Mixed Surface Morphologies of Well-Defined Smectic Diblock Copolymer Ultrathin Films

Jung-Sheng Wu,[†] **Michael J. Fasolka,**[‡] **and Paula T. Hammond***,[†]

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

Received July 13, 1999
Revised Manuscript Received January 4, 2000

Liquid crystalline (LC) block copolymers present a number of interesting applications; for these reasons, the interest in bulk polymer morphologies and ordering of LC block copolymer systems has increased greatly in recent years.[1] Despite the interest in the solid state properties of these materials, there have been only a few reports of their behavior as ultrathin films on surfaces.[2] Surface segregation of fully amorphous block copolymers produces interesting nanostructures, which are the basis for chemical patterning, lithography, or textured surfaces, as illustrated by several groups.[3−6] A base of knowledge has been established in the formation of thin films of amorphous block copolymers, which serves to direct these applications.[7−10] On the other hand, the surface morphology of LC diblock copolymer thin films encompasses the interplay between two different levels of order, both of which may be influenced by energy and ordering effects at the substrate surface or air interface. These systems consist of a LC mesophase nested within a larger mesophase, and the relative orientation and wetting behavior of the block copolymer and the LC smectic layers are at issue. An understanding of the thin film morphologies of these materials could lead to interesting approaches to surface modification, such as electro- or photoswitchable wetting properties, unique thin film membranes, or smart coatings.

To investigate the possibility of forming microdomain structures on surfaces, we have begun to probe the ordering behavior of ultrathin films of side chain LC block copolymers spun cast onto silicon. An unusual stepped morphology has been observed due to incommensurations between the block copolymer morphological domain period (L_0), the smectic LC period (s_0), and the film thickness. These studies yield two significant implications. First, upon close examination of the films using TEM, we have found that although an asymmetric film is formed with the PS block on top, perforations of the LC block are found to wet the air interface in the copolymer thin films, presumably driven by similarities in the interfacial free energy presented by PS and the ordered LC, and by anchoring interactions with the substrate and air interfaces. Second, the LC smectic layers in ultrathin films actually lie parallel to the lamellar block copolymer domains at the surface, despite the fact that perpendicular packing is preferred in the bulk state.[11] This observation suggests that interfacial effects direct the arrangement of the mesogens, regardless of the potential entropic cost of unfavorable conformations of the polymer main chain. Sentenac et al. have also recently observed similar behavior in a different set of LC block copolymers.[12]

The block copolymer investigated here is one of a series of diblock copolymers, PS−*b*-PHBPB in Figure 1. PHBPB is a methyl methacrylate containing (*s*)-2-methyl-1-butyl-4′-(((4-hydroxyphenyl)carbonyl)oxy)-1,1′-biphenyl-4-carboxylate mesogens separated from the main chain with hexyl ($n = 6$) alkyl spacers. These materials were prepared using direct anionic synthesis, and their bulk phase behavior has been fully characterized in previous papers.[13,14] The diblock copolymer, PS−*b*-PHBPB41, has a molecular weight of 18 300 (PS/PHBPB = 11K/7.3K), a polydispersity of 1.06, and a LC volume fraction of approximately 0.39. The LC domains exhibit a smectic C* phase with a layer spacing $s_o = 3.5$ nm, and the lamellar period of the block copolymer is $L_o = 17.3$ nm, as determined by small-angle X-ray scattering (SAXS) of bulk samples. Oriented samples indicate that in the bulk state the smectic layers orient perpendicular to the block copolymer interface.[15] Thin films were spun cast directly from 0.2−2% toluene (a nonselective solvent) solutions onto silicon wafers precleaned by piranha solution (H_2SO_4/H_2O_2). All films were kept under vacuum at room temperature to remove residual solvent for 1 day and then annealed at 170 °C for 3 days, well above the glass transition of both blocks and just below the clearing point of the smectic LC phase. Films were characterized using ellipsometry, atomic force microscopy (AFM), and transmission electron microscopy (TEM). AFM was performed with a Digital Instruments Nanoscope IIIa in D3000 standard tapping mode. Samples for bright field TEM (JEOL 200CX) were prepared by a known carbon replica technique.[1] The PS domains were selectively stained with ruthenium tetroxide. Surface compositions were determined by a Surface Science X-ray photospectrometer (XPS) SSX-100. The average film thickness of each sample was determined using ellipsometry. AFM was used to determine the surface topography.

