Communications to the Editor

Observation of Transverse Cylinder Morphology in Side Chain Liquid Crystalline Block Copolymers

Eric Verploegen,[†] LaRuth C. McAfee,[‡] Lu Tian,[‡] Darren Verploegen,[‡] and Paula T. Hammond*[,‡]

Department of Materials Science and Engineering and Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

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Molecular alignment of block copolymers typically involves the orientation of nanoscale domains. Examples of various techniques utilized to achieve well-aligned materials include annealing,[1] various shear fields,[2−10] and electric and magnetic fields.[11] Side chain liquid crystalline elastomers (SCLCEs) have attracted recent interest due to their ability to combine the properties of small molecule liquid crystals and polymers.[12] The increased mechanical integrity of attaching a liquid crystalline moiety to a block copolymer backbone can be beneficial for applications such as electromechanical or mechanooptical materials. Additionally, a thermoplastic elastomer can be created utilizing the phase segregation of block copolymers, where the high-T_g minority blocks serve as physical cross-links, allowing the elastomer to be processed by heating above the T_g of the minority block to achieve an oriented liquid crystalline monodomain. The intermaterial dividing surface (IMDS) of the block copolymer mesophase can be used to orient the liquid crystalline mesophase due to surface stabilization effects. In this way a well-oriented block copolymer mesophase can be used to template order in the LC mesophase.

In this work the smectic liquid crystals are attached to the functionalized siloxane block of a poly(styrene)−poly(vinylmethylsiloxane) (PS−PVMS) diblock copolymer.[13] Gaining a more complete understanding of the interactions between the block copolymer and the liquid crystalline mesophases is key for enabling control over the morphologies and thus the properties of these systems; thus, recent research has increased in the area of LC block copolymers.[9,10,13−23] The system discussed here has a unique advantage over other liquid crystalline block copolymers—a low-T_g siloxane block that makes a room temperature elastomer feasible. Here we investigate the morphologies and the effects of oscillatory shear on the orientation and order of these LC block copolymers and find that the orientation of the block copolymer domains is heavily influenced by the LC orientation. A few means of orientation have been previously reported for lamellar and cylindrical LC block copolymer systems, including melt fiber drawing,[10] roll casting,[3] and oscillatory shear.[4] In this work, the effects of oscillatory shear have been shown to introduce preferential orientation of both block copolymer and liquid crystalline mesophases. Ultimately, transverse orientation of the block copolymer domains is observed in these systems at temperatures above the LC clearing point, which has never been previously observed.

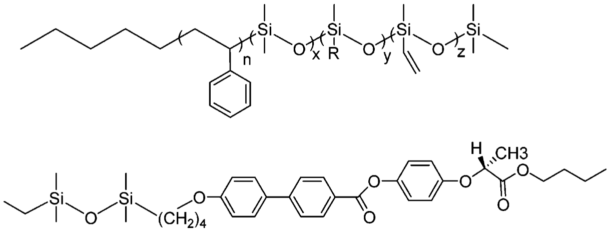

Figure 1. Schematic of side chain liquid crystalline block copolymer (with *y* and *z* random). The number-average molecular weights (M_n) of the polystyrene (PS), liquid crystalline polymer (LCP), and overall block copolymer were determined to be 26 900, 79 400, and 106 300 g/mol, respectively, with a polydispersity index (M_w/M_n) of 1.28. The NMR-based mesogen percent substitution was 55%, yielding a LCP that is 75% of the overall block copolymer by weight.[13]

Structural Characterization of Side Chain Liquid Crystalline Block Copolymer. PS−PVMS functional diblock copolymer was synthesized with anionic polymerization; LCs were synthesized and attached to the block copolymer backbone via hydrosilylation (Figure 1) (see Supporting Information).

Differential scanning calorimetry (DSC) was used in order to determine the thermal transitions of the SCLCBCP. Two glass transition temperature temperatures (T_g) were observed at −14 and 100 °C, corresponding to the T_g for the LCP and the styrene, respectively. The smectic-to-isotropic transition temperature (T_{iso}) of the LC mesophase was observed at 67 °C. (The smectic-to-isotropic transition temperature was also confirmed by POM and SAXS; see Supporting Information.) The presence of a disordered smectic C* liquid crystalline phase was confirmed via small-angle X-ray scattering (SAXS). The *d*-spacings observed are indicative of the presence of smectic layers. Accelrys Materials Studio Molecular Modeling Software was used in order to calculate the molecular lengths of the 4BPP4 mesogen attached to the siloxane backbone. The calculated mesogen length was ∼3.6 nm. Comparing the experimentally observed *d*-spacings (3.45 nm) with the calculated molecular length of the liquid crystalline molecule, it was concluded that the liquid crystals form smectic C* single layers with a tilt angle of ∼16.6°.

