

Transverse Cylindrical Microdomain Orientation in an LC Diblock Copolymer under Oscillatory Shear

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The development of oriented microdomain morphologies by shearing lamellar and cylindrical microdomain block copolymers has been studied by many researchers, and observed orientations were found to depend on such variables as temperature (in particular proximity to ODT), strain amplitude, strain rate, mechanical contrast, chain architecture, and molecular weight.^{1–10} Good reviews of work in this area are available.^{11,12} For lamellae and for cylinders, three distinct orientations are possible, viz. parallel, perpendicular, and transverse, discriminated by the orientation of the cylinder long axes and lamellar repeat vector with respect to the flow and flow gradient directions in each case. Processing conditions of lamellar systems have been found that lead to all three types of orientation as well as mixed orientations.¹¹

In cylindrical microdomain forming coil–coil block copolymers subjected to steady and oscillatory shear, parallel orientation, in which the cylinder long axes are aligned along the flow direction, is the overwhelming orientation observed to date,^{3,5,9} with the sole exception of Gronski et al., who found cylinders in the perpendicular orientation for an LC diblock copolymer due to strong homeotropic anchoring of the cyano end groups of the LC mesogens to the glass surfaces of the oscillatory shear cell.¹⁰ Here, we report on the selection of the transverse cylinder orientation, with cylinder long axes aligned along the vorticity direction, by a liquid crystalline (LC) diblock copolymer subjected to large amplitude oscillatory shear within the LC regime, and a subsequent rapid transition to the parallel cylinder orientation upon the thermal clearing of the LC phase.

The material investigated is an 80 000 g/mol styrene, mesogen-functionalized isoprene diblock copolymer, denoted P(S-*b*-ILC) 27/53, containing a polystyrene block of 27 000 g/mol and a polyisoprene–LC block of 53 000 g/mol. The volume fraction of PS is 0.34, leading to the formation of hexagonally packed cylinders in the bulk. The isoprene block was modified using polymer analogous chemistry as detailed elsewhere¹³ to produce an azobenzene side-group liquid crystal diblock copolymer, depicted schematically in Figure 1. We also studied the PI–LC homopolymer (MW = 78 000). Both materials formed smectic A LC mesophases with a layer spacing of 31 Å and intermesogen distance of 4–5 Å. The PI–

LC and P(S-*b*-ILC) 27/53 materials undergo a smectic to isotropic transition at 171 and 165 °C, respectively.

Samples are prepared by slow evaporation from a 5 wt % toluene solution of the polymer over a period of 3–4 days, followed by drying under vacuum for 12 h at ambient temperature. The polymer is then placed between the quartz plates of a Linkham CSS 450 shear cell to form a sample about 3 mm in diameter and 1 mm thick. The block copolymer was sheared for 2 h at 150 or 180 °C with a strain amplitude of 100% and an oscillation frequency of 0.50 Hz. The PI–LC homopolymer was sheared at 150 °C under the same conditions. After cooling, the polymers were carefully removed and mounted so that X-ray diffraction could be performed, at room temperature, along two orthogonal axes. For in-situ experiments, the shear cell was modified to permit collection of forward scattered synchrotron X-ray radiation, and mounted on beamline X27C at Brookhaven National Laboratory. The same procedures described above for the ex situ measurements were employed, and data were taken at suitable intervals for up to 3 h of shearing in the LC state.

As expected, the ex situ experiments showed that the smectic layers of the LC homopolymer assumed the parallel orientation common to layered structures such as block copolymer lamellae and that the PS cylinders were aligned parallel to the flow direction when the block copolymer was sheared above its clearing temperature (see Figure 2a). Interestingly, when the block copolymer was sheared in the LC state, the initially randomly arranged set of grains developed a preference for grain orientations with cylinders oriented *transverse* to the shear flow and with the smectic layers in the *perpendicular* orientation (see Figure 2b). The quality of the orientation of the respective LC and microphase-separated structures is comparable.

The data of the ex situ experiment were well verified by the in situ investigation in which the initially random uniform distribution of scattered intensity due to the (10 $\bar{1}$ 0) planes of the cylinders gradually narrowed around the azimuth corresponding to the development of the transverse orientation over a period of 2–3 h, and the smectic (001) scattering gradually narrowed around the azimuth corresponding to the development of the perpendicular orientation, while under shear at 150 °C (see Figure 3a–c). Heating to 175 °C cleared the LC scattering and brought about a reorientation of the cylinders into the parallel orientation (see Figure 3d), as had been observed previously in the ex situ experiments. Cooling the sample back into the smectic A regime with continued shearing did not result in the reemergence of the transverse orientation on the time scale of the experiment.

