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Ordering of Cylindrical Microdomains in Thin Films of Hybrid Isotropic/Liquid Crystalline Triblock Copolymers

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ABSTRACT: We have investigated the roles of liquid crystallinity (LC) and substrate interactions on the ordering of isotropic cylindrical microdomains in thin films of two hybrid isotropic/LC triblock copolymers. Each copolymer consists of polystyrene (PS) end blocks and a side-chain LC midblock that exhibits either a nematic or smectic mesophase up to temperatures beyond the glass transition temperature (T_g) of PS. In thin films measuring on the same order as the lattice period, the orientation of the cylinders relative to the substrate is sensitive to the interactions of the mesogens at internal microdomain boundaries and external interfaces. Upon annealing such copolymer films at temperatures below the LC → isotropic transition but above the PS T_g on a neutral NaCl substrate, the PS cylinders within the nematic matrix adopt a long-range parallel orientation, whereas those within the smectic matrix lie perpendicular to the substrate and exhibit liquidlike order. After long annealing times, the cylinders residing near the film surface within the smectic matrix reorganize from perpendicular to parallel orientation due to surface tension at the film/air interface. On a polished Si substrate that promotes homeotropic mesogen anchoring, the perpendicular cylindrical orientation within the smectic mesophase remains stable.

Introduction

Depending on their degree of thermodynamic incompatibility, isotropic block copolymers can microphase-separate into several ordered morphologies within the bulk state. The spherical, cylindrical, lamellar, and bicontinuous morphologies observed to date develop primarily in response to balancing the enthalpic repulsion and configurational entropy of the blocks and depend on factors including molecular weight and composition, as well as the asymmetry and interaction between the repeat units comprising the blocks.[1] In a thin block copolymer film, additional considerations govern the ordering and orientation of lamellae or cylinders relative to the surfaces in contact with the film. In the case of thin films composed of a lamellar block copolymer, the lamellae generally orient parallel to the surface, with lamellae of lowest surface energy in contact with the surface, in the absence of selective surface patterning. If d_0 denotes the equilibrium period of a block copolymer in the bulk state, the film thickness must assume discrete values of d_n, where d_n is given by $(n + {}^1/_2)d_0$ or nd_0 depending on the interaction of the blocks with the surfaces.[2] In unconfined thin films, the film thickness can adjust to satisfy these conditions by partitioning into coexisting domains of thicknesses d_n and d_{n+1}. In contrast, analogous films confined between two rigid surfaces can become frustrated due to incommensuration of the film thickness and the block copolymer period, which may result in the formation of layers with a perturbed period. Minimization of the interaction between the blocks and the surfaces may relieve the frustration through perpendicular ordering of the lamellae.[3]

Cylindrical microdomains in a comparably confined block copolymer thin film tend to adopt a perpendicular orientation relative to its surfaces if the elastic distortion of the chains and the resulting free energy penalty are larger than the gain in surface free energy due to preferential surface segregation of one of the blocks at the surfaces. This has been verified for poly(styrene-*b*-butadiene-*b*-styrene) (SBS) triblock copolymers.[4] According to predictions from the theoretical framework recently proposed by Suh et al.,[5] cylindrical microdomains can undergo a transition from parallel to perpendicular when the film thickness approaches the order of d_0. Cylinders oriented perpendicular to the surfaces of a thin film have been observed by Mansky et al.,[6] who attribute the orientation to the metastability of the morphology generated during the course of solvent evaporation. Mayes and co-workers[7] have, on the other hand, reported that the onset of parallel lamellar microdomain orientation occurs when the thickness of a block copolymer film supported on one side exceeds ${}^1/_2d_0$. For films measuring less than ${}^1/_2d_0$, the perpendicular orientation is observed. Recent annealing studies conducted by Libera[8] on poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] (SEBS) triblock copolymers likewise support the existence of cylindrical microdomains oriented perpendicular to the surfaces of a block copolymer thin film.

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In this work, we present results on the morphological development in the liquid crystalline mesophase of thin unconfined films of hybrid LC/isotropic (LC/i) block copolymers exhibiting the cylindrical morphology. More precisely, we have investigated two ABA block copolymers in which A constitutes an isotropic polymer and B is a nematic or smectic side-chain LC polymer. In thin films, the morphology and orientation of the cylindrical microdomains composed of the isotropic A-block are influenced by the following additional contributions to the free energy: (i) the elastic energy of the LC mesophase, (ii) mesogen anchoring at microdomain boundaries, and (iii) orientational wetting of the LC mesophase at the film surfaces. Recent studies[9,10] of nematic triblock copolymers have demonstrated that considerable interplay exists between the LC mesophase and the microdomains resulting from microphase separation. It has been shown, for instance, that a morphological transition from a body-centered-cubic (bcc) spherical morphology to a hexagonally close-packed (hcp) cylindrical morphology can be induced at the nematic → isotropic (n → i) transition of the LC block, with homogeneous anchoring along internal interfaces being responsible for the orientation of the isotropic cylinders along the nematic director.[9] In a similar vein, Anthamatten and Hammond[11] and Figueiredo et al.[12] have found that the smectic → isotropic (s → i) transition of the LC block can likewise induce microphase separation in an otherwise homogeneous LC/i block copolymer. The existence of molecular orientational effects on block copolymer microdomains in the presence of smectic mesophases has also been investigated.[13−16]