Contact angle measurements of the two homopolymer films illustrated quite similar surface free energies for the two blocks (within 4° in value). In blends of the two homopolymers, XPS indicates that the liquid crystal homopolymer resides at the top surface of phase separated thick films. On the basis of optical microscopy observations of the homopolymer, a planar arrangement of the mesogens is preferred on the silicon oxide surface; this is consistent with observations made of similar block copolymers.[2] To determine whether the copolymer thin films wet symmetrically or asymmetrically, AFM was used to measure the height of the edges of microdroplets of the polymer on the silicon surface. The heights exhibited along the terraced droplets were of values $L_o/2$ and $3L_o/2$, suggesting that this diblock copolymer forms asymmetric films on the silicon substrate.[16,17] Indeed, in the PS−LC methacrylate block copolymer, a significant fraction of the PS block predominately wets the air interface, as determined by XPS, unlike the homopolymer blend. Thus, while it appears that the LC block prefers to wet both interfaces in polymer blends, in block copolymer thin films, substrate surface energetics result in the presence of PS at the air interface, as discussed below.

[†] Department of Chemical Engineering.
[‡] Department of Materials Science and Engineering.

10.1021/ma991135w CCC: $19.00

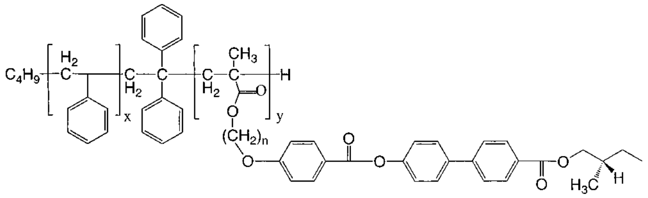

Figure 1. Molecular structure of PS-b-PHBPB41.

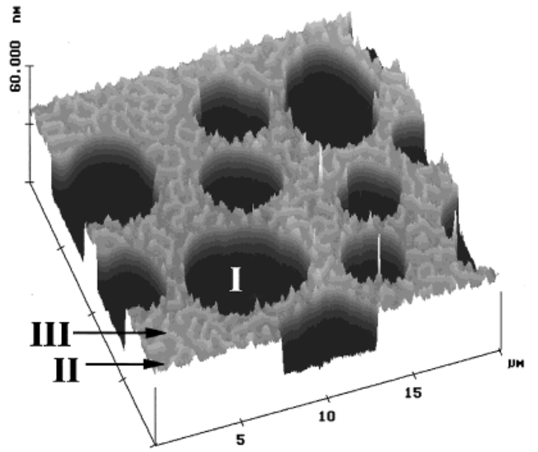

Figure 2. AFM (20 × 20 μm^2 viewing area) of hole structures of a 21 nm thick diblock copolymer film morphology. Region I is the bottom layer of $L_o/2$ thickness, region II is the top layer, and region III indicates smectic terraces.

Depending on the overall film thickness, surface morphologies with holes or islands were observed, as shown by the AFM micrograph in Figure 2. The average film thickness of 21 nm was determined from ellipsometry to fall between L_o and $1.5L_o$. In the micrograph in Figure 2, there exists an underlying bottom layer of $L_o/2$ thickness (region I). The top layer of the film (region II) exhibits holes with depth equal to approximately 17.8 nm, close to the block copolymer lamellar periodicity (L_o). The surface of this top layer contains irregularly shaped ribbons of material on the surface (region III), which are consistently 2.7−3.5 nm, the height of the LC smectic layer (s_o = 3.5 nm). Similar observations of isolated islands appear for the overall film thickness of 16 nm, between $L_o/2$ and L_o. The presence of the smectic layer height step indicates a homeotropic arrangement of the LC mesogens at the air interface. The coexistence of holes or islands of L_o periodicity indicate that the block copolymer lamellae must be parallel to the substrate throughout the film thickness. When the film thickness approaches a half-integral multiple of L_o greater than one, the holes disappear, but the thin top smectic layer terraces remain. The opposite of this coplanar arrangement is seen in the bulk state in oriented films from SAXS, for which the smectic and copolymer domains are perpendicular.