We have shown in prior work on bulk samples that the mesogens in our PI–LC block exhibit homogeneous anchoring at the IMDS for the lamellar, cylinder and inverse cylinder microdomain structures.^{13,14} This arrangement thus places the layer normal of the LC mesophase parallel to the long axes of the PS cylindrical microdomains. We can qualitatively evaluate various candidate structural models for this block copolymer (see Figure 4). In model 4a, the cylinders are in their preferred parallel orientation but the smectic layers are constrained by the boundary condition to be in the

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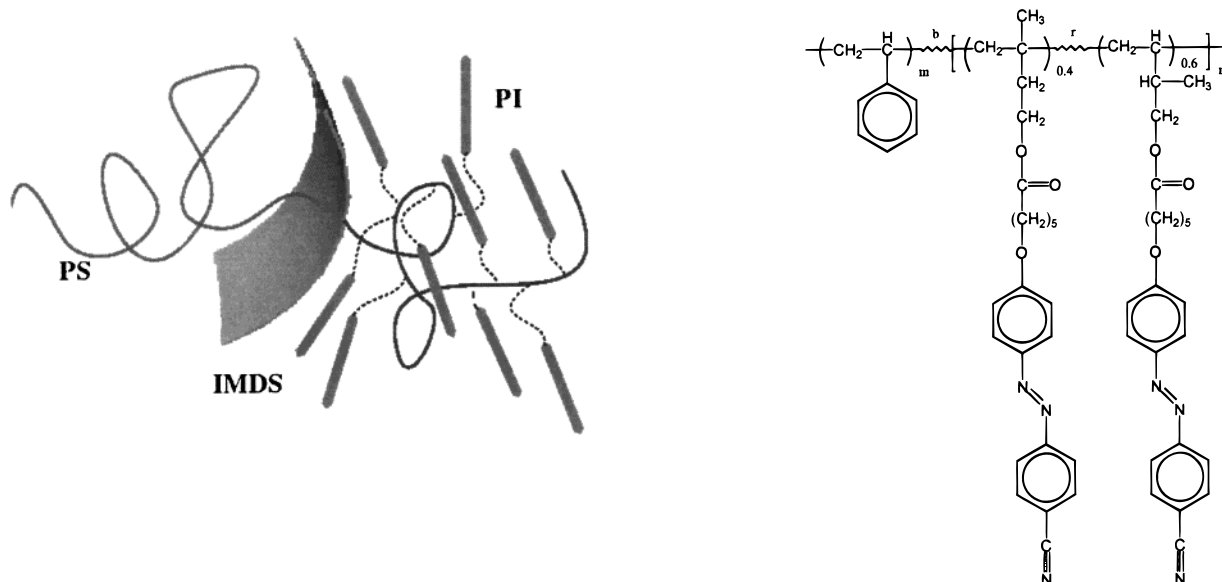


Figure 1. Schematic and chemical structure of the coil block–side-group LC block copolymer. The polystyrene (PS) coil block is separated from the LC functionalized polyisoprene block by the intermaterial dividing surface (IMDS).