A fundamental understanding of the influence of surfaces on the morphology and orientation of both the LC director and the microdomains of the isotropic block in LC/i block copolymers is critical for potential application of these copolymers as electrooptical devices[17] or surface nanotemplates.[18] Despite the obvious importance of these considerations, only three studies[19−21] have been reported thus far in which orientational wetting in lamellar hybrid isotropic/smectic diblock copolymers has been investigated in requisite detail. While the lamellae of a compositionally symmetric diblock copolymer have been observed to orient perpendicular to the substrate, the lamellae of asymmetric diblock copolymers appear to prefer the more general parallel orientation. Wong et al.[19] attribute their observation to block-specific interface wetting and incommensuration between the smectic spacing and the smectic block size. It was also shown that homeotropic anchoring of the mesogens on the substrate may induce an unusual parallel orientation of both smectic and amorphous layers in contrast to their orthogonal arrangement in the bulk.[20,21] In the present study, we anneal thin films of the two LC/i triblock copolymers mentioned earlier at temperatures within the LC mesophase and above the glass transition temperature (T_g) of the isotropic block to discern the effects of two different LC fields, as well as surface interactions, on microdomain ordering and orientation.

Scheme 1

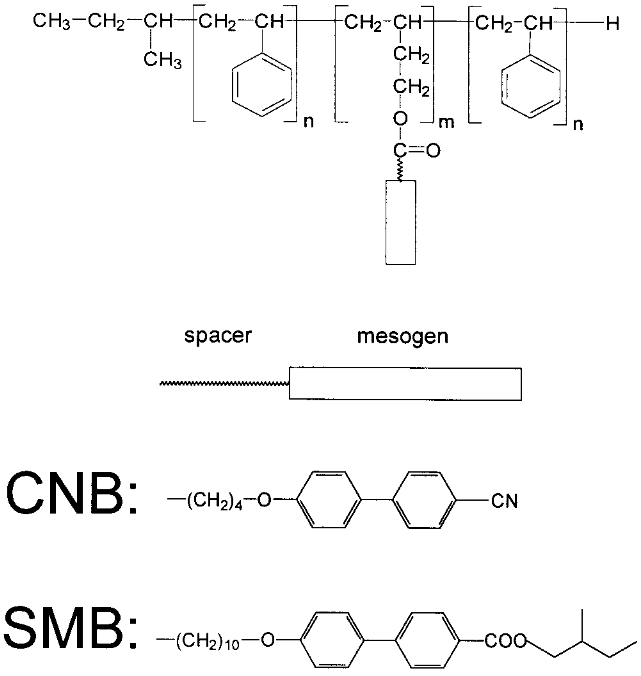

Table 1. Thermal Characteristics of the LC Blocks of the CNB and SMB Block Copolymers[a]

copolymer	mesophase	T_g, °C, [Δc_p, J/(g K)],	LC trans temp, °C (trans enthalpy, J/g)	
CNB	nematic (n)	34.5 [0.41]		N 122 (2.6) I
SMB	smectic (s)[b]	6.8 [0.12]	Sc* 64 (13.5) Sa	Sa 112 (7.3) I

[a] Measured by DSC and extrapolated to zero heating rate. [b] While the SMB homopolymer exhibits both Sc* and Sa mesophases, we refer to its general s mesophase throughout this work.

Table 2. Molecular Characteristics of the CNB and SMB Block Copolymers

copolymer	wt % PS[a]	M_w[b]	polydispersity[b]	N_{LC}[c]	N_{PS}[c]
CNB	11.9	84 000	1.08	$m = 211$	$n = 2 \times 48$
SMB	7.4	582 000	1.13	$m = 1053$	$n = 2 \times 207$

[a] Measured by ^{1}H NMR. [b] Measured by SEC. [c] Number of repeat units (based on ^{1}H NMR and SEC results), with *m* and *n* defined in Scheme 1.

Experimental Section

Materials. Hybrid LC/i triblock copolymers were synthesized via conversion of the poly(1,2-butadiene) (PB) block of SBS triblock copolymers prepared by living anionic polymerization. Side-chain mesogens were introduced by hydroboration of the PB block and subsequent esterification with activated mesogenic units.[22] Two triblock copolymers were prepared in this manner. One copolymer, designated CNB, was modified with a cyanobiphenyl mesogen and exhibited a nematic mesophase. The other copolymer, denoted SMB, possessed a chiral (*S*)-2-methylbutyl 4-biphenylcarboxylate mesogen and exhibited two smectic mesophases. The chemical structures of these mesogens are provided in Scheme 1. The thermal characteristics of the LC midblocks in the two copolymers, according to differential scanning calorimetry (DSC) results extrapolated to zero heating rate, are listed in Table 1, and pertinent molecular information obtained from ^{1}H NMR and SEC is provided in Table 2. Due most likely to the low polystyrene (PS) content of the CNB and SMB copolymers, no PS T_g for the copolymers were detectable by DSC or dynamic mechanical themal analysis. In comparison, however, PS with 48 repeat units (N_{ps}) as in the CNB copolymer is estimated to have a T_g of about 82 °C, whereas the T_g of PS with $N_{ps} = 207$ (as in the SMB copolymer) is ca. 96 °C.[23] Note that the M_w of PS in each compound was less than or comparable to the critical molecular weight of entanglement of PS. The CNB copolymer was previously found[9] to order into the bcc spherical morphology in the isotropic melt and the hcp cylindrical morphology in the nematic mesophase. In the latter case, the periodicity in the bulk (d_0) was measured to be 26 nm, and the cylinder radius (R) was 5.0 nm. The SMB copolymer has been observed[12] to undergo microphase separation into the hcp cylindrical morphology at the smectic → isotropic (s → i) transition with $d_0 = 48$ nm and $R = 7.7$ nm.