SAXS and TEM were used in order to investigate the morphology of the block copolymer mesophase (Figure 2). A TEM of PS27-LCP$_{4BPP4}$79 indicates a HCP cylinder morphology. The TEM results are corroborated with SAXS, where several higher order reflections were seen for PS27-LCP$_{4BPP4}$-79. The observed higher order peaks correspond to scattering characteristic of a HCP cylinder morphology (see Supporting Information).

Temperature-dependent SAXS was performed to investigate morphological changes in the block copolymer mesophase as a

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* Corresponding author. E-mail: hammond@mit.edu.
[†] Department of Materials Science and Engineering.
[‡] Department of Chemical Engineering.

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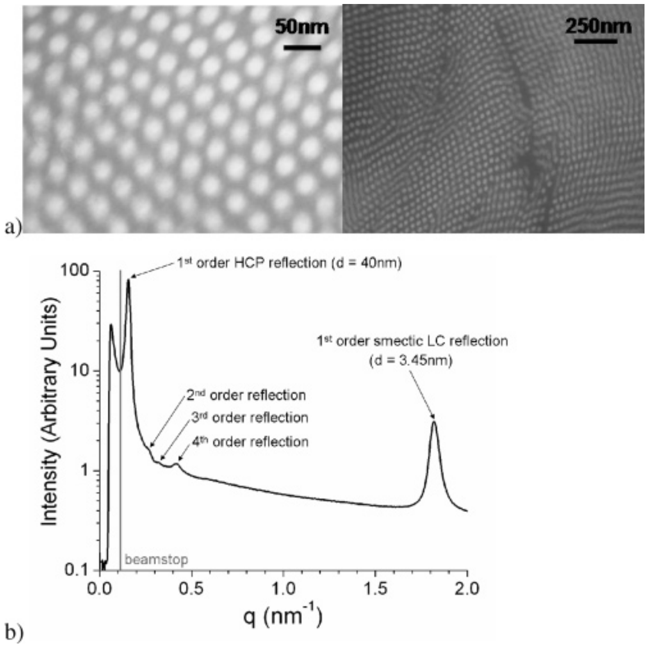

Figure 2. (a) TEM and (b) SAXS of solvent-cast PS27-LCP$_{4BPP4}$79 displaying the HCP cylinder morphology.

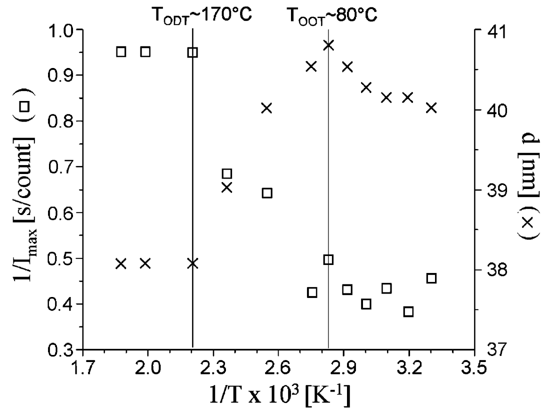

Figure 3. Plots of $1/I_{max}$ vs $1/T$ and d vs $1/T$. The smectic-to-isotropic transition temperature (T_{OOT}) and the order−disorder transition temperature (T_{ODT}) are marked with solid lines, where I_{max} is the maximum intensity of the scattering in the q range of interest and d is the spacing of the ordered phase below the T_{ODT} and the length scale of concentration fluctuations above the T_{ODT}.

function of temperature. At elevated temperatures the scattering intensity from the first-order peak was observed to decrease. In order to systematically determine the order−disorder transition (ODT), the reciprocal of the maximum scattering intensity ($1/I_{max}$) was plotted vs the reciprocal temperature ($1/T$). Additionally, the wavelength of concentration fluctuations, above T_{iso}, and the d-spacing, below T_{iso}, denoted as d was plotted vs reciprocal temperature, similar to the technique used by Anthamatten et al.[24−26]

I_{max} and d are both observed to decrease with increasing temperature (moving from right to left in Figure 3), above 80 °C, and reach a plateau near 170 °C. The smectic-to-isotropic temperature was observed at 67 °C via DSC, SAXS, and POM (see Supporting Information). It is concluded that there is the order−order transition (OOT) near 80 °C related to the smectic-to-isotropic transition. Additionally, this data along with the disappearance of higher order peaks leads to the conclusion that the order−disorder transition (ODT) occurs near 170 °C.