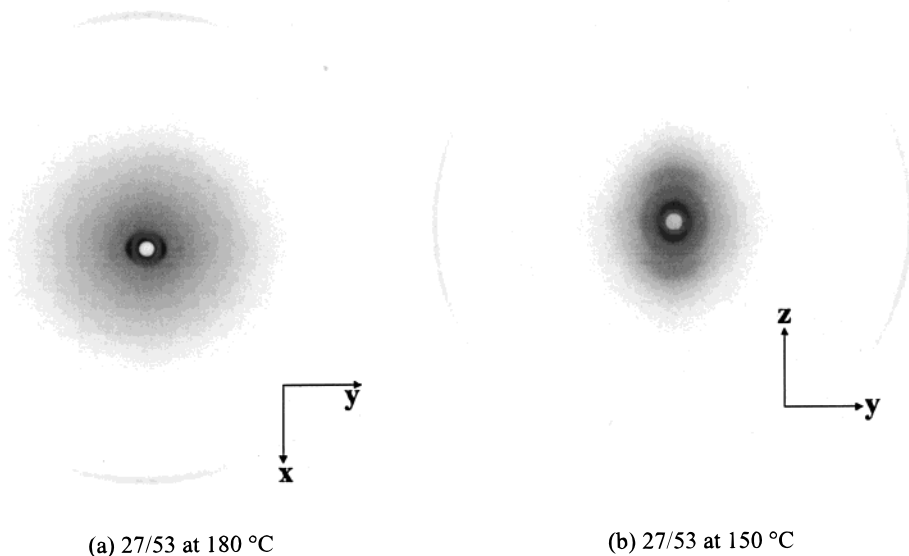


Figure 2. Ex situ scattering results. (a) P(S-*b*-ILC) 27/53 sheared at 180 °C – X-ray beam directed along z , parallel to the velocity gradient. Flow is along x . Scattering from the $d_{10\bar{1}0}$ and d_{1120} reflections of the hexagonal lattice of the PS cylinders is enhanced along the y direction, indicating the cylinder axes have aligned with the flow direction (parallel alignment). The d_{001} smectic layer reflection appears only after cooling and implies a preferred homogeneous anchoring of the mesogens with the respect to the IMDS. (b) P(S-*b*-ILC) 27/53 sheared at 150 °C, with X-rays incident parallel to the flow direction. Scattering from the $d_{10\bar{1}0}$ reflection of the PS cylinders is now enhanced along the z direction indicating that the cylinder axes are aligning along the vorticity direction of the flow (transverse alignment). Simultaneously, the d_{001} reflection of the smectic layers concentrates along the y direction indicating that the LC layers take on a perpendicular alignment. This arrangement also allows the preferred homogeneous anchoring of the mesogens with respect to the IMDS during flow alignment in the LC regime (see structural model 4d).

transverse orientation which is unfavorable as it would lead to layer dilation and compression. In model 4b, the smectic layers are now in their preferred parallel orientation, but the cylindrical microdomains are in the unfavorable perpendicular orientation. Given that both the smectic layers and the cylinders individually prefer the parallel orientation, the model in 4c is a possible, but demands the breaking of the homogeneous boundary condition, and creates defects within the LC mesophase. The most probable structure is therefore model 4d, which has transverse cylinders and perpendicular smectic layers, and represents a compromise between two antagonistic orientation tendencies present in one material. The invariant homogeneous anchoring of the

mesogens with respect to the IMDS that we find in this LC block copolymer is most likely the key feature leading to the emergence of the transverse cylinder orientation under shear, as it makes the mutual existence of parallel oriented cylinders with parallel smectic layers impossible. Similar results have recently been obtained from shearing an LC cylinder forming composition, P(S-*b*-ILC) 176/55, i.e., transverse cylinder orientation by shearing below the clearing temperature and parallel orientation above the clearing temperature, without any breaking of the homogeneous boundary condition. The notable difference was the greater length of time that it took to achieve significant transverse orientation of the cylinders, this explained by the

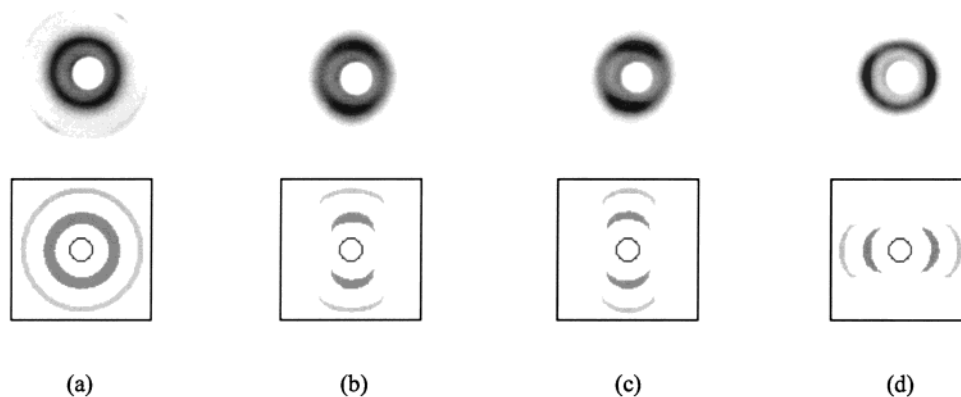


Figure 3. In situ scattering results (low q region only) and schematic representations. Incident X-ray beam directed along the velocity gradient with flow direction vertical on the page for P(S-*b*-ILC) 27/53 sheared at 150 °C. (a) Initial randomly oriented grains of PS cylinders give rise to a uniform ring of scattered intensity. (b) After 0.75 h of shearing, the d_{1010} reflection displays enhanced intensity along the flow direction. (c) After 2.5 h of shearing, the d_{1010} reflection is strongly concentrated along the flow direction indicating transverse alignment. (d) Sample was heated to 175 °C while shearing for an additional 0.5 h—the cylinders have reoriented to align parallel to the flow in the absence of the LC layers.