Methods. Films were prepared by spin-coating a 1.0 wt % solution of copolymer in tetrahydrofuran on freshly cleaved NaCl single crystals and Si wafers. The NaCl single crystals measured $11 \times 30 \times 7$ mm^3 and were purchased from Aldrich, whereas the polished Si(100) wafers were obtained from Aurel GmbH. Prior to measurement, the films were annealed for various periods of time at 105 °C (which is above the T_g's of the PS blocks in the CNB and SMB copolymers) in the nematic or smectic mesophase, respectively. The thickness of annealed and unannealed films on NaCl and Si substrates was determined by Rutherford backscattering in the 7.5 MV van de Graaff laboratory at the Universität Freiburg. Film thicknesses of 50 ± 10 nm for CNB and 55 ± 10 nm for SMB were measured with $^4He^+$ ions at an energy of 2 MV. Similar results were independently obtained by atomic force microscopy (AFM) and ellipsometry. X-ray reflectivity measurements were performed at the BW4 USAX beamline of the DORIS III storage ring at HASYLAB/DESY in Hamburg. Details regarding the beamline are available elsewhere[24] and are not reproduced here. The wavelengths (λ) selected for two separate experiments were 0.138 and 0.154 nm, and reflected intensities from the CNB and SMB films were detected over 8 orders of magnitude. By analyzing these reflectivity data according to the protocol provided earlier,[25] the total film thickness and the surface and interface roughness were deduced.

The evolution of film surface morphology as a function of annealing time was observed by AFM in tapping mode using a Nanoscope III instrument (Digital Instruments). Standard AFM tips with ~10 nm radii and a cantilever resonant frequency of ~300 kHz were used to scan the samples. The AFM topographies showed no evidence of tip-induced modification during successive scans. The global morphology of the films spin-coated onto NaCl and subsequently annealed was studied by transmission electron microscopy (TEM) after dissolving the NaCl substrate in deionized water and collecting pieces of the films on copper grids. The films were exposed to the vapor of RuO_4(aq), which stains the phenyl rings of the PS more readily than the phenyl rings on the mesogens, thereby yielding sufficient contrast between the PS and LC microdomains to permit discrimination of the microphase-ordered morphology. Images were collected on a Leo 912 Omega electron spectroscopic microscope operated at an accelerating voltage of 120 kV and an energy loss of 0 eV. Further characterization of the microdomain characteristics of the CNB and SMB bulk samples was performed with small-angle X-ray scattering (SAXS), as described previously.[9] The critical surface tension (γ_c) of each block was determined by static contact angle measurements conducted with the homopolymer analogues in the presence of a series of liquid standards: 1-bromonaphthalene, CH_2I_2, glycerol, and water, as prescribed elsewhere.[22] By doing so, the following values for γ_c (in mN/m^2) were extracted: $\gamma_c(PS) = 42 \pm 2$, $\gamma_c(SMB) = 42 \pm 6$, and $\gamma_c(CNB) = 44 \pm 6$.

Results

X-ray Reflectivity Measurements. Reflectivity data collected from annealed CNB and SMB films on Si are presented as a function of the scattering vector (q_z) in Figure 1. As seen in this figure, the reflectivity curve corresponding to the CNB copolymer does not show a Bragg peak over the entire measured angular range. Thus, it can be concluded that the CNB film does not exhibit a layered structure perpendicular to the sample surface. Fitting a one-layer model to these data yields a total film thickness of 51.2 nm and a surface roughness of 0.8 nm. The reflectivity data acquired from the SMB copolymer after 48 and 123 h of annealing at 105 °C, on the other hand, clearly exhibit up to 5 orders of pronounced Bragg peaks. On the basis of these data, the spacing of the smectic layers is discerned to be 3.4 nm. Fitting the model to the data results in a total film thickness and surface roughness of 61.9 and 0.5 nm, respectively, for the SMB copolymer annealed for 48 h and 58.3 and 0.8 nm, respectively, for the SMB copolymer annealed for 123 h. These thickness values correspond to 18 (48 h) and 17 (123 h) smectic layers. Note that the experimental error on all these measurements is estimated to be on the order of ±0.1 nm. Comparison of the data for the SMB copolymer in Figure 1 therefore indicates that an increase in annealing time is accompanied by a slight increase in surface roughness and a slight decrease in film thickness without any substantial change in the degree of order in the layered structure.

