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Communications to the Editor

Competition between Liquid Crystalline Phase Symmetry and Microphase Morphology in a Chiral Smectic Liquid Crystalline−Isotropic Block Copolymer

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Introduction. In recent years, many research groups have focused their interests on the synthesis and characterization of liquid crystalline (LC)−isotropic (I) AB block copolymers.[1−5] These block copolymers are of particular scientific interest, since they have the fascinating ability to show two different ordering phenomena: (i) the morphology, due to microphase separation of the linked blocks, and (ii) the liquid crystalline phase behavior due to the mesogenic units of the LC block. Compared to isotropic AB block copolymers, where the morphology is mainly determined by the Flory−Huggins interaction parameter χ, the degree of polymerization N, and the volume fraction of the blocks, in LC−I block copolymers the influence of the liquid crystalline phase on the structure formation cannot be neglected. On one hand, morphologies, leading to a highly distorted director field of the LC block, increase the free elastic energy of the system, and therefore their formation should be unfavorable. On the other hand, one can expect an influence of the morphologies on the liquid crystalline phase behavior because of packing restrictions and finite size effects.

This delicate competition between the liquid crystalline phase behavior and morphology is still under investigation by many scientists. Recently, Sänger et al. reported an order−order transition in the morphology of a block copolymer accompanied by the loss of the anisotropic phase structure above the clearing temperature of the LC block.[6]

In this communication we show the influence that the morphology and the liquid crystalline phase structure of a novel chiral LC−I block copolymer has on each other. By means of transmission electron microscopy (TEM), it is possible to observe both the morphology and the orientation of the mesogens in the same image.

Experimental Section. The investigated AB block copolymer consists of poly(hexyl methacrylate) (the isotropic block) and a chiral liquid crystalline azobenzene moiety (the liquid crystalline block) (see Figure 1). A detailed description of the synthesis of this block copolymer by direct anionic polymerization will be presented in a separate publication.[7] The molecular weight M_n and the polydispersity M_w/M_n were estimated from a SEC profile based on standard polystyrene calibration. The liquid crystalline phase behavior was determined by differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS), and polarizing optical microscopy (POM). For the TEM investigations the samples were annealed at elevated temperatures for 5 days and microtomed below the glass transition temperature of the sample. Exposure of the sample to RuO_4 for 10 min leads to a selective staining of the LC block.

Results and Discussion. In this paper, the self-assembling behavior of a block copolymer with molecular weight of $M_n = 32\,800$ g/mol and a narrow molecular weight distribution of $M_w/M_n = 1.08$ will be described. The block length of the liquid crystalline part of the sample is $M_n = 12\,800$, estimated by ^{1}H NMR spectroscopy, which led to a block copolymer with a liquid crystalline mass fraction of $w = 39\%$. The liquid crystalline block exhibits a T_G at 78 °C and a smectic A* to isotropic phase transformation at $T_{S,I} = 95$ °C, while the isotropic block shows a T_G at −13 °C.

To investigate the interplay between the morphology and the liquid crystalline phase behavior, one sample was annealed for 5 days in the smectic phase at 85 °C

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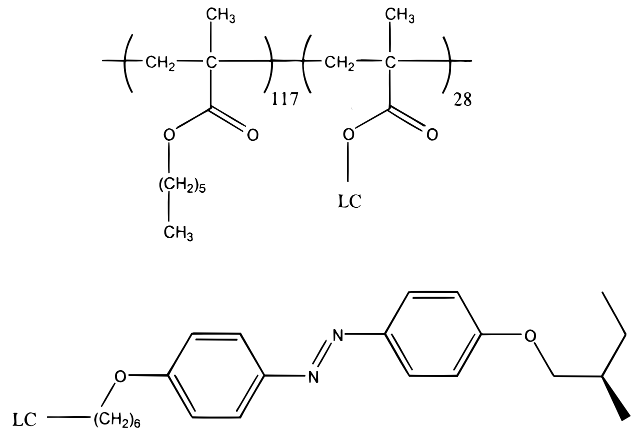

Figure 1. Chemical structure of the investigated LC−I block copolymer.

and allowed to cool slowly to room temperature. The other sample was annealed in the isotropic phase at 105 °C and quenched in liquid nitrogen to prevent the formation of a smectic structure.

The morphologies of this block copolymer in the liquid crystalline and the isotropic phase are presented in Figure 2, a and b, respectively.

