Hierarchical Order in a Side-Group Liquid Crystalline Block Copolymer

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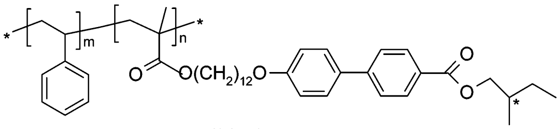
The coupling of a mesogenic block to an isotropic block in a side-group liquid crystal block copolymer (SGLC−BCP) leads to a fascinating interplay between liquid crystalline order and the microphase-separated order of the block copolymer. The mesogen influences the microphase structure of the block copolymer and vice versa. Microphase separation is expected also to affect the conformation of the liquid crystalline block and the orientational ordering of the mesogens. The conformation of the liquid crystalline block is constrained by the coupling of this block to the isotropic block.[1] This is similar to the situation in amorphous−crystalline block copolymers, where the folding of the crystalline block is influenced by the amorphous block.[2] At the same time, the conformation of the amorphous block (isotropic block for SGLC−BCPs) is influenced. The orientation of the mesogens with respect to the microstructure can be probed in samples aligned by flow.[3−6] It will depend on the composition of the copolymer (which in turn controls the microphase symmetry) and on the size of the microphase-separated domains (finite size effect).[1] If the liquid crystal is confined within spheres, smectic phase formation is suppressed, and instead a nematic phase has been observed.[3,4] In contrast, when the liquid crystalline domain is continuous, smectic phases can form. Considering, for example, lamellar phases, the smectic layers are usually aligned perpendicular to the block copolymer lamellae.[1,4,5,7,8] However, a parallel alignment has been reported for a smectic C*-forming mesogen.[9] It was proposed that the distinct orientation resulted from a decoupling of mesogenic order from that of the block copolymer due to the longer spacer attaching the mesogen to the backbone. A homogeneous orientation of mesogens confined within cylinders, parallel to the walls, has been reported.[5] For the inverse structure (continuous liquid crystalline phase) smectic layers lie parallel to the cylinders[4,10] or tilted with respect to them.[6] Liquid crystal phase transition temperatures are usually found to be similar to those of the corresponding homopolymers (although the transition enthalpy may differ).[1] However, Zheng and Hammond report a stabilization of the smectic phase by a lamellar block copolymer microstructure.[11]

Here, we report the characterization of hierarchical order in the bulk and in thin films of the side chain liquid crystalline polymer **Z11**. Small-angle X-ray scattering (SAXS) indicates hierarchical ordering in the bulk: microphase separation between the two blocks together with smectic ordering of the mesogens. The combination of SAXS and atomic force microscopy (AFM) provides the most compelling evidence for the block copolymer microstructure, which consists of hexagonally arranged polystyrene cylinders in a matrix of the block bearing the mesogens. Compared to SGLC−BCPs studied previously in which the mesogen is attached to a methacrylate block, the alkyl chain spacer is much longer (dodecyl vs hexyl[6,10] or butyl[3,4]), and it is interesting to examine whether this leads to a decoupling of smectic order and microphase-separated structure. This can have important consequences for shear orientation, as we show. We also comment on the relationship between these observations and those of Ikkala and co-workers on a diblock system with amphiphilic molecules attached via hydrogen bonds to one block. In particular, they investigated hierarchical order in polystyrene−poly(4-vinylpyridine) (PS−P4VP) diblocks with pentadecylphenol side chains attached via hydrogen bonding to the P4VP block.[12,13] Although the hydrogen bond is much weaker than a covalent bond, the side-chain length is similar in their system and in our side-group liquid crystal block copolymer.