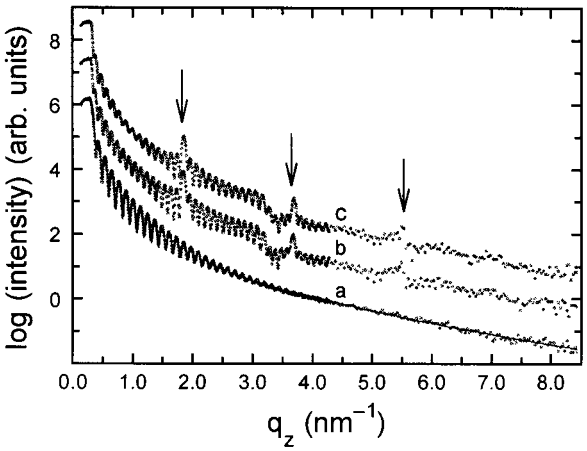

Figure 1. X-ray reflectivity profiles of block copolymer thin films prepared on Si, along with an example of a theoretical fit (solid curve). The nematic block copolymer (CNB, a) was measured after it was annealed for 86 h, whereas the smectic block copolymer (SMB) was measured after it was annealed for 48 (b) and 123 (c) h, at 105 °C in the LC mesophase.

Nematic Block Copolymer Films on NaCl. The time-dependent evolution of global morphology in the CNB copolymer, as discerned by TEM, is presented as a function of annealing time in Figure 2. The image of the as-cast (unannealed) film (Figure 2a) reveals the existence of disordered PS microdomains that appear darker than the matrix due to staining with RuO_4, thereby confirming that the film underwent microphase separation during solvent evaporation. Under crossed polars in an optical microscope, the film appears uniform, suggesting that the matrix of the copolymer is not in its LC mesophase. The most likely reason for this to occur is that the LC block vitrified below its T_g (34.5 °C, according to DSC; see Table 1) prior to its i → n transition during rapid solvent evaporation. As expected from the low PS content (11.9 wt %) in the CNB copolymer and verified by the TEM image in Figure 2a, dispersed PS microdomains lacking any substantial degree of positional order develop upon microphase separation of the copolymer. It is not clear whether the microdomains are altogether cylindrical (exhibiting random orientation), a combination of cylindrical and spherical, or residually disorded (due to spin-casting).

As the CNB copolymer film is annealed for up to 12 h at 105 °C (Figure 2b,c), the matrix of the copolymer enters into its nematic mesophase. After 3 h of annealing, a morphology consisting of small grains approximately 50 nm in size develops. Within these grains, PS cylinders aligned parallel to the substrate surface are clearly evident. If spherical PS microdomains are initially present, the transition from a spherical to cylin-

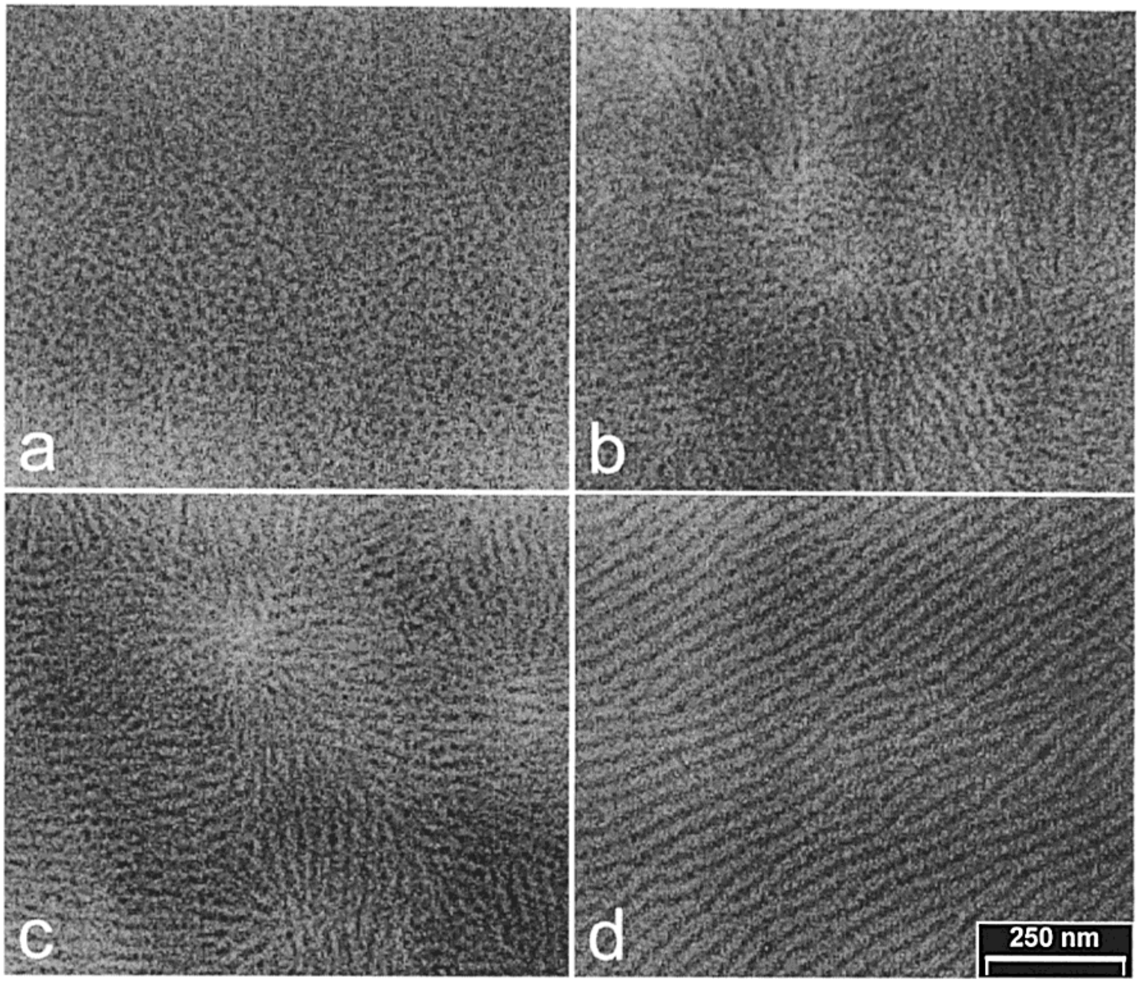

Figure 2. TEM images of CNB block copolymer thin films deposited on NaCl and annealed for different times (in h) at 105 °C in the nematic mesophase: (a) 0, (b) 3, (c) 12, and (d) 86. The PS microdomains appear electron-opaque (dark) due to staining with RuO_4.