These observations suggest that, despite the preferred perpendicular “bookshelf” morphology observed in the bulk state for these materials and several others,[18−21] a parallel arrangement relative to the lamellae can be induced by surface effects. It is relevant to note here that in the case of the block copolymers with decyl (n = 10 rather than 6) spacer group, the LC smectic layers exhibit parallel arrangements even in the bulk equilibrium state due to the effective decoupling of the mesogen from the main chain and favorable anchoring interactions at the interface.[22] At the surface, the hexyl spacer block copolymer described here takes on this configuration, minimizing the interfacial free energy at the air interface. Notably, the bottom regions of holes (region I), which are approximately $L_o/2$ in film thickness determined by AFM, show no topographical features at the top surfaces. This observation suggests that the orientation of the smectic layers in the bottom monolayers is not the homeotropic arrangement seen in the top regions of the film. In the case of cholesteryl LC block copolymers investigated by de Jeu and co-workers,[2] the smectic layers were consistently perpendicular rather than parallel to the domain morphology. These differences are probably due to the less polar nature of the cholesteryl groups. In the more recent report from this group involving a biphenyl mesogen with an ethyl ester tail group. Sentenac et al. report a similar type of parallel alignment of the smectic layers as that observed here;[12] however, the stable homeotropic smectic terraces observed in our system were not reported by these groups.

TEM images of the films, in parts a and b of Figure 3, reveal a complex surface morphology, in which PS and LC blocks coexist at the air interface. Other researchers[9,10] have shown that submonolayer films can exhibit laterally ordered polymer microdomains. More recently, perforations or columnar structures have been observed to occur in lamellar PS−poly(n-butyl methacrylate) copolymer systems[6] and in PS−b-poly(methyl methacrylate) films.[8,23] Figure 3a is an unstained TEM image, which clearly illustrates the size and shape of individual regions of LC blocks (darker regions) immersed in a continuous PS matrix (lightest regions). At the bottom level (region I), the tiny circular regions are approximately $L_o/2$ in diameter and randomly dispersed. The top of the film (region II) consists of coarser LC domains. While larger than the regions in (region I), close inspection reveals that these regions are aggregates of $L_o/2$ sized domains. Because the influence of the silicon substrate is lessened in this layer, the LC block can be expressed to a greater extent at the free surface. In the region III, large, submicrometer-sized terraces form puddlelike areas of height s_o on the film surface, indicating the presence of homeotropic LC orientation in these areas. Figure 3b contains a complementary TEM image of a stained film, in which the analogous (I, II, III) regions are labeled; dark regions indicate PS domains in this image.

A proposed model, which combines these observations, is shown in Figure 4. Region I is a single monolayer of height $L_o/2$. Here, the LC block wets the silicon surface, and the PS block predominately wets the air interface with random perforations of the LC block. Planar LC anchoring should be favored by the silicon substrate based on the behavior of the LC homopolymer. The top regions (II) of the film are no longer strongly influenced by the substrate, so a larger fraction of the surface is taken up with the LC block. As a result, coarser LC domains form in region II. At the top surface (region III), a homeotropic LC arrangement is present due to the low surface energy provided by the alkyl tails at the ends of the mesogens. These homeotropic regions consist of one parallel smectic layer in which the mesogens are perpendicular to the surface. Preliminary cross-sectional TEM images confirm that an interconnected morphology is present within the layers. Given the volume fraction of LC at 0.39 and the value of L_o = 17.3 nm, the anticipated size of the LC domains is 6.8 nm, which is approximately two smectic layers ($2s_o$ = 7 nm). It is noted that this layer might consist of a more tilted

