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Preliminary communication
Lyotropic mesomorphism of AB block copolymers in a nematic solvent

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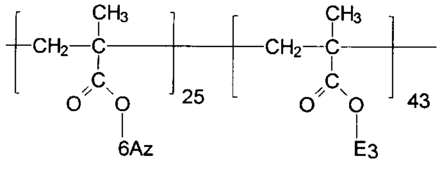
A lyotropic hexagonal mesophase is identified in a mixture of a low molecular mass nematic solvent and an AB block copolymer with a liquid crystalline block A and an isotropic block B by polarizing microscopy. A highly ordered striated texture evolves spontaneously that exhibits an additional striated fine structure within the stripe domains.

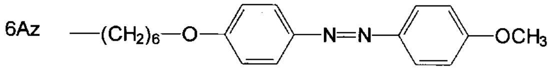
AB block copolymers in selective solvents in many ways resemble low molecular mass surfactants in aqueous solutions. Above a critical concentration, the insoluble blocks associate to form micelles with a core consisting of the insoluble blocks and a corona of solvated soluble chains. The micellar structure is controlled by the specific molecular design of the copolymer as well as by thermodynamic parameters. At higher copolymer concentrations (>20%) the closely packed micelles can form lyotropic liquid crystalline (LC) phases. Cubic, hexagonal and lamellar mesophases have been reported [1–5] that additionally exhibit a distinct thermotropic behaviour, i.e. temperature-induced phase transformations at a constant copolymer concentration.

Recently we reported that a low molecular mass nematic phase is a selective solvent for an AB block copolymer with a thermotropic LC block A and an isotropic block B (LC/I block copolymer) [6]. The differential solubility is driven mainly by forces of entropic origin. The anisotropic state of order of the nematic solvent imposes severe restrictions on the conformation of a macromolecule and strongly affects the entropy of mixing. In the nematic state, a macromolecule has to depart from the statistical chain conformation and that costs conformational entropy. Normally this is avoided by phase separation, where the nearly pure nematic solvent coexists with the isotropic polymer. On the other hand, miscibility is achieved if mesogenic groups are attached to the polymer main chain. For the combination of a soluble LC block and an insoluble isotropic block into an LC/I block copolymer the differential solubility of the nematic solvent leads to structure formation by microphase separation that has been investigated in dilute nematic solution [6,7]. In this paper we demonstrate that a lyotropic hexagonal mesophase is formed in the high concentration regime of an LC/I block copolymer in a nematic solvent.

The LC/I block copolymer used in this investigation is poly(4-(6-(4′-methoxyphenylazo)-phenoxy)hexyl methacrylate)-*block*-poly(3,6,9-trioxydecanyl methacrylate) (**P6Az-b-PE3**) having the structure:



P6Az-b-PE3



E3 —$(CH_2CH_2O)_3OCH_3$

The LC block exhibits a smectic A to nematic phase transformation at 88°C and the nematic to isotropic phase transformation temperature T_{NI} is 117°C. The glass transition temperature T_g of the LC block is 80°C, whereas the isotropic block exhibits a T_g of −49°C. To ensure selective solubility, the corresponding homopolymers **P6Az** ($M_n = 13{\cdot}400\,\mathrm{g\,mol^{-1}}$; $M_w/M_n = 1{\cdot}23$) and **PE3** ($M_n = 10{\cdot}300\,\mathrm{g\,mol^{-1}}$; $M_w/M_n = 1{\cdot}12$) were

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Figure 1. Contact preparation of the nematic solvent N5 (left side) and the copolymer **P6Az-b-PE3** (right side) at room temperature. The crossed polarizers are parallel to the edges of the photograph, magnification 175X.

investigated with respect to their miscibility behaviour in the nematic solvent. The polymer synthesis and detailed characterization will be presented elsewhere [7]. The low molecular mass nematic solvent N5 was obtained from E. Merck (Darmstadt) and is a commercial mixture of azoxybenzene derivatives. The phase behaviour of N5 is Cr< −5°CN73°CI.

To determine miscibility and mesomorphic phase behaviour, samples were prepared between glass slides (thickness 20 μm) and investigated by polarizing microscopy using a Leitz Ortholux II Pol BK polarizing microscope equipped with a hot stage Mettler FP 80/82. The miscibility behaviour of the nematic solvent and the isotropic and LC homopolymer was studied by contact preparation. For the LC/I block copolymer and the nematic solvent, the phase sequence and the upper temperature limits of the mesomorphic phases were determined by contact preparation, where all mesomorphic phases appear in the concentration gradient between the pure copolymer and the pure nematic solvent. Additionally, homogenous mixtures with fixed weight fractions were prepared by dissolving the copolymer in the nematic solvent and stirring the mixture above T_{NI}. Small angle X-ray diffraction experiments were performed using Cu-K$_\alpha$ radiation ($\lambda = 1{,}542$ Å) and a 0·8 mm pinhole collimator. The scattered intensity was detected with an image-plate system.

Investigating the miscibility behaviour of the LC homopolymer **P6Az** and the nematic solvent N5 revealed complete miscibility in the isotropic and nematic state. The isotropic homopolymer **PE3** showed complete miscibility with N5 in the isotropic state, whereas in the nematic state demixing took place below T_{NI}. Accordingly, the nematic solvent N5 is a selective solvent for the LC block that matches the conditions for microphase separation of the LC/I block copolymers.