drical morphology is induced by the i → n transition, as occurs in bulk specimens of the same copolymer.[9] Enhanced orientation of the cylinders is likewise commensurate with this transition. As the annealing time is increased, the grain structure grows and becomes more highly ordered. After 86 h of annealing (Figure 2d), PS cylinders lying parallel to the substrate surface and exhibiting long-range order are prevalent throughout the film. Under crossed polars, the film appears highly birefringent, verifying that the mesogens are also aligned parallel to the substrate. Since previous studies on oriented bulk samples have demonstrated parallel orientation of cylinders and mesogens,[10] we conclude that also in the film the orientation of the PS cylinders likely follows the orientation of the nematic director of the side-chain mesogens. The increasing degree of microdomain order with increasing annealing time reflects defect healing/annihilation within the nematic mesophase until a near-equilibrium state is attained after 86 h. The distance between the PS cylinders is uniform at about 35 nm, which is significantly larger than the 26 nm measured in bulk specimens of the same CNB copolymer. This discrepancy is consistent with the formation of only one layer of cylinders. Since the TEM image is a two-dimensional projection of the three-dimensional morphology, a smaller distance would be observed if more than one layer is present.

The surface of the CNB films at the film/air interface, as observed in AFM phase images, does not reveal any characteristic morphological features irrespective of the annealing time. In particular, the surface appeared very flat and homogeneous after the longest annealing time of 86 h, strongly suggesting that the film/air surface was uniformly covered by one of the blocks. If the LC mesogens locate preferentially at the surface, the mid-blocks of the copolymer must form highly distorted loops, if one considers the film thickness and the microdomain period. Since this scenario is improbable, the film/air surface is most likely covered with PS. Recall that the value of γ_c measured for PS (42 ± 2 mN/m^2) is slightly lower than that of the CNB homopolymer (44 ± 6 mN/m^2). Similar reasoning can also be applied to the substrate surface.

Smectic Block Copolymer Films on NaCl. Figure 3 shows the morphological development that occurs in SMB copolymer films, as observed by TEM. In the case of the unannealed film (Figure 3a), a disordered morphology grossly similar to the CNB film (Figure 2a) is apparent. The contrast between the PS and LC blocks is rather weak, implying incomplete microphase separation of the copolymer. Unlike the CNB block copolymer, the SMB copolymer is not microphase-separated in the isotropic melt above the isotropization temperature. Microphase separation in this copolymer only occurs as a direct consequence of the i → s transition.[12] Although the T_g of the SMB block is lower than the T_g of the CNB block, the morphology obtained after solvent evaporation is not well microphase-separated. In as-cast films,