Diblock **Z11**

Polymer **Z11** was synthesized by atom transfer radical block copolymerization of styrene with (*S*)-(−)-methylbutyl 4′-(12-methacryloyloxydodecyloxy)biphenyl-4-carboxylate, following a method developed earlier.[14] ^{1}H NMR spectra were measured in CDCl$_3$ on a Bruker AC-F 250 MHz NMR spectrometer. The molecular weight was found to be $M_n = 33\,900$ g mol^{-1}, and the volume fraction of side-group liquid crystalline segments was $\phi = 0.61$. The polydispersity was determined to be $M_w/M_n = 1.14$ by gel permeation chromatography using a Knauer Instruments chromatograph equipped with two PL gel 10 μm mixed columns and controlled by Polymer Laboratories GPC SEC V5.1 software. THF was used as the eluent. A calibration curve was obtained using polystyrene standards. The thermal properties were determined by differential scanning calorimetry (DSC) using a Metter-Toledo 821 DSC equipped with an autocool accessory and calibrated using indium and zinc standards. Two aliquots were used and the results averaged. Phase identification was performed by polarized light microscopy using an Olympus BH-2 optical microscope equipped with a Linkam THMS 600 heating stage and TMS 91 control unit.

For AFM, samples were spin-coated from a 2% solution of polymer in toluene onto Si wafers and annealed under vacuum overnight at 130 °C. Tapping mode AFM (Nanoscope III, Digital Instrument) was used to image the polymer surface. The AFM was operated under ambient conditions with commercial silicon microcantilever probe tips. The manufacturer's values for the probe tip radius and force constant are <10 nm and in

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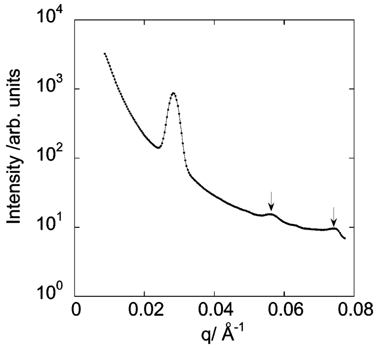

Figure 1. SAXS data obtained after cooling from liquid crystal phase to 25 °C. Arrows indicate higher order reflections.

the range 31−71 N m^{-1}, respectively. Topographic and phase images were obtained simultaneously using a resonance frequency of approximately 165 kHz for the probe oscillation.

SAXS experiments were performed at the Synchrotron Radiation Source (SRS) at the Daresbury Laboratory, Warrington, UK. Samples were studied both at rest and during shear (the latter experiments were performed separately) on beamlines 2.1 and 16.1 (X-ray wavelength $\lambda = 1.5$ Å and $\lambda = 1.41$ Å, respectively). WAXS data were also acquired during measurements on station 16.1. A sample in sheet form (previously annealed overnight at $T = 130$ °C) was mounted in a TA Instruments DSC pan fitted with mica windows to allow transmission of the X-ray beam. The loaded pans were placed in the cell of a Linkam DSC of single-pan design. The experiments were carried out for temperatures ranging between 25 and 125 °C. Additional experiments were performed in which the sample was subjected to large-amplitude oscillatory shear (LAOS) in the melt using a modified Rheometrics RSA II rheometer.[15] For all SAXS measurements, scattering patterns from wet collagen (rat-tail tendon) were used for calibration of the **q** scale ($|\mathbf{q}| = 4\pi \sin \theta/\lambda$, where the scattering angle is 2θ), and corrections for detector response were made.

DSC was used to locate phase transition temperatures in polymer **Z11**. As expected for a microphase-separated system, two glass transitions were observed. The first occurs at about 15 °C and corresponds to the methacrylate block bearing the mesogens. The second (for polystyrene) is hidden under the liquid crystal−isotropic phase transition temperature, which occurs at $T = 102.2$ °C during a second heating ramp at 10 °C min^{-1}, with an associated transition enthalpy $\Delta H = 1.01$ kcal mol^{-1}. The presence of a liquid crystal phase was confirmed by polarized optical microscopy.