The phase behaviour of the LC/I block copolymer and the nematic solvent was investigated by contact preparation. In the isotropic phase, complete miscibility was observed over the whole concentration range. Below the isotropic to nematic phase transformation, a homogeneous nematic phase was observed down to temperatures of 65°C. On cooling the sample below 65°C, a birefringent fan-shaped texture emerged from the pure copolymer (figure 1). The phase boundaries between the nematic state and the pure copolymer were clearly

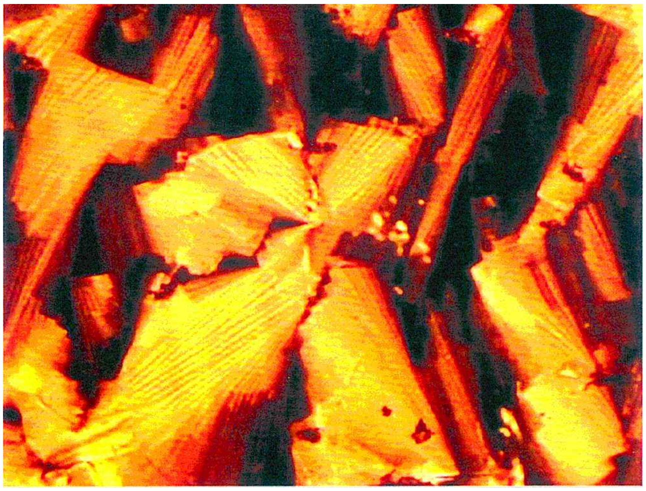

Figure 2. Fan shaped texture of a mixture of 20 wt % copolymer in the nematic solvent at room temperature. The crossed polarizers are parallel to the edges of the photograph, magnification 70X.

Figure 3. Striated texture of a mixture of 20 wt % copolymer in the nematic solvent at room temperature after annealing (see text). The crossed polarizers are parallel to the edges of the photograph, magnification 70X.

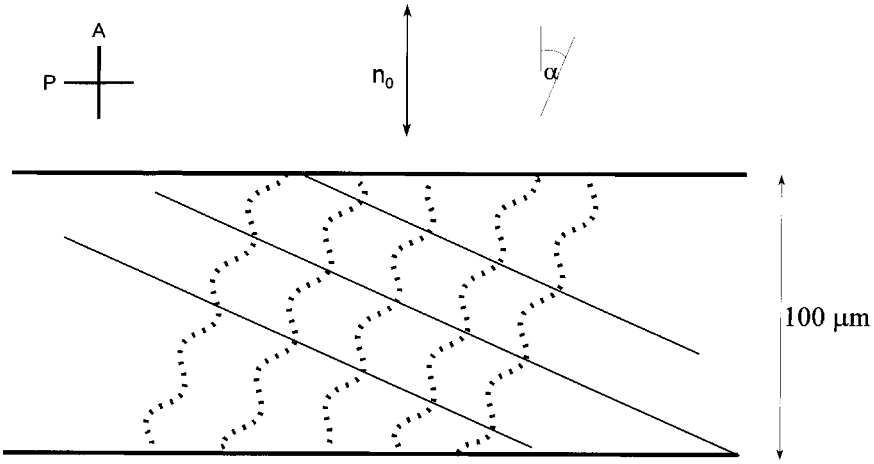

Figure 4. Schematic representation of the director field of the striated texture (figure 3).

detected using parallel polarizers. Cooling the sample to room temperature caused an increasing concentration width where the fans exist. Further investigations of the fan-shaped texture were performed on a sample containing 20 wt % of the block copolymer. Below 63°C, the thermo-reversible formation of a fan-shaped texture was observed with a fine structure in the fans, as shown in figure 2. A smectic phase can be excluded based upon the X-ray diffractograms where in the small angle region no reflections of a smectic layered structure were detected. The mixture exhibited the same diffraction pattern as the pure nematic solvent. The expected reflections from a micellar superstructure with typical dimensions beyond 30 nm cannot be resolved in our X-ray apparatus.

On annealing the sample at room temperature, a highly ordered striated texture was slowly formed where two different length scales can be distinguished (figure 3). The UV/VIS dichroism of the mesogenic chromophores allows one to determine the mean direction of the optical axis in the sample n_0. The director field is analysed by rotating the sample between crossed polarizers as schematically depicted in figure 4. Perpendicularly to n_0, large stripe domains are observed with a typical width of 80–100 μm. The sharp black lines between the domains are disclination walls. Within these domains the director is tilted at an angle $\pm\alpha$ of 12° with respect to n_0. Due to an undulation of the director, an additional striation is found within the domains at an angle of 7°, exhibiting a periodicity of 10 μm. In general, fan-shaped and striated textures are commonly found in lyotropic hexagonal phases, where striations result from a thermo-mechanical undulation of the columns in oriented samples [8–12].

From these observations we conclude that the LC/I block copolymer associates in the nematic solvent forming micelles in dilute nematic solution. At copolymer concentrations above ≅20 wt %, the micelles are sufficiently closely packed to form a lyotropic hexagonal phase. The hexagonal phase is built up by cylindrical block copolymer micelles. In contrast to lyotropic hexagonal phases in aqueous solution, we observe a spontaneous ordering of the sample on a macroscopic length scale without surface alignment or mechanical shear. Furthermore, the striated texture exhibits two distinct length scales with a periodicity that clearly exceeds the dimensions of conventional hexagonal phases in aqueous solution. The fine structure and the spontaneous ordering is assumed to arise from the anisotropic molecular field of the nematic phase and the minimization of the Frank elastic energy. Further investigation of the texture is in progress and the detailed phase diagram will be presented in a following paper.

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