The interfacial thickness was determined by the method of Hashimoto,[24,25] where the $\ln[I(S)S^2]$ is plotted vs S^2, where $S = 2\sin(\theta)/\lambda$ and $I(S)$ is the scattering intensity as a function of S. From the slope or this graph the interface thickness (t) can be determined, $t = (|\text{slope}|/2\pi)^{0.5}$ as $I(S)S^2$ is proportional to $\exp(-2\pi t^2 S^2)$. Using this method, interface thicknesses of ~3 nm were calculated.

Mechanical Orientation. In-situ SAXS studies were performed by applying oscillatory shear with a Linkam CSS450 shear cell at the NSLS beamline X27C at BNL (see Supporting Information). Initial results indicated that shearing must take place above the PS T_g in order for there to be sufficient mobility in the system for orientation of the smectic LC or block copolymer mesophases to occur on the time scales studied (5 min−1 h). Samples of PS27-LCP$_{4BPP4}$79 were subjected to 100% shear at a frequency of 1 Hz at 120 °C, which is above the smectic-to-isotropic transition and the order−order transition for this sample. The development of preferential orientation of the HCP cylinders was initially observed within several minutes (in the absence of scattering from smectic layers), and after ~20 min no further significant increase in the alignment of the domains was observed.

Upon slow cooling (5 °C/min) after the cessation of shear, smectic layers were observed to form preferentially oriented in a manner that is consistent with the homogeneous boundary condition relative to the orientation of the HCP cylinder morphology. Both the cylinder axis and the smectic layer normal were preferentially oriented transverse to the shear direction, i.e., parallel to the vorticity direction (see Figure 4). It was also observed that samples that had been previously deformed could be heated above the smectic LC clearing temperature and the PS T_g to 120 °C, and with a cooling rate of 5 °C/min the smectic layer preferential orientation was regained. However, when the cooling rate is increased to 20 °C/min, significantly less preferred orientation was observed in the smectic layers. This result indicates that kinetics play an important role in the formation of the smectic LC mesophase.

It is important to note that the cylinders align in the transverse orientation while the liquid crystalline mesophase is in the isotropic phase. The lack of smectic ordering is confirmed by the lack of scattering over the relevant q range throughout the in-situ shear experiment. The cylinders would be expected to align in the parallel orientation for an amorphous−amorphous block copolymer;[26−28] however, since the cylinders are observed in the transverse orientation, it is clear that even in the isotropic phase, the LC mesophase has an effect upon the physics of the block copolymer orientation (contrary to previous results from other work[4]).

This observation leads to the conclusion that there is residual order in the isotropic LC mesophase, and this anisotropy is the driving force for the transverse orientation of the cylinders. It is generally known that liquid crystals at a surface or interface can retain orientation even when transverse fields or temperatures above the clearing point are introduced. The periodicity of the PS cylinders is only ~40 nm, resulting in a situation where surface-induced ordering could persist through the entire LC mesophase. Ordering of the LC moieties parallel to the IMDS (i.e., homeotropic anchoring) is consistent with the orientation of the smectic layers observed upon cooling. Additionally, the large size and aspect ratio of the LC moieties in this system could lead to stronger homeotropic anchoring than in other systems, thus having a greater influence upon the orientation of the block copolymer morphology.

The SAXS pattern taken with the beam incident parallel to the vorticity direction clearly shows a hexagonal scattering pattern, indicating that the entire sample is well aligned (the

