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Preparation of a Liquid Single-Crystal Triblock Copolymer by Shear

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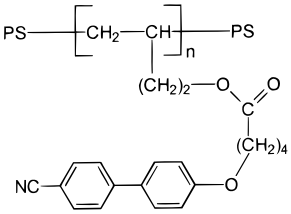
ABA triblock copolymers having well-defined block lengths belong to the class of materials that form microdomains on a scale of 10 nm. The microdomains are ordered in randomly oriented grains of a typical size of about 1000 nm. By shearing techniques[1] or extrusion[2] the microdomains can be oriented to a high degree. The generated macroscopic lattice has the properties of a single crystal. Perhaps the best known example are uniaxial crystals formed by extrusion of polystyrene/polydiene/polystyrene triblock copolymers with cylindrical microdomain morphology.[2] In these experiments the cylinders were nearly perfectly oriented along the direction of extrusion and extended practically over the total length of the extruded plug. Techniques of generation of oriented styrene−diene triblock copolymers and the impact of orientation on mechanical properties have been reviewed recently.[3] Active research is currently being devoted to clarify the mechanism of orientation of lamellar diblock copolymers under large amplitude oscillatory shear.[4]



I

Recently we synthesized an ABA triblock copolymer with polystyrene A-blocks and a liquid-crystalline side-chain center block. The structure of the block copolymer is shown in structure **I**. The block copolymer was synthesized by hydroboration of the poly(1,2-butadiene) center block of a corresponding precursor triblock copolymer prepared by anionic polymerization and subsequent introduction of the mesogens by esterification of the hydroxyl groups.[5] The synthesis of the mesogen and details of the specific preparation and characterization of the triblock copolymers **I** are published elsewhere.[6] The LC phase behavior of the block copolymers is dependent on the number x of methylene groups of the spacer. In this work a nematic system with $x = 4$ is investigated. The LC phase behavior is characterized by the sequence g/34/n/122/i.[6] The styrene content is 12 wt % and the total molecular weight is 84 000. The triblock copolymer belongs to a novel class of thermoplastic liquid-crystalline elastomers (TPLCE's). It exhibits reversible elasticity between 50 and 80 °C and is thermostable up to 180 °C.[6] In the isotropic phase the block copolymer has a morphology of PS spheres of bcc symmetry. It was shown that the spherical morphology is transformed to a hexagonally packed cylindrical (hpc) morphology by cooling from the isotropic to the nematic phase.[7]

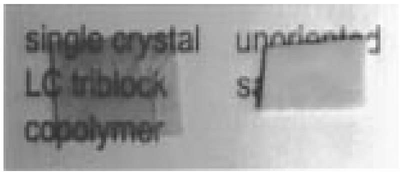


Figure 1. Photograph of a sheared liquid single crystal triblock copolymer and an unsheared sample with a polydomain morphology.

It was of interest to see whether the block copolymer can be oriented in the nematic phase by suitable mechanical fields and which orientations can be achieved for the nematic director and the polystyrene cylinders. The first attempt to achieve orientation by uniaxial strain below T_g of polystyrene was not successful. Though a block copolymer film could be reversibly stretched to 200% at 70 °C the extension did not produce significant orientation. The film remained cloudy in the strained state. Successful experiments were carried out by subjecting a block copolymer film to reciprocating shear between two parallel plates. The technique was introduced by Skoulios and Hadziioannou[1] to orient block copolymers of cylindrical and lamellar morphology. Our experiments were carried out on 0.5 mm thick films which were melt pressed at 160 °C. The shearing was carried out at 120 °C in the nematic phase. The sample was sheared for 3 min at a frequency of 0.1 Hz with a shear amplitude of 4.5 mm.

In Figure 1 the transparency of the film before and after shearing is compared. Without shear the film is turbid due to the polydomain structure of the directors in the liquid-crystalline phase and due to the grain structure of the microdomain morphology. After shearing, the film becomes transparent, indicating a high degree of orientation of the nematic director and the cylindrical microdomains. The nature and degree of orientation was investigated by X-ray scattering with a Kiessig camera and a 2D detector. In Figure 2 the intensity pattern in the wide angular range is displayed from which information on the orientation of the mesogens is obtained. In Figure 2a the X-ray beam is directed along the direction of shear flow. At the largest angles corresponding to a distance of 4.4 Å we see the reflection of the lateral spacing of the mesogens. From the pattern we conclude that the mesogens are oriented either normal to the shear plane or tilted in the direction of shear. According to the pattern of Figure 2b where the X-ray beam is directed in the neutral direction the mesogens appear to be tilted in the direction of shear. Because of the manual alignment of the sample in the sample holder the tilt angle could not be determined precisely. In Figure 2c the X-ray beam is incident normal to the shear plane. The nearly isotropic intensity pattern indicates that the mesogens are essentially aligned along the normal of the plane. From the azimuthal intensity distribution in Figure 2a,b an order parameter $\langle P_2(\cos\,\theta)\rangle = 0.66$ is calculated by the procedure of Mitchell and Windle.[8] A similar value was found in uniaxial liquid single crystal elastomers[9] in which the strain induced order was fixed by chemical cross-links. The weak equatorial reflections at 28.5 and 14.3 Å indicate the presence of oriented smectic clusters which are not detected in the unsheared sample. The first order reflection corresponds to 1.4 times the length of the mesogen, which is 20.5 Å including the spacer