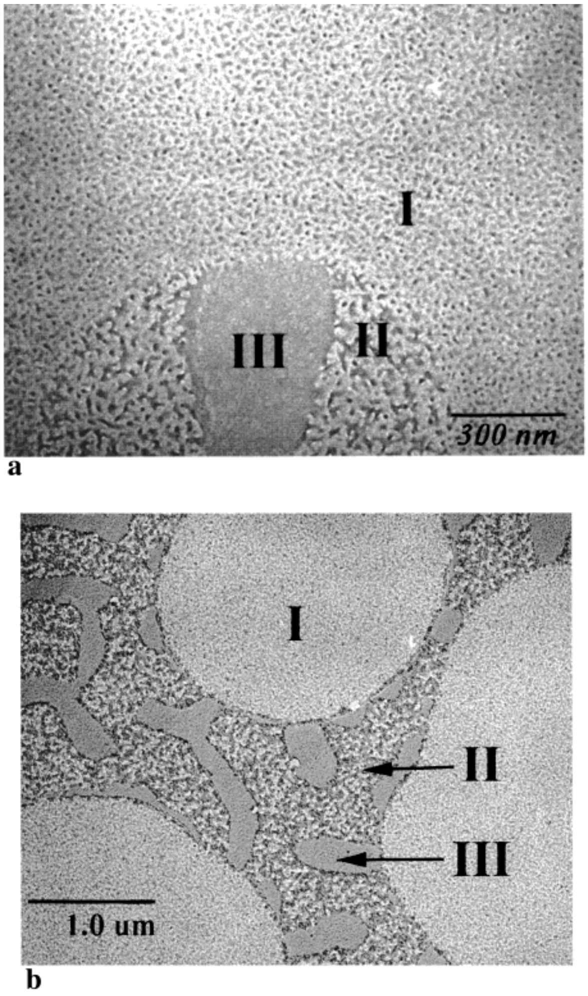

Figure 3. TEM micrographs of ultrathin films cast on silicon, and lifted onto grids. (a) Unstained micrograph of a film in which the LC regions appear dark and the PS regions are light. It is apparent that PS regions are continuous, but LC domains increase in size on tops of islands. (b) Stained micrograph of a 21 nm film with hole defects. The darker regions are preferentially stained PS phase.

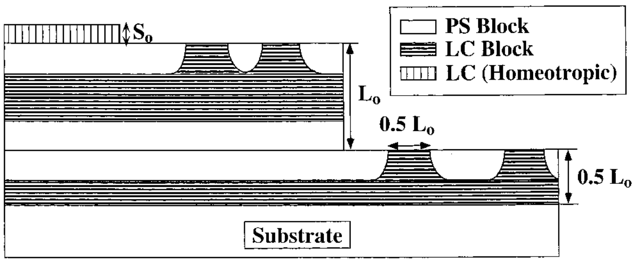

Figure 4. Proposed model based on AFM and TEM evidence.

smectic C phase than that observed in the bulk, as the values of the terrace spacings are lower than s_0 by 0.5–0.7 nm. The premise of asymmetric wetting would dictate that the surface be predominately PS; however, at the top layer, there are large regions of LC, which implies a kind of inversion of the block copolymer lamellar arrangement to allow wetting of the LC layer. Although the smectic LC in the top terraces are homeotropic, it is possible that the LC regions in region II exhibit planar rather than hometropic anchoring; further experiments using reflectivity measurements will be used to determine LC ordering within the film.

Thicker films (thicker than $5L_0$) of the same block copolymer indicate that the topography eventually damps out and disappears as the influence of the substrate and the confinement effects of the film subside. In this arrangement, the LC smectic layers can arrange in the more desirable homeotropic manner at the air interface. It appears that once the film is thick enough to overcome the strong preferential interactions of the silicon substrate with the LC layer, the block copolymer arrangement approaches the wetting exhibited by the homopolymer blend, i.e., LC at both the air and silicon interfaces. The terraced and perforated morphologies observed in mono- and bilayer films are due to the strongly preferential wetting of the substrate by the mesogens in the LC block. Further investigation and confirmation of the arrangement of the LC layers is required to confirm this model, and will be pursued using X-ray reflectivity studies, to be reported separately.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation Division of Materials Research Polymer Program under Award No. DMR-9526394. This work was partially supported by the MIT Center for Materials Science and Engineering, NSF MRSEC under DMR-9400334. P.T.H. also thanks the DuPont Corporation for its support.