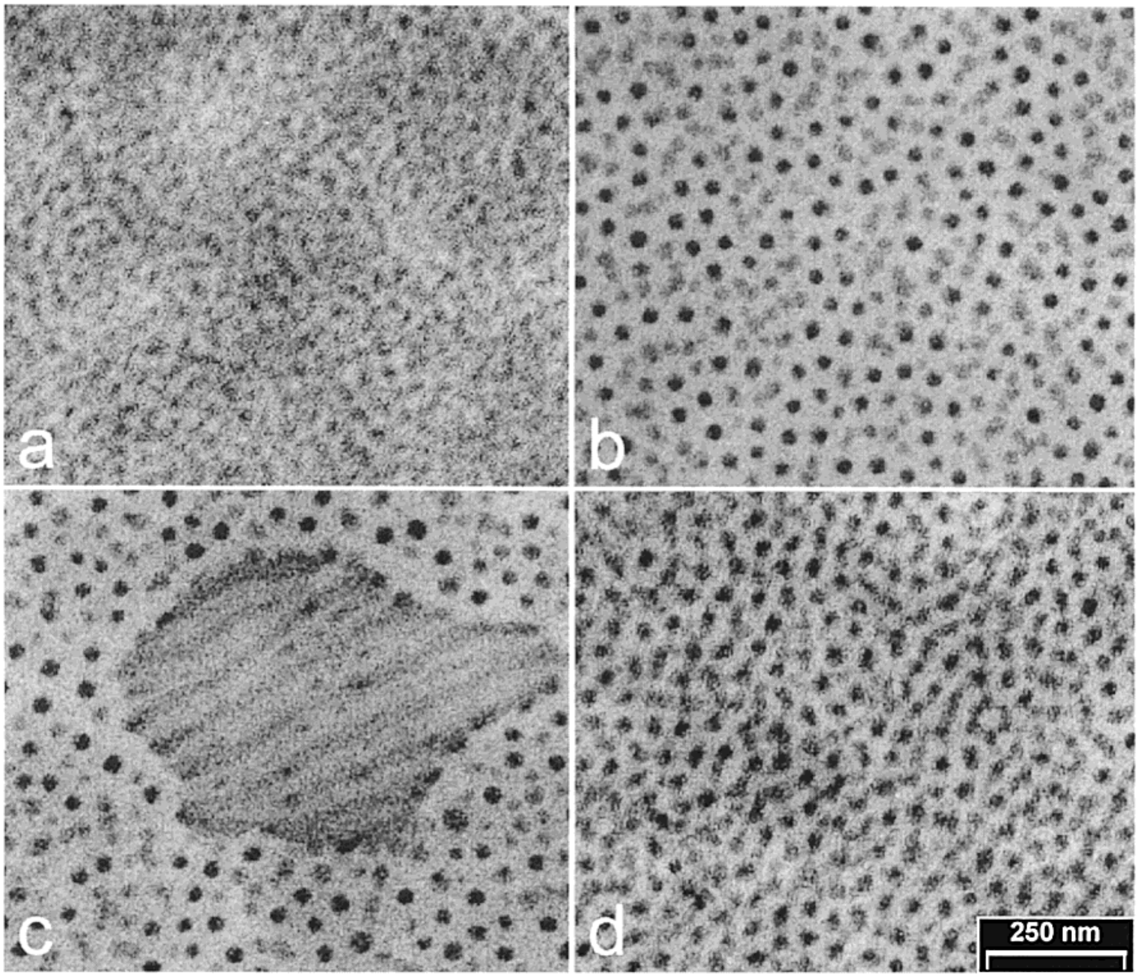

Figure 3. TEM images of CNB block copolymer thin films deposited on NaCl and annealed for different times (in h) at 105 °C in the smectic mesophase: (a) 0, (b) 12, (c) 24, and (d) 86. The PS microdomains appear electron-opaque (dark) due to staining with RuO_4.

the SMB mesogens nevertheless exhibit LC behavior, as confirmed by the presence of birefringence when viewed with an optical microscope under crossed polars. Free-standing as-cast films collected after dissolution of the NaCl substrate exhibit homeotropic mesogen orientation, since the films become birefringent only when they are rotated out of the polarization plane. Another apparent difference between the CNB and SMB film morphologies in Figures 2a and 3a is that the PS microdomains are larger in the SMB copolymer due to the higher molecular weight of the copolymer (see Table 2).

After 12 h of annealing at 105 °C (Figure 3b), the contrast between the blocks has improved noticeably, indicating that annealing in the smectic mesophase has improved the extent of phase separation between the PS and LC blocks. In marked contrast to the CNB film, the SMB film no longer appears birefringent upon annealing. This observation can only be translated to mean that the mesogens are homeotropically anchored to the substrate, in which case it immediately follows that the smectic layers are oriented parallel to the substrate. Recent SAXS measurements obtained from bulk specimens of the SMB copolymer have shown that the $i \rightarrow s$ transition at 112 °C (see Table 1) induces microphase separation in the copolymer, resulting in the formation of the cylindrical morphology.[12] As a consequence of these findings and TEM images acquired at different tilt angles (not shown), the electron-opaque circular projections visible in Figure 3b must correspond to PS cylinders oriented perpendicular to the surface. Since the aspect ratio of the cylinders (i.e., the ratio of the film thickness to the cylinder diameter) is only about 3−4, these cylinders are best described as short and stubby, but not quite disklike. Note in Figure 3b that the cylinders are not ordered on a hexagonal lattice, but rather exhibit liquidlike order. Another interesting feature of this image is that the cylindrical cross sections appear to possess different gray levels, which can be attributed to differences in mass density due to different cylinder lengths. Short cylinders exhibiting low levels of contrast (i.e., low gray levels) tend to form stringlike aggregates within the film.

As seen in Figure 3c, SMB copolymer films annealed for 24 h exhibit essentially the same morphological features as those in films annealed for 12 h (Figure 3b). This is likewise true for annealing times of 6 and 48 h (not shown). In some of the images collected from SMB films annealed for more than 24 h, discrete regions are observed in which the PS cylinders adopt a parallel orientation to the substrate surface. Examples of such regions are included for the sake of completeness in Figure 3c. Within these regions, the length of the cylinders is on the order of several hundred nanometers and is considerably longer than the film thickness. The microdomain period within these regions is about 60 nm, which is again larger than that in bulk specimens of the copolymer (48 nm). Note that the ends of the