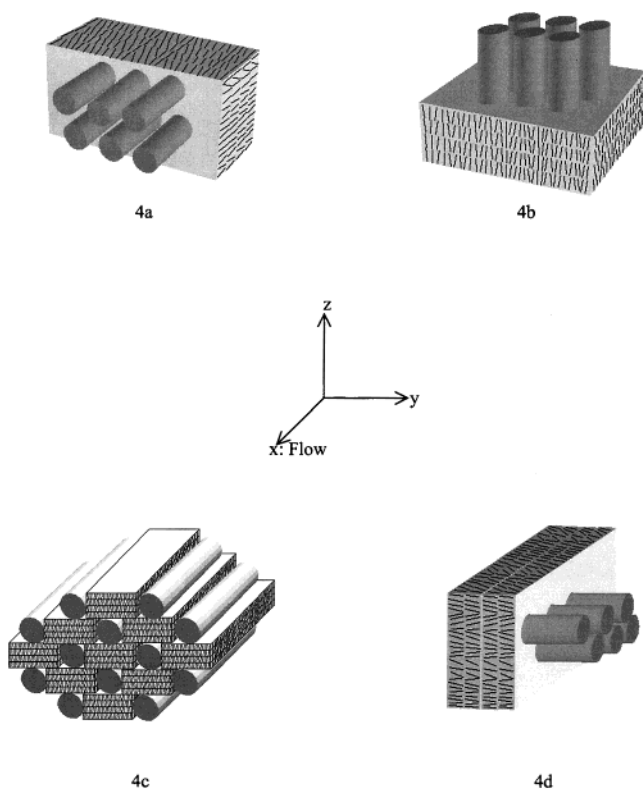


Figure 4. Schematic structural models of smectic layers and cylindrical microdomains with various boundary conditions for the mesogens with respect to the IMDS. Flow is along x and vorticity along y . (a) Model which places the cylinders in their preferred orientation along the flow direction and with homogeneous boundary conditions for the mesogens. The smectic layers are in the unfavorable transverse orientation. (b) Model which places the smectic layers in their preferred orientation parallel to the shear flow with homogeneous boundary conditions for the mesogens. The cylinders are in the unfavorable perpendicular orientation. (c) Model which places both the cylinders and the smectic layers in their preferred orientations but the homogeneous boundary condition for the mesogens is lost. (d) Model which provides a compromise structure in which the cylinders are transverse and the layers are perpendicular but which maintains homogeneous boundary conditions of the mesogens.

smaller volume fraction of the LC component, which, as we suggest, provides the driving force for the assumption of the compromise structure discussed above.

The results of this study suggest that the invariant boundary condition observed in this system may be more the product of geometric constraints than of an independent thermodynamic selection of orientation at the IMDS by the mesogen. Other workers have reported on the occurrence of homeotropic as well as homogeneous anchoring in different copolymers.^{15,16} In our system, the stretching of the isoprene backbone away from the IMDS and especially the relatively short C_5 spacer used to decouple the mesogen from the backbone make anchoring other than homogeneous geometrically difficult.

The presence of hierarchical structure in the LC block-coil block copolymers presents opportunities for manipulating the antagonistic or cooperative actions that occur when the material is placed in a field that interacts with both structures, representing a useful approach for engineering functional polymers.^{17,18} Similar effects of shear alignment in LC-coil block copolymers have been used to successfully align LC groups in a stable bookshelf pattern in a ferroelectric block copolymer. In this polymer, bistable switching could be induced when the LC side groups were aligned homogeneously with respect to the cylinders of the non-LC block. The use of processing variables to control final morphology is clearly possible, and is the subject of work in progress. Prospects exist for the preparation of piezoelectric and electrooptic materials using similar molecular design and processing principles.

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