SAXS provides evidence for a hierarchically ordered structure formed by self-assembly in **Z11**. Figure 1 shows SAXS data obtained after cooling from the liquid crystal phase to 25 °C. A sharp peak from a microphase-separated structure is evident at $q^* = 0.0285 \pm 0.0005$ Å^{-1} and corresponds to a structural period $d_{\mathrm{m}} = 220 \pm 4$ Å. Weak higher-order peaks at $2q^*$ and $\sqrt{7}q^*$ indicate that the morphology is hexagonal-packed cylinders. (In separate experiments a $\sqrt{3}q^*$ peak also expected for a hexagonal structure was observed, at higher temperatures in the melt.) A strong peak was observed at higher q that is due to smectic layering. This is illustrated in Figure 2, which presents scattering data obtained with a shorter sample-to-detector distance than in Figure 1. This enables the observation of two orders of reflection. The smectic period is found to be $d_{\mathrm{s}} = 35.0 \pm 0.3$ Å. The smectic phase melts at $T = 95 \pm 2$ °C, in reasonable agreement with the value from DSC. The first-order smectic reflection was observed to orient under LAOS. Figure 3 presents SAXS data obtained in the smectic phase at $T = 90$ °C. Arcs are observed, oriented toward the (vertical) shear direction. Unfortunately, we were not able to simultaneously record the diffraction peaks from the cylindrical microphase-separated structure. In separate experiments under similar conditions ($T = 95$ °C, $\omega = 100$ rad s^{-1}, $A = 60\%$) no shear alignment was observed. It is particularly interesting to note that Ikkala and co-workers, studying a diblock with hydrogen-bonded side chains attached to one block, observed that microphase-separated lamellae oriented under LAOS ($f = 1$ Hz, $A = 75\%$) parallel to the flow direction.[13] At the same time, the smectic layers (from the hydrogen-bonded amphiphiles) were oriented perpendicular to the shear direction, as in our data. Also, as for **Z11**, the orientation of the mesogens was not exactly perpendicular to the shear direction. This misorientation has previously been observed for the smectic phase of a flow-aligning side-chain liquid crystal polymer,[16] as well as in the nematic phase of liquid crystal polymers,[17,18] and results from the balance of hydrodynamic torques on the liquid crystal director that selects a particular angle, termed the Leslie angle.[17,18] We propose that in our SGLC−BCP flow

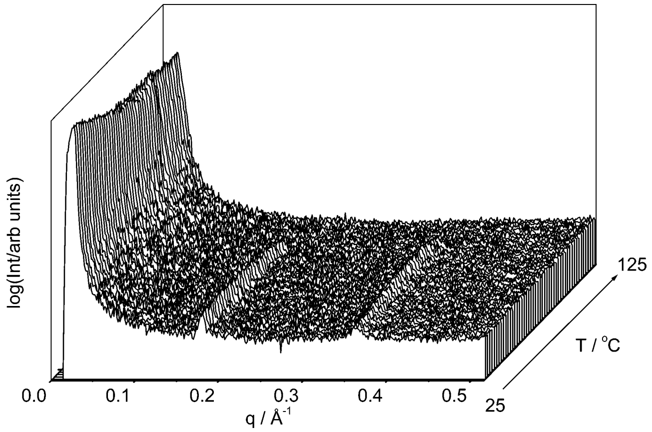

Figure 2. SAXS data obtained during a heating ramp from 25 to 125 °C at 5 °C/min.

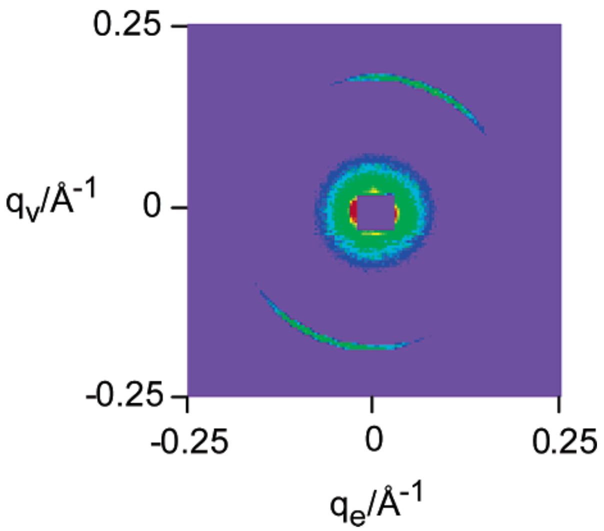

Figure 3. SAXS pattern obtained during shear at 90 °C at a frequency $\omega = 100$ rad s^{-1} and a strain amplitude $A = 100\%$.