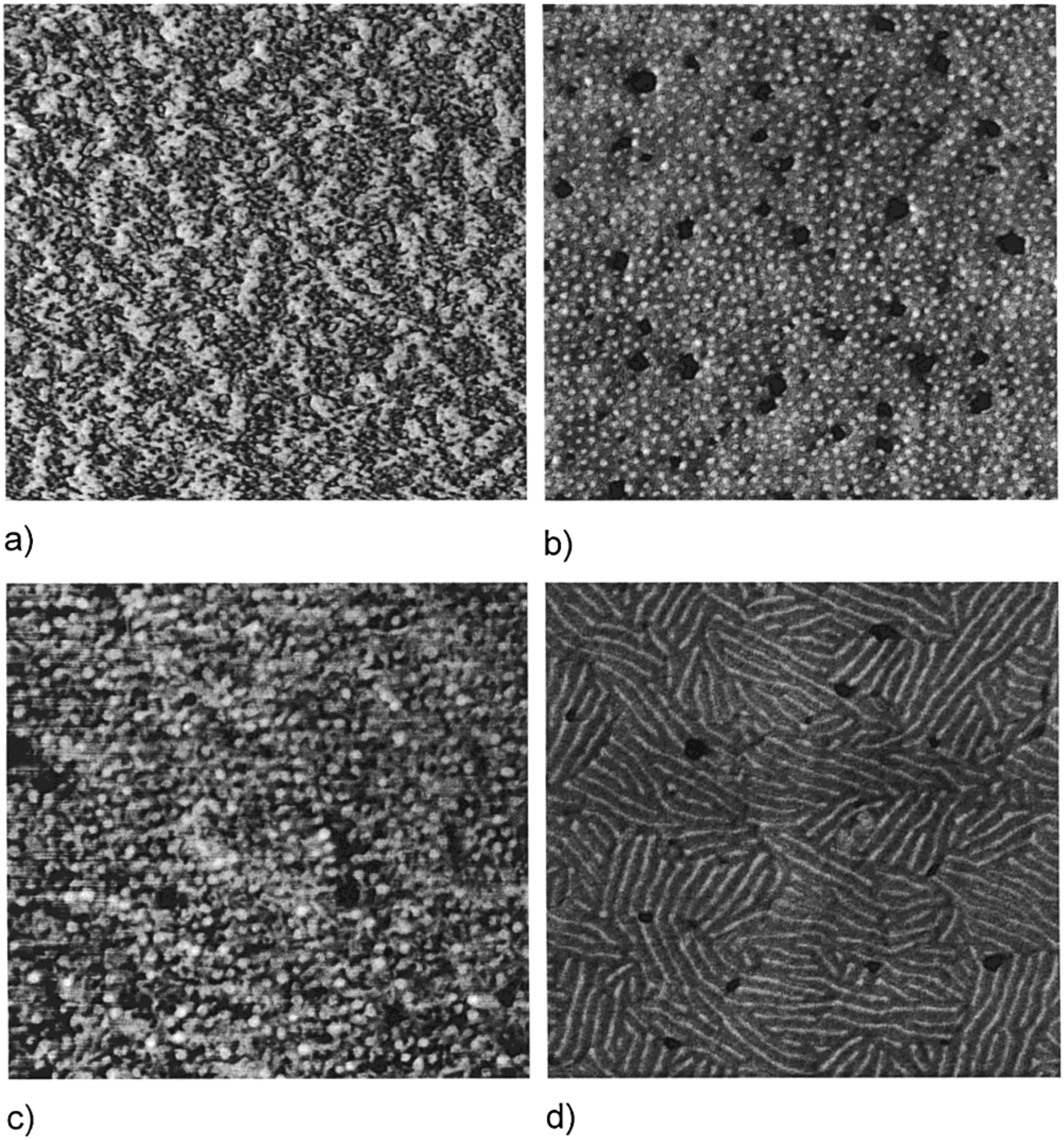

Figure 4. AFM phase images of a 2 × 2 μm^2 area of SMB block copolymer thin films deposited on NaCl and annealed for different times (in h) at 105 °C in the smectic mesophase: (a) 0, (b) 6, (c) 24, and (d) 86.

cylinders residing in the regions terminate in a disk possessing higher contrast. This feature indicates that the cylinders are not necessarily aligned parallel to the substrate but are instead curved in a plane normal to the film surface. The higher mass density evident at the end of the cylinders is indicative of a near perpendicular orientation of the cylinder axis. Accompanying the curved cylinders within these isolated regions are discrete entities, which appear to be remnants of vertically oriented cylinders that have not yet merged with the curved cylinders. A representative TEM image acquired of the SMB copolymer film after the longest annealing period (86 h) is presented in Figure 3d. While cylinders oriented parallel to the substrate surface have not been identified in the imaged regions, this observation should not be construed that such regions do not exist. Rather, it is more reasonable to suspect that they do not occur frequently. Compared to the images collected from films subjected to shorter annealing times (Figure 3b,c), the imaged regions show an increased propensity for the cylinders to aggregate and form connected strings.

Unlike the CNB block copolymer, the SMB copolymer exhibits a distinct surface morphology when prepared as a thin film. Phase images (obtained by AFM in tapping mode) of such films are provided as a function of annealing time in Figure 4. The contrast in these images originates from differences in hardness (or modulus) between the constituent block species. On the basis of this contrast mechanism, the bright regions are assigned to PS, which possesses a higher T_g than the SMB block. The surface of the unannealed film (Figure

4a) displays an irregular morphology comparable to the global morphology seen in the TEM image shown in Figure 3a. After 6 h of annealing at 105 °C (Figure 4b), any existing continuous PS-rich regions have disappeared, and the surface reveals a well-developed morphology composed of discrete PS cylinders possessing liquidlike positional order. The average distance between the disks is approximately 54 ± 2 nm, in favorable agreement with TEM. Recall that $d_0 = 48$ nm for this copolymer. Note that holes have formed on the surface of the annealed SMB copolymer film, because the film thickness does not accommodate an integral number of smectic layers. This surface morphology remains relatively constant up to annealing times of 12 h (not shown). Up to this point, the AFM phase images agree completely with images acquired by TEM.