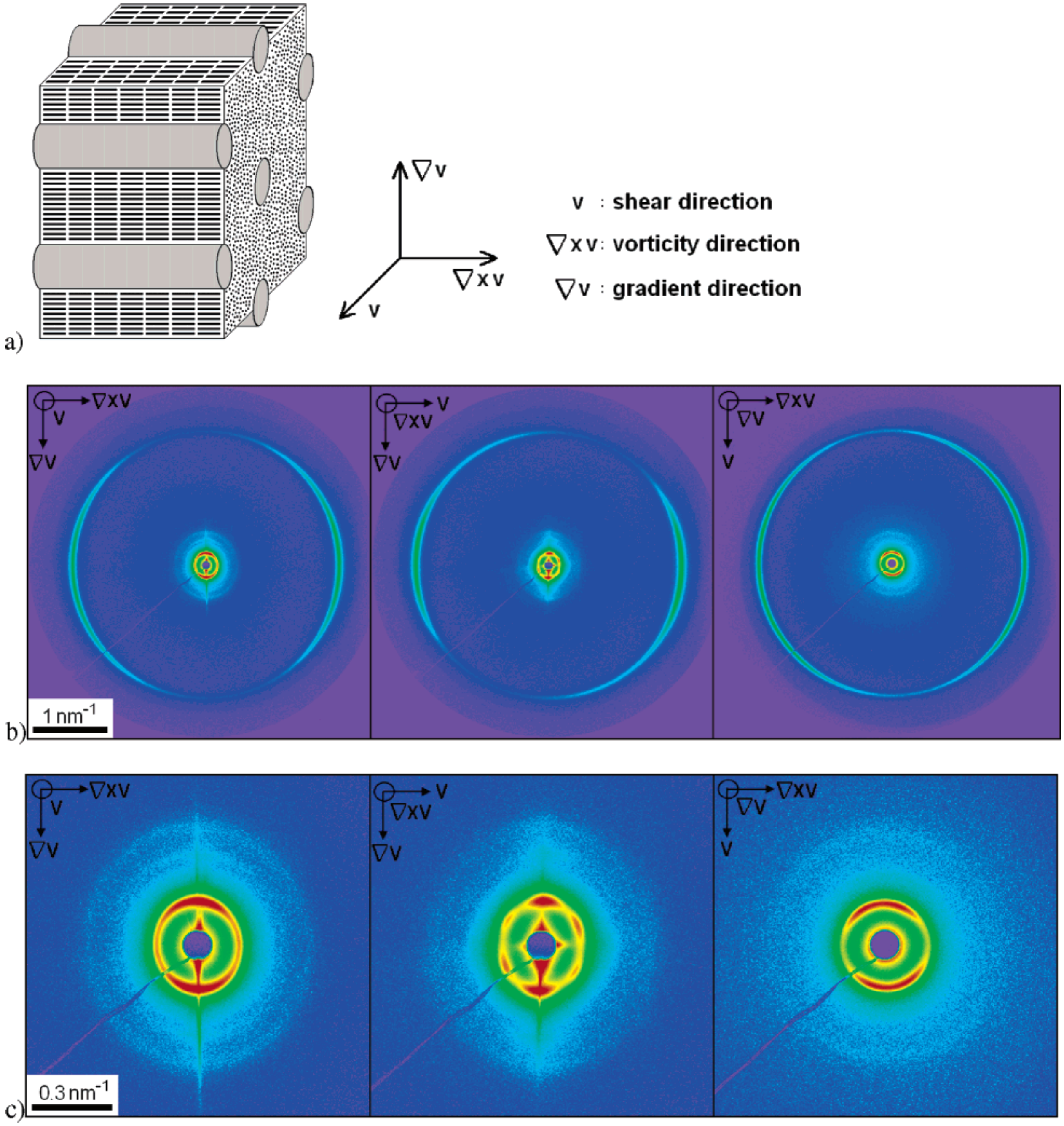

Figure 4. (a) Cartoon depicting observed predominant structure relative to the direction of shear. (b) 2-D SAXS images of sample after shear of 100% at a frequency of 1 Hz took place at 120 °C for 1 h. Moving from left to right, the images were taken with the incident beam parallel to the shear, vorticity, and gradient directions, respectively. (c) Enlarged views of the 2-D SAXS images, displaying the low-angle scattering for each direction, confirming the transverse cylinder orientation. Each image indicates that the cylinder axis is preferentially aligned along the vorticity direction.

sample and the beam are both ~400 μm). This image was taken slightly off axis, leading to the apparent increase in intensity along the gradient direction at low *q* and the higher *q* smectic LC scattering seen along the shear direction. (Calculations of orientation parameters are described in the Supporting Information.) Additionally, anisotropy was observed in the *d*-spacings of the cylinders relative to the direction of the applied shear. This result indicates the HCP lattice has been distorted, such that the cylinder spacings are larger along the shear direction than along the gradient direction (see Supporting Information).

Conclusion. A well-defined smectic C* side chain liquid crystalline block copolymer has been synthesized and characterized. For the polymer studied a cylindrical morphology was observed via TEM and SAXS. When mechanically deformed, the preferential orientation of the smectic LC and the block copolymer mesophases was observed, and the homogeneous boundary condition between the smectic LC mesophase and the IMDS of the cylindrical block copolymer mesophase was maintained.

The transverse HCP cylinders orientation was observed for liquid crystalline block copolymers that experienced oscillatory shear. The transverse orientation was observed while shearing took place above the smectic-to-isotropic transition temperature. The significance of this result is that it indicates that the presence of the isotropic liquid crystalline phase alters the orientation of the block copolymer morphology in response to shear, which has not been previously reported. PS27-LCP$_{4BPP4}$79 was deformed using oscillatory shear, resulting in a nearly uniform oriented HCP cylindrical morphology across the thickness of the sample, as observed via SAXS. Achieving macroscopic orientation of the block copolymer and LC morphologies is critical for a material that can be used for electromechanical applications.

Future work in this area includes study and optimization of the effects of the morphology and orientation of the block copolymer and the liquid crystalline polymer mesophases on thermo- and electromechanical response in these liquid crystalline thermoplastic elastomers.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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