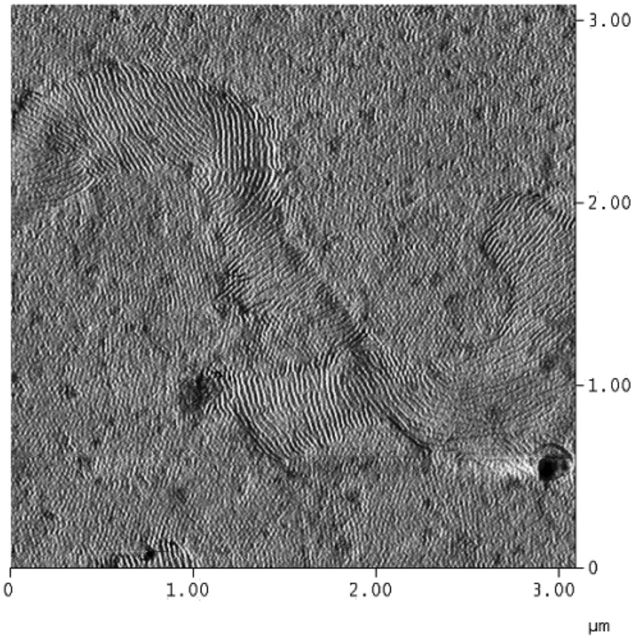

Figure 4. AFM image (phase contrast mode) obtained at room temperature for a sample annealed overnight at 130 °C.

orientation of mesogens occurs and that this is possible because these are highly decoupled from the polymer backbone. We do not observe alignment of the cylindrical microstructure. Our system differs from that of Ikkala et al.[13] since the hydrogen-bonded amphiphiles act as plasticizers in their system, aiding shear alignment of the block copolymer structure. The side groups in **Z11** in contrast are covalently bonded and contribute to a very high melt viscosity. We do not rule out the possibility to align the block copolymer superstructure under more extreme shear conditions than those accessible when performing LAOS in our modified soft solids rheometer, for example roll casting or fiber drawing.[6]

Evidence that the hexagonal-packed cylinder structure is retained in thin films is provided by AFM. Figure 4 shows a phase contrast image of the polymer surface, containing prominent domains of stripelike patterns coexisting with domains of local hexagonal ordering (particularly evident in the center right portion of the image). The combination of these two features supports the presence of a hexagonal-packed cylinder phase, two projections of which are imaged at the surface. The stripe domains correspond to cylinders viewed "edge-on", and the regions of circular domains correspond to "end-on" cylinders. Coexisting parallel and perpendicular cylinders were previously observed by AFM for a nonmesogenic PS−PB−PS triblock.[19] It is interesting that this mixed morphology persists even after annealing overnight at high temperature (130 °C)—it would be expected on surface energy grounds that the lower surface energy component would preferentially segregate to the polymer−air interface. It may be that we are imaging (in phase contrast mode) buried "hard" cylinders through a thin top layer. Alternatively, there may be PS cylinders at the surface due to reduced kinetics of microstructure rearrangement for the confined structure, an effect already noted for PS-based block copolymers with a nonmesogenic block.[20] It is not possible to differentiate these two possibilities at present. We note that the structure in very thin films probed by AFM does not necessarily correspond to the bulk structure, although the bulk limit is recovered for sufficiently thick films.[21] Ellipsometry (phase-modulated spectroscopic ellipsometer, Beaglehole Instruments) was employed to measure the thickness of the film on silica studied by AFM, which was found to be 933 ± 7 Å, corresponding to just over four layers, i.e., definitely not the bulk limit. However, the SAXS data presented in Figure 1 provide strong evidence for a hexagonal structure in the bulk also (striped domains, possibly cylinders, were also observed by transmission electron microscopy on a microtomed and stained section, data not shown).