Upon further annealing, however, the surface morphology imaged by AFM begins to change. Comparison of a typical AFM image acquired after an annealing time of 24 h (Figure 4c) to a comparable TEM image (Figure 3c) clearly reveals that the PS cylinders oriented perpendicular to the substrate appear much less distinct at the film surface. The surface consists of bright circular microdomains (the PS cylinders) on a more diffuse pattern of faint clusters composed of circular microdomains. The apparent difference between these TEM and AFM images can be explained if one assumes that the low-contrast clusters of PS observed by TEM are not resolved by AFM because they are located below the surface. In this case, the modulus contrast is lower than for cylinders protruding from the surface. Further comparison between the global morphology from TEM and the surface morphology from AFM gives the impression that the fluctuation of PS microdomains is enhanced near the film surface. This is attributed to the comparable surface tension of PS and the SMB block ($\gamma_c \approx 42$ mN/m). Unlike the case of the CNB copolymer in which PS covers the surface of the film at the film/air interface, the SMB copolymer undergoes substantial surface reorganization upon long-term annealing, first to a morphology composed of platelike structures (not shown) and eventually (after an annealing time of 86 h) to a morphology consisting of PS cylinders lying parallel to the surface (Figure 4d). Close examination of the image displayed in Figure 4d reveals that many of the PS microdomains terminate with bright spots, indicating that these ends extend through to the film surface. In addition, the thickness and contrast level of the microdomains are not completely homogeneous. These microdomains possess thick regions followed by thin regions that seem to have some memory of their formation from the original perpendicular cylinders observed in the early stages of annealing. Recall that TEM images of the SMB copolymer after identical annealing times (Figure 3d) show the development of stringlike aggregates in thin films of the SMB copolymer.

Images of the surface morphology, acquired by AFM, reveals that the morphological transformation most likely proceeds from the film/air interface to the interior of the film. This conclusion is formed on the basis of the pronounced change from perpendicular to parallel cylinder orientation evident at the film surface. Under comparable annealing conditions, the global morphology observed in TEM images continues to show a predominantly perpendicular cylindrical orientation. To better understand these morphological transformations, it is important to realize the concurrent development of LC order within the SMB films. A macroscopic measure of LC order and director orientation is the degree of birefringence. As mentioned earlier, as-cast films of the SMB copolymer do not yield any evidence of birefringence, indicating homeotropic orientation of the mesogens relative to the substrate. After 48 h of annealing at 105 °C, an increase in film birefringence is observed, suggesting that the smectic layers in regions of parallel cylindrical orientation are reoriented. This explanation is corroborated by a high-resolution TEM image (Figure 5) that shows regions wherein PS cylinders are oriented both perpendicular and parallel to the film surface. Close examination of the region with parallel cylinders shows the regular repeating pattern of another level of molecular organization due to the smectic layers of the SMB mesogens. The spacing of the smectic layers measured from this image is about 4−5 nm, in good agreement with the X-ray reflectivity results (3.4 nm) presented earlier in this work. Visualization of the smectic layers provides evidence that the layers are oriented perpendicular to the cylindrical axis and that the mesogens are homogeneously anchored to the surface of the PS cylinders. When the cylinders are oriented perpendicular to the film surface in Figure 5, the smectic layers are no longer detectable since they are viewed along their normal. On the basis of these considerations, the appearance of birefringence accompanying the morphological transition from perpendicular to parallel cylinders in SMB films must be related to reorientation of the smectic layers.

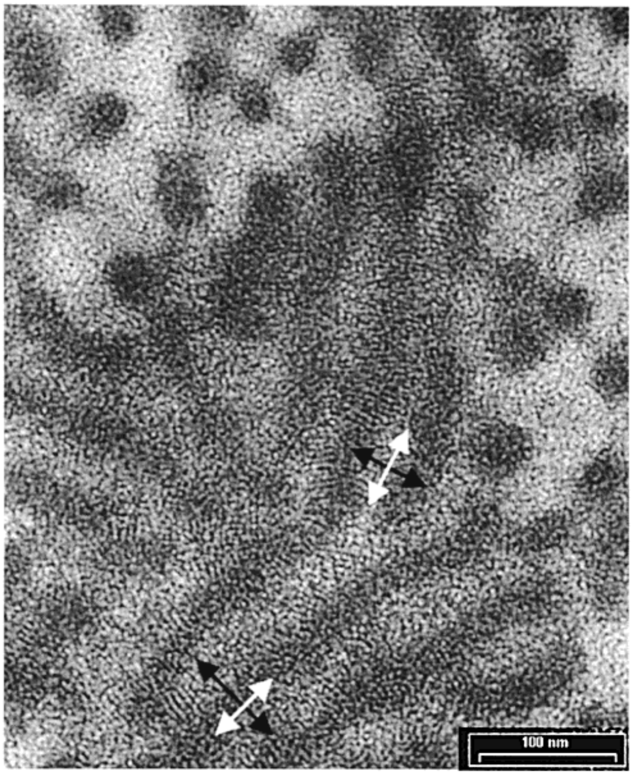

Figure 5. High-resolution TEM image of a smectic (SMB) block copolymer thin film obtained after solvent evaporation and annealing for 72 h at 105 °C in the smectic mesophase. Cylinders (dark) oriented both perpendicular and parallel to the film surface are evident, as are the smectic layers (in the lower left-hand corner). Examples of local smectic layers and cylinders oriented parallel to the surface are shown as black and white arrows, respectively.

