficult to decide if these changes in handedness are showing the real structure of the system. During the microtoming process, PS cylinders could be cut into halves. Depending on which half remains on the grid, the projection could imply a change in handedness. This microtoming artifact could occur on a single cylinder as well as on different cylinders. To confirm or discard the existence of reversals, additional studies are necessary. There are no energetic favors which could distinguish between the two types of handedness (i.e., left or right-handed helix). According to this, it is not likely that only one species is formed during the casting process.

The helical morphology has been obtained by casting the block copolymers from various solvents with different solubilities for the three components (e.g., methyl isobutyl ketone (solubility parameter $\delta = (8.4\ (\text{cal/cm}^3)^{1/2})$, THF ($\delta = 9.1\ (\text{cal/cm}^3)^{1/2}$), $CHCl_3$ ($\delta = 9.3\ (\text{cal/cm}^3)^{1/2}$), and dioxane ($\delta = 10\ (\text{cal/cm}^3)^{1/2}$)). It also does not change with annealing time. This is a strong indication that the helical morphology is the equilibrium structure of the system.

The formation of the helical structure in the present polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) triblock copolymers can be explained on the basis of the theory of block copolymers in the strong segregation limit which was originally developed by Meier[15] and Helfand[16,17] and later extended by Semenov.[18] This approach was successful for the description of symmetric ABC block copolymer systems.[11] The details of the calculations for the helical morphology will be published elsewhere.[19] Here we only wish to summarize qualitatively the arguments which explain the formation of the helical structure.

As discussed above, one could have expected that the polybutadiene (B) would form cylinders at the PS/PMMA (A/C) interface. The formation of the PB cylinders lowers the surface free energy and enhances the degrees of configurational freedom for the PS and PMMA chains. The helical structure is just one possibility for realizing such a "cylinder at the cylinder surface" structure. Two other cases would be B cylinders parallel to the A cylinder (Figure 3b) or B rings surrounding the A cylinder (Figure 3c). An example of such a morphology has been observed in a symmetric ABC polymer with an even lower B content.[12] The structures given in parts b and c of Figure 3 would be the extreme situations of "cylinder at the cylinder surface" morphologies, and the various helical structures (single, double, and triple stranded) would correspond to intermediate situations.

As mentioned above, the formation of a specific microphase morphology mainly results from the balance of the contributions of the interface energy and the elastic energy.

In asymmetric AB diblock copolymers with B as the major component, the formation of curved "micellar" structures (A cylinders or A spheres) results from a considerable lowering of the elastic energy of the major component which counterbalances the higher interface free energy as compared to a lamellar phase. The same principles hold for ABC block copolymers with the fundamental difference that additional constraints act on the B chain: i.e., a B chain starts at the A/B interface and ends at the B/C interface. As a consequence, the elastic contribution of the B chains at a given B domain size is considerably larger than in AB diblock copolymers.[11]

As we have shown previously,[9] a morphology with PB rings surrounding PS cylinders (Figure 3c) forms at an even smaller volume fraction of B. Increasing the B volume fraction at the same overall molecular weight and PS cylinder diameter would involve an increase in the ring diameter. Since the elastic potential of the B chains is proportional to the square of the ring diameter, the system will tend to reduce the deformation of the B chains (reducing the ring diameter). This can be achieved by the formation of the helix which only has a slightly larger surface area but keeps the stretching of the B chains lower than the equivalent ring system. Finally, if the B fraction becomes too large, a core–shell structure will be formed.

To our knowledge, this is the first example for a spontaneous assembly of a nonchiral amorphous block copolymer into a helical, i.e., chiral, superstructure. It has to be pointed out that the chirality in this system is not the result of an inherent molecular chirality of the polymer chain. Moreover, it is an example of a chiral structure on the level of the dimensions of the microphases. Upon appropriate functionalization of the helical polybutadiene phase, the noncentrosymmetric morphology may be used as a building block of a variety of optical devices based on organic materials.

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