Considering that the mesogenic block is the majority component, the observation of hexagonal-packed cylinders implies a structure comprising PS cylinders in a matrix of the mesogen-bearing block. Furthermore, the mesogen forms a smectic liquid crystal phase. A similar morphology was previously reported.[3,4,6] Aligned samples of polymers with shorter spacers than **Z11** were studied, and it was concluded that the smectic layers were aligned parallel to the cylinder long axis[4] or were tilted.[6] Compared to the perpendicular orientation, this is expected to cause less distortion of the liquid crystal director field.[1] In our case smectic layers are observed perpendicular to the flow direction due possibly to the greater decoupling of the mesogens from the backbone, which allows them to align with the shear direction.

In summary, atomic force microscopy together with SAXS confirms that hierarchical order exists in a side-group liquid crystal block copolymer with a lengthy alkyl chain between mesogen and main chain. The morphology consists of hexagonal-packed PS cylinders in a matrix that contains smectic layers. The decoupling of the mesogens enables them to be oriented by LAOS, parallel to the shear direction, although the cylinders are not aligned under the same flow conditions. AFM indicates a thin film structure consisting of coexisting parallel and perpendicular cylinders that may be kinetically trapped.

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References and Notes

(1) Walther, M.; Finkelmann, H. *Prog. Polym. Sci.* **1996**, *21*, 951.
(2) Hamley, I. W. *Adv. Polym. Sci.* **1999**, *148*, 113.
(3) Fischer, H.; Poser, S.; Arnold, M.; Frank, W. *Macromolecules* **1994**, *27*, 7133.
(4) Fischer, H.; Poser, S.; Arnold, M. *Liq. Cryst.* **1995**, *18*, 503.
(5) Mao, G.; Wang, J.; Clingman, S. R.; Ober, C. K.; Chen, J. T.; Thomas, E. L. *Macromolecules* **1997**, *30*, 2556.
(6) Anthamatten, M.; Zhang, W. Y.; Hammond, P. T. *Macromolecules* **1999**, *32*, 4838.
(7) Adams, J.; Gronski, W. In *Liquid Crystal Polymers*; Wein, D. A., Ober, C. K., Eds.; American Chemical Society: Washington, DC, 1990; Vol. 433.
(8) Yamada, M.; Iguchi, T.; Hirao, A.; Nakahama, S.; Watanabe, J. *Macromolecules* **1995**, *28*, 50.
(9) Zheng, W.-Y.; Albalak, R. J.; Hammond, P. T. *Macromolecules* **1998**, *31*, 2686.
(10) Anthamatten, M.; Hammond, P. T. *Macromolecules* **1999**, *32*, 8066.
(11) Zheng, W. Y.; Hammond, P. T. *Macromolecules* **1998**, *31*, 711.
(12) Ruokolainen, J.; Mäkinen, R.; Torkkeli, M.; Mäkelä, T.; Serimaa, R.; ten Brinke, G.; Ikkala, O. *Science* **1998**, *280*, 557.
(13) Polushkin, E.; van Ekenstein, G. A.; Dolbnya, I.; Bras, W.; Ikkala, O.; ten Brinke, G. *Macromolecules* **2003**, *36*, 1421.
(14) Itoh, T. Ph.D. Thesis, Tokyo Institute of Technology, 2002.

(15) Hamley, I. W.; Pople, J. A.; Gleeson, A. J.; Komanschek, B. U.; Towns-Andrews, E. *J. Appl. Crystallogr.* **1998**, *31*, 881.
(16) Castelletto, V.; Noirez, L. *Mol. Cryst. Liq. Cryst.* **2001**, *362*, 79.
(17) Zhou, W.-J.; Kornfield, J. A.; Burghardt, W. R. *Macromolecules* **2001**, *34*, 3654.
(18) Kempe, M. D.; Kornfield, J. A. *Phys. Rev. Lett.* **2003**, *90*, 115501.
(19) van Dijk, M. A.; van den Berg, R. *Macromolecules* **1995**, *28*, 6773.
(20) Kim, G.; Libera, M. *Macromolecules* **1998**, *31*, 2670.
(21) Knoll, A.; Horvat, A.; Lyakhova, K. S.; Krausch, G.; Sevink, G. J. A.; Zvelindovsky, A. V.; Magerle, R. *Phys. Rev. Lett.* **2002**, *89*, 035501.

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