Figure 2a shows a lamellar morphology in the smectic phase of the liquid crystalline block with an average periodic structure of 16 nm. In between these lamellae one can observe a second periodicity of about 4 nm arising from the smectic layers of the liquid crystalline block, which is consistent with the results of wide-angle X-ray scattering experiments in which the periodicity of 4.9 nm corresponds to a smectic bilayer structure. More interestingly, one can see the relative orientation of the smectic layers to the lamellae, and it can be clearly observed that parallel, as well as perpendicular, orientations are present. Furthermore, it seems that the lamellae are thinner in regions of parallel rather than perpendicular orientation in the smectic layers. Recently, the direct imaging by means of TEM of such a structure-in-structure morphology was also reported by Ikkala et al.[8] However, they reported only a orientation of the smectic layers perpendicular to the layer morphology.

A completely different behavior of the morphology can be observed in the isotropic state of the liquid crystalline block, in which the microphase-separated structure seems to be a bicontinuous cubic phase, as shown in Figure 2b. Indeed, fast Fourier transformation (FFT) of this image (see the inset in Figure 2b) reveals reflexes corresponding to a ratio of 1:1.16, in accordance with the theoretical ratio of $\sqrt{3}$:$\sqrt{4}$ (or 1:1.155) for a gyroid structure. Although this $\sqrt{3}$:$\sqrt{4}$ ratio would be consistent with hexagonally packed cylinders and bcc spheres, there is no evidence for such morphologies, since in both cases a reflex with a ratio of 1 should be observed. Also, an ordered bicontinuous double-diamond morphology, for which a reflex in the ratio of $\sqrt{2}$ is expected, can be excluded. However, we have to point out that these preliminary results have to be confirmed by small-angle X-ray scattering experiments.

Nevertheless, these investigations clarify the delicate competition between the morphology and the liquid crystalline phase structure as shown in the schematic illustration in Figure 3.

In the liquid crystalline phase, the morphology will tend to be consistent with the symmetry of the smectic layers. Therefore, in lamellar morphologies both the parallel and the perpendicular orientations of the smectic layers to the interface do not disturb the anisotropic phase structure. Since it is well-known that in block copolymers the polymer chain is stretched perpendicular to the interface and the orientation of the smectic layers is normally parallel to the stretching direction of the polymer backbone, then one expects a perpendicular orientation of the smectic layers to the lamellae, which was indeed demonstrated by several authors by means of X-ray investigations.[9−12] This orientation, however, limits the size of the smectic layers in one direction with the dimension of the periodicity of the lamellar morphology.

On the other hand, very recently, Hammond et al. reported the parallel orientation of the smectic layers to the lamellar morphology, which was explained by a