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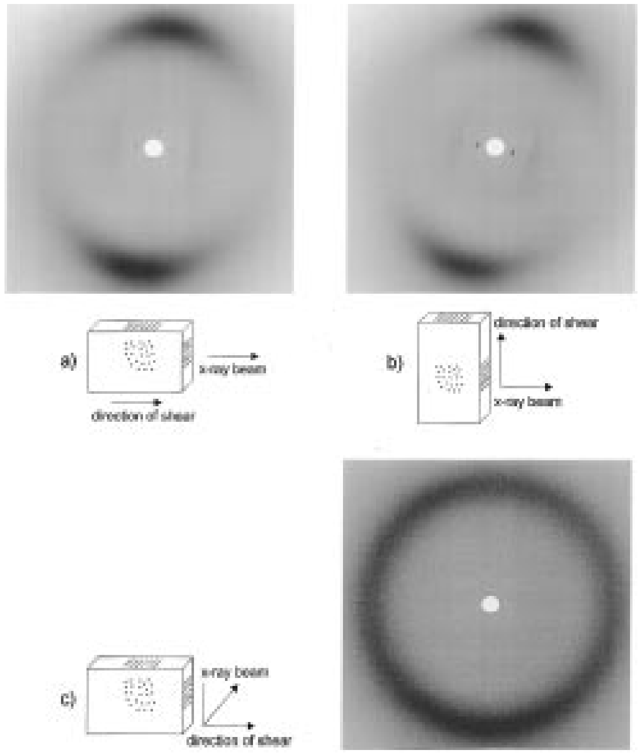

Figure 2. Wide-angle x-ray pattern of the sheared triblock copolymer showing the orientation of the mesogens. X-ray beam (a) directed along the direction of shear, (b) directed along the neutral direction, (c) directed normal to the shear plane.

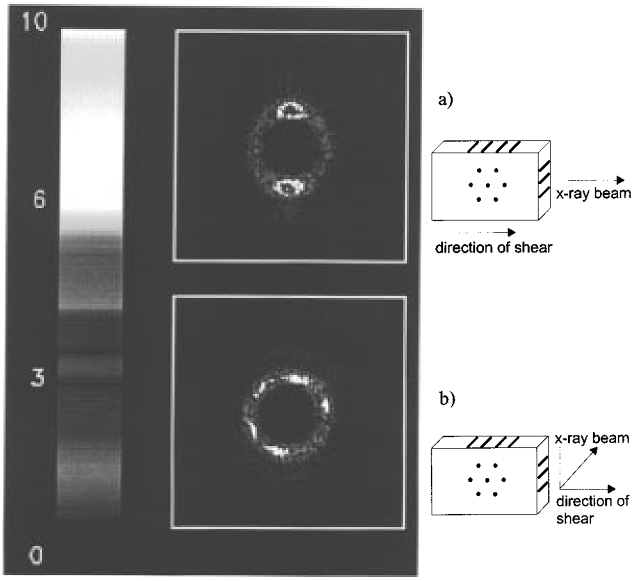

Figure 3. Low-angle x-ray pattern of the sheared triblock copolymer showing the orientation of the cylindrical microdomains. X-ray beam (a) directed along the direction of shear (upper part) and (b) directed normal to the shear plane (lower part). One of the reflections is obscured by the holder of the beam stop.

length. This indicates the existence of clusters of bilayers in which the side chains are partly interleaved. It is known that in low molecular weight liquid crystals with a cyanobiphenyl moiety the mesogens aggregate to pairs with antiparallel orientation of the dipole moments. The length of the aggregates is also 1.4 times the length of a single mesogen.[10]

The orientation of the polystyrene cylinders is derived from the low-angle region of the X-ray scattering. In Figure 3a the X-ray pattern is displayed for the same geometry as in Figure 2a. One concludes that the cylinders are oriented in the same direction as the mesogens, i.e., essentially vertical to the shear planes. This is in contrast to shear induced orientation in isotropic block copolymers with cylindrical morphology where the cylinders are oriented in the direction of shear.[1] From the first order reflection one obtains 26 nm for the distance between the cylinders in accordance with the value obtained by SAXS measurements on unoriented samples.[7] The evaluation of the order parameter of the cylinders from the azimuthal intensity distribution yields $\langle P_2(\cos\theta)\rangle = 0.5$, somewhat less than the orientation of the mesogens. In Figure 3b the geometry is the same as in Figure 2c with the X-ray beam being directed normal to the shear plane, i.e., in the direction of the cylinder axes. Consequently we see the reflections of oriented hexagonally packed cylinders. The reflections are superimposed on an isotropic ring of much lower intensity showing that the orientation is not perfect.

In summary we have shown that a film of a nematic triblock copolymer with cylindrical microdomains of the isotropic component can be oriented to a high degree by simple shear. The oriented film has the properties of an optically uniaxial single crystal. The optical axis is given by the uniform direction of the nematic director and the cylinder axes. Both coincide and are directed essentially along the normal of the shear plane according to X-ray measurements. Conoscopical measurements with a polarizing microscope show that the nematic director is tilted by 15° on average with respect to the normal of the shear plane. The director exhibits a smooth ondulation about the average tilt angle by about ±10° on a scale of about 1 mm along the direction of shear. Apparently this behaviour is related to the history of the shearing procedure.

As the orientation mechanism is concerned we can only say the following at present: Since the cylinders are oriented in the same direction as the director and since this orientation is vertical to the orientation obtained by shearing isotropic blockcopolymers the mechanical stress must primarily interact with the director field. The cylinders are following the director orientation such that they cause the least distortion of the director field. This is the case for a parallel alignment of the cylinders for which the mesogens have a planar orientation with respect to the cylinder surface. This alignment at the interior interfaces is consistent with the known preferential orientation of the main chains perpendicular to the cylinder surface and with the tendency of the mesogens to orient perpendicular to the main chains for the present polymer. The latter can be inferred from stretching experiments.[6] The reason why the director is oriented preferentially normal to the shear plane is probably caused by the strong homeotropic anchoring of the mesogens at the exterior surfaces which appears to be a property of mesogens with cyano end-groups.[10]

References and Notes

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