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Communications to the Editor

Antiferromagnetic Ordering in a Helical Triblock Copolymer Mesostructure

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Chirality is of utmost importance in nature due to its relevance in biochemistry and its ubiquity in the living world.[1,2] Most helical structures found in nature are based on specific molecular structures favoring a regular twist of the molecules around a given axis. Quite intriguingly, helical superstructures can as well be found in systems where no chirality is present on the molecular scale. A few years ago, a helical mesophase was observed in a microphase-separated ABC triblock copolymer with all three components being nonchiral, amorphous homopolymers.[3] In the present communication, we describe a chiral mesophase formed in a *thin film* of an ABC triblock copolymer. In such thin films, neighboring helices exhibit perfect antiferromagnetic order; i.e., left-handed and right-handed helices strictly alternate, leading to a favorable packing of the polymeric material. This antiferromagnetic behavior seems to be limited to monolayers of helices and is not observed in the bulk material.

Block copolymers are known to form of a rich variety of ordered mesophases of molecular dimensions (10−100 nm).[4,5] This is particularly true for ABC triblock copolymers, for which a wealth of different structures can be created depending on the mutual interactions and the volume fractions of the constitutents.[5−7] A few years ago, Stadler and co-workers reported on the observation of a helical superstructure in a bulk polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (SBM) triblock copolymer in a narrow window of volume fractions of the three components.[3,8] The morphology is composed of straight cylinders of the polystyrene (S) minority component arranged in a hexagonal lattice within a poly(methyl methacrylate) (M) matrix. The polybutadiene (B) middle block arranges into cylinders as well, which wind helically around the S cylinders (Figure 1c). Both left-handed and right-handed helices were observed by transmission electron microscopy (TEM). A detailed study of the helicity, however, was hardly possible in the bulk, as a single helix may appear both left-handed or right-handed depending on the exact location of the slice cut for TEM inspection. Neighboring helices, however, did not show any correlation of their helicities.

Here, we communicate preliminary results on the morphology of ultrathin films of a polystyrene-*block*-poly(2-vinylpyridine)-*block*-poly(*tert*-butyl methacrylate) (SVT) triblock copolymer ($M_w = 110$ kDa, $\varphi_S = 0.17$, $\varphi_V = 0.26$, $\varphi_T = 0.57$). The polymers were synthesized by anionic polymerization.[9] The films were deposited onto polished silicon wafers by dip-coating from chloroform solution. After drying, the films were exposed to tetrahydrofuran (THF) vapor to induce mobility and to allow microphase separation to occur. After 1 h at 94% saturation, the THF vapor pressure was linearly reduced to 30% saturation over a period of 4 days. Subsequently, the films were dried and investigated by field emission scanning electron microscopy (FE-SEM). Images were taken on a LEO 1530 scanning electron

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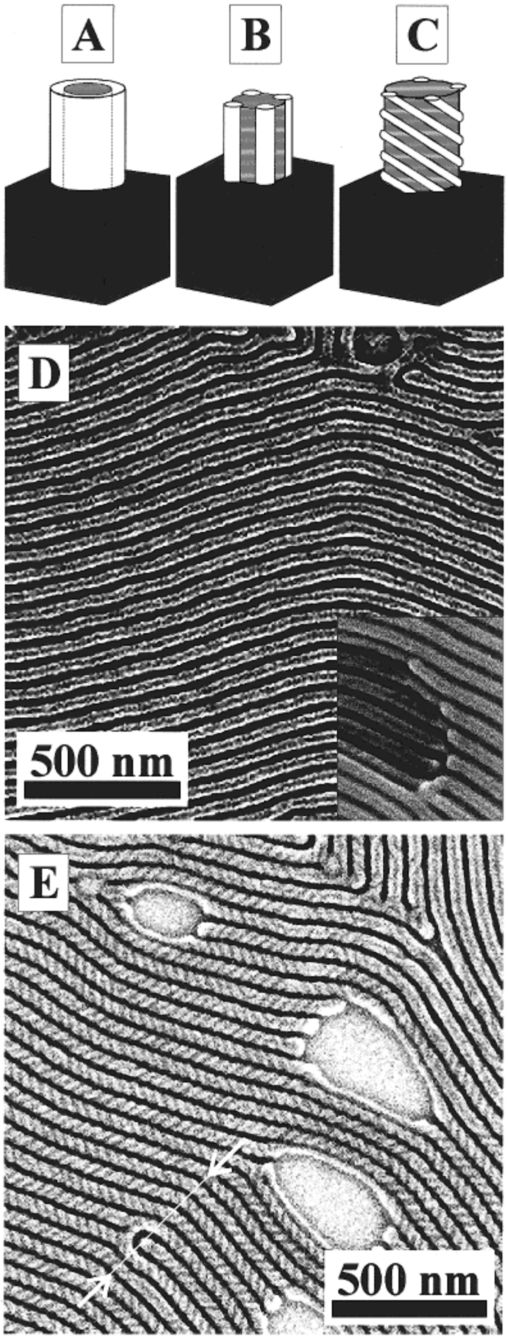

Figure 1. (A−C) Sketch of ABC triblock copolymer morphologies: core−shell cylinders (A), cylinder at cylinder (B), and helices wound around a cylindrical core (C). (D, E) SEM images of a 60 nm thick SVT film after staining with OsO_4. The bright structures are expected to be poly(2-vinylpyridine) blocks, and the gray ones should be polystyrene blocks, while the poly(*tert*-butyl methacrylate) blocks should appear darkest.[9,14,15] The white line indicates a change of the helicity along single cylinders induced by line defects. The inset to (D) shows a detail of a thicker region of the film displaying both the first and the second layer of cylinders. (The scale of the inset is equal to that of the whole figure.)

microscope with an in-lens detector (voltage: 0.8 kV; sample−detector distance: 2 mm). To enhance material contrast, the respective samples were stained in OsO_4 vapor for 3 min prior to the SEM experiments.

On exposure to THF vapor, the initially flat films develop areas of well-defined, "quantized" film thickness, indicative of the formation of ordered microphases aligned with respect to the substrate surface.[10,11] The thinnest regions of the films consist of a 5 ± 1 nm thick layer of copolymer chains physisorbed onto the polar SiO_x surface via the polar V-block.[12,13] More interestingly, thicker regions of the films do exhibit well-defined lateral order. Figure 1d shows an SEM secondary electron image of an area of thickness 60 ± 2 nm. Here, a nicely ordered stripe pattern is visible with a characteristic periodicity of $L_0 = 64 \pm 2$ nm. Given the volume fractions of the three blocks and the preferential staining of the V-middle block by OsO_4, the pattern reflects a monolayer of cylinders composed of a polystyrene core (gray) surrounded by a poly(2-vinylpyridine) shell (bright) embedded in a matrix of poly(*tert*-butyl methacrylate) (dark). The poly(2-vinylpyridine) shell may be either continuous (*core−shell morphology*, Figure 1a) or else broken into cylinders as well (*cylinder at cylinder morphology*, Figure 1b). The present experiments do not allow to distinguish between the two. A cylindrical morphology however is strongly corroborated by the fact that an identical surface morphology is observed in areas where the film thickness is increased by multiples of 55 ± 3 nm. For a hexagonal packing of cylinders, the layer spacing d should be related to the nearest-neighbor distance L_0 by $d = \sqrt{3}/2L_0 = 55 \pm 3$ nm, in perfect agreement with the experimental finding. Moreover, in some regions the second layer of core−shell cylinders exhibits holes, which give access to the relative lateral positions of the cylinders in the first and second layer, respectively (Figure 1d, lower right corner). Clearly, the inset shown in Figure 1d indicates a hexagonal packing of cylindrical objects. We note that the notion of core−shell cylinders is in partial agreement with earlier transmission electron images of bulk samples, in which both core−shell cylinders and distorted lamellae were observed.[9]

In some areas of thickness $d = 60 \pm 3$ nm (corresponding to a single layer of cylinders) the observed striped morphology turns into a quite spectacular, herringbone-like morphology, a characteristic SEM secondary electron image of which is displayed in Figure 1e. Given the assignment of gray values to the different components of the block copolymer, the SEM image indicates a helical morphology with the V-middle block winding about the S-core resembling the helical morphology observed in the SBM bulk experiments mentioned above.[3] In contrast to the TEM experiments performed in the bulk, however, a single layer of cylinders is formed which nicely aligns with respect to the substrate plane. Therefore, no cutting artifacts as in TEM experiments exist, and the helicity can unambiguously be determined. The average distance between neighboring S-cylinders is somewhat smaller than the value found for the core−shell cylinders discussed above and amounts to 56 ± 2 nm. Three remarkable observations are made: At first, the helical structure is only observed for a film thickness corresponding to a single layer of cylinders. Second, the helicity is found to strictly alternate between neighboring cylinders within the plane, leading to an almost perfect antiferromagnetic superstructure. Finally, the helicity does not change along a single cylinder except if the cylindrical lattice itself exhibits a defect. In the latter case (see lower right corner in Figure 1e), the helicity along a couple of neighboring cylinders changes in such a way that irrespective of the defect the antiferromagnetic superstructure is preserved (see arrows and white line in Figure 1e).

The fact that the S-cylinders appear to be somewhat closer packed in the case of the helical morphology and the antiferromagnetic superstructure of the helices points to packing arguments responsible for the observed effects. Indeed, two screws of same pitch but opposite helicity can be fit tightly together while this is not possible for screws of same helicity. Consequently, the observation of a strictly alternating helicity of neighboring cylinders yields a closer packing possibly releasing unfavorable chain stretching. Therefore, the average distance between neighboring cylinders is smaller in the helical superstructure as compared to the core−shell cylinders. From these considerations, one would expect the antiferromagnetic superstructure to be a favorable morphology in the bulk as well. It must be realized, however, that a strict alternation of helicity is possible only in a two-dimensional array, i.e., if individual helices have two nearest neighbors only. In the hexagonal arrangement of cylinders present in the bulk, strict alternation between nearest neighbors is impossible, and the antiferromagnetic superstructure is frustrated. Indeed, while multilayers of core−shell cylinders are found in thicker regions of the films, no indication of two or more layers of helices is observed in our experiments.

In summary, we have shown that a helical mesophase with well-defined chirality of neighboring helices can be stabilized in a monolayer of an ABC triblock copolymer, which in thicker films reveals a core−shell cylindrical structure. An almost perfect antiferromagnetic superstructure of helicity is observed which is expected to lead to a more favorable packing of microdomains. The antiferromagnetic ordering is possible in two dimensions only. It is expected to be frustrated in a bulk hexagonal mesophase, while it could exist, in principle, in a bulk phase of tetragonally packed cylinders surrounded by helices. The apparent coexistence between the helical morphology and core/shell cylinders in the monolayer regime indicates that the films may not have fully equilibrated. A detailed study of the conditions under which the different mesophases appear is under way and will be subject of a forthcoming publication.

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