References and Notes

(1) Geil, P. H. *Polymer Single Crystals*; Huntington, NY, 1973; pp 69–70.
(2) Wong, G. C. L.; Commandeur, J.; Fischer, H.; de Jeu, W. H. *Phys. Rev. Lett.* **1996**, *77*, 5221.
(3) Amundson, K.; Helfand, E.; Quan, X.; Hudson, S. D.; Smith, S. D. *Macromolecules* **1994**, *27*, 6559.
(4) Morkved, T. L.; Lu, M.; Urbas, A. M.; Ehrichs, E. E.; Jaeger, H. M.; Mansky, P.; Russell, T. P. *Science* **1996**, *273*, 931.
(5) Park, M.; Harrison, C.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. *Science* **1997**, *276*, 1401–1404.
(6) Fasolka, M. J.; Harris, D. J.; Mayes, A. M.; Yoon, M.; Mochrie, S. G. J. *Phys. Rev. Lett.* **1997**, *79*, 3018.
(7) Mansky, P.; Harrison, C. K.; Register, R. A.; Chaikin, P.; Yao, N. *Appl. Phys. Lett.* **1996**, 2586.
(8) Russell, T.; Menelle, A.; Anastasiadis, S. H.; Satija, S. K. *Macromolecules* **1991**, *24*, 6263–6269.
(9) Koneripalli, N.; Levicky, R.; Bates, F. S.; Ankewer, J.; Kaiser, H.; Satija, S. K. *Langmuir* **1996**, *12*, 6681–6690.
(10) Kellog, G. J.; Walton, D. G.; Mayes, A. M.; Lambooy, P.; Russell, T. P.; Gallagher, P. D.; Satija, S. K. *Phys. Rev. Lett.* **1996**, *76*, 2503.
(11) First reported by Wu, J.-S.; Hammond, P. T. Surface Morphologies in Ultrathin Films of Liquid Crystalline Block Copolymers. Presented at the American Physical Society Annual Meeting, Atlanta, GA, March, 1999.
(12) Sentenac, D.; Demirel, A. L.; Lub, J.; de Jeu, W. H. *Macromolecules* **1999**, *32*, 3235–3240.
(13) Zheng, W. Y.; Hammond, P. T. *Macromol. Rapid Commun.* **1996**, *17*, 813–824.
(14) Zheng, W. Y.; Hammond, P. T. *Macromolecules* **1998**, *31*, 711–721.
(15) Anthamatten, M. L.; Hammond, P. T. *Macromolecules* **1999**, *32*, 4838–4848.
(16) Coulon, G.; Collin, B.; Ausserre, D.; Chatenay, D.; Russell, T. P. *J. Phys.* **1990**, *51*, 2801–2811.
(17) Maaloum, M.; Ausserre, D.; Chatenay, D.; Coulon, G.; Gallot, Y. *Phys. Rev. Lett.* **1992**, *68*, 1575.
(18) Mao, G.; Wang, J.; Clingman, S. R.; Ober, K.; Chen, J. T.; Thomas, E. L. *Macromolecules* **1997**, *30*, 2556–2567.
(19) Fischer, H.; Poser, S.; Arnold, M. *Liq. Cryst.* **1995**, *18*, 503–509.
(20) Adams, J.; Gronski, W. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 553–557.
(21) Yamada, M.; Iguchi, T.; Hirao, A.; Nakahama, S.; Watanabe, J. *Macromolecules* **1995**, *28*, 50–58.
(22) Zheng, W. Y.; Albalak, R.; Hammond, P. T. *Macromolecules* **1998**, *31*, 2686–2689.
(23) Morkved, T. L.; Jaeger, H. M. *Europhys. Lett.* **1997**, *40*, 643.

MA991135W