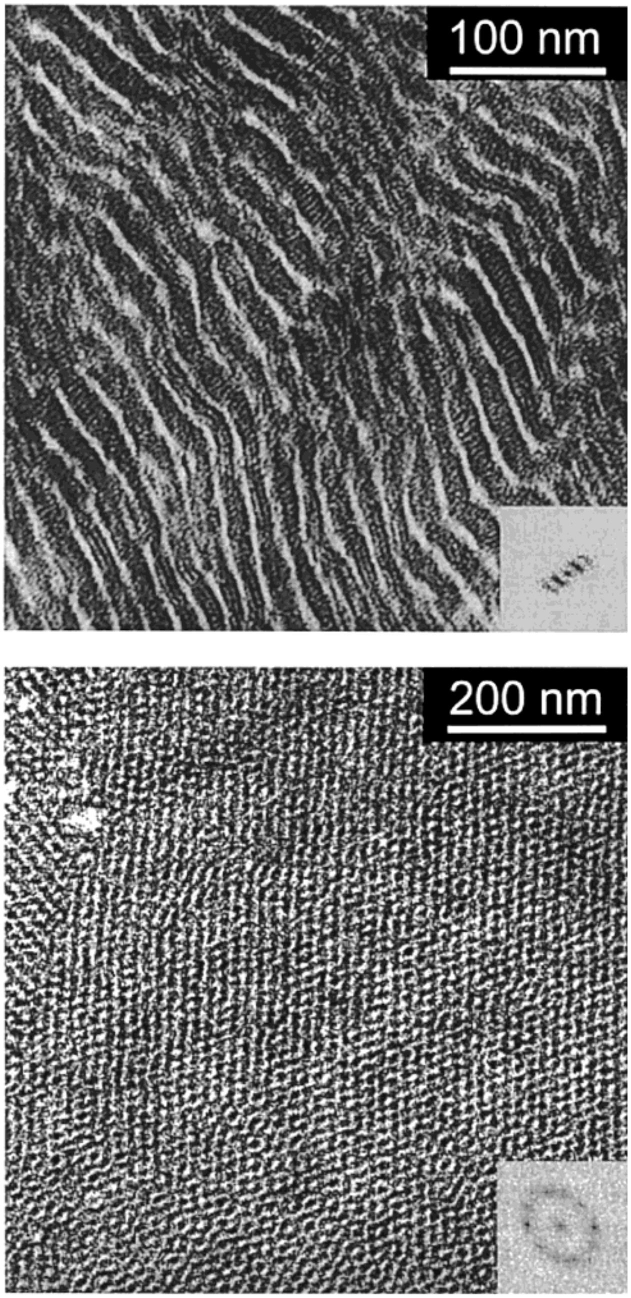

Figure 2. TEM images of the block copolymer morphology annealed at (a, top) 85 °C and (b, bottom) 105 °C. The FFT of the images are inserted into both micrographs.

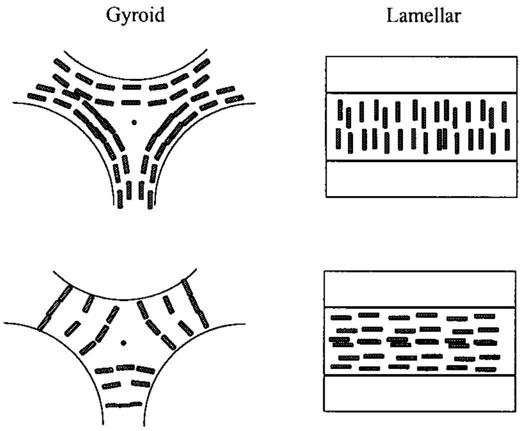

Figure 3. Schemes explaining the symmetry arguments between the morphology and a liquid crystalline phase; gyroid morphology (left) leading to a strong deformation of the mesogens orientation (left) for both the planar and the homeotropic orientation; on the contrary, lamellar morphology (right) is consistent with the smectic phase symmetry (lines represent the shape of the interface between the LC and the I block; mesogens are represented by rods).

decoupling between the main-chain and the mesogenic side groups.[13,14] Since the dimensions of the smectic layers are not longer restricted by the morphology, this situation is energetically more favorable. However, with this orientation the morphology has to accommodate a whole number of smectic layers, which limits the lamellar morphology to a distinct periodicity.

This is clearly seen in Figure 2a, where this orientation of three layers forces a periodicity in the morphology of about 12 nm, in contrast to the average periodicity of 16 nm.

Moreover, this arrangement of only three layers parallel to the lamellar morphology is not correlated to specific defects and can be observed all over the sample.

It is important to note that, because of the two-dimensional visualization of the morphology, only the parallel orientation of the smectic layers can be observed in all positions, whereas the perpendicular orientation appears only in certain cases. In regions where no smectic layers are seen, a perpendicular orientation can then be assumed. Therefore, the perpendicular orientation is the main one (roughly 90%), which corroborates the macroscopic observation in a paper by Walther et al.[3] In any case, our image clearly shows the possibility of obtaining a parallel orientation of the smectic layers in some limited areas of the morphology.

Unlike the lamellar morphology, a gyroid morphology would lead to defects and a strong deformation of the smectic layers, as shown in Figure 3. As soon as the smectic phase disappears, steric arguments concerning the volume fraction of the blocks remain the only relevant parameter, and an order−order transition to a gyroid morphology is observed.

Although a similar change from a lamellar to a gyroid morphology has been observed in a polystyrene (37 wt %)-*b*-polyisoprene diblock copolymer simply by increasing the temperature,[15] a stabilizing effect of the smectic phase on the lamellar morphology can be assumed. A similar behavior was observed by order−disorder transitions of the block copolymer morphology accompanied by the loss of the liquid crystalline phase structure.[5,12]

In conclusion, these LC−I block copolymers exhibit a fascinating competition between the formation of an anisotropic phase structure in the liquid crystalline block and microphase separation. We have shown by means of TEM that the smectic layers of the LC block are orientated either parallel or perpendicular to the lamellar morphology. In addition, the dimensions of the lamellae are directly influenced by the mesogenic orientation. Furthermore, the loss of the anisotropic phase structure leads to the formation of a gyroid morphology.

Further experiments are in progress to investigate this interplay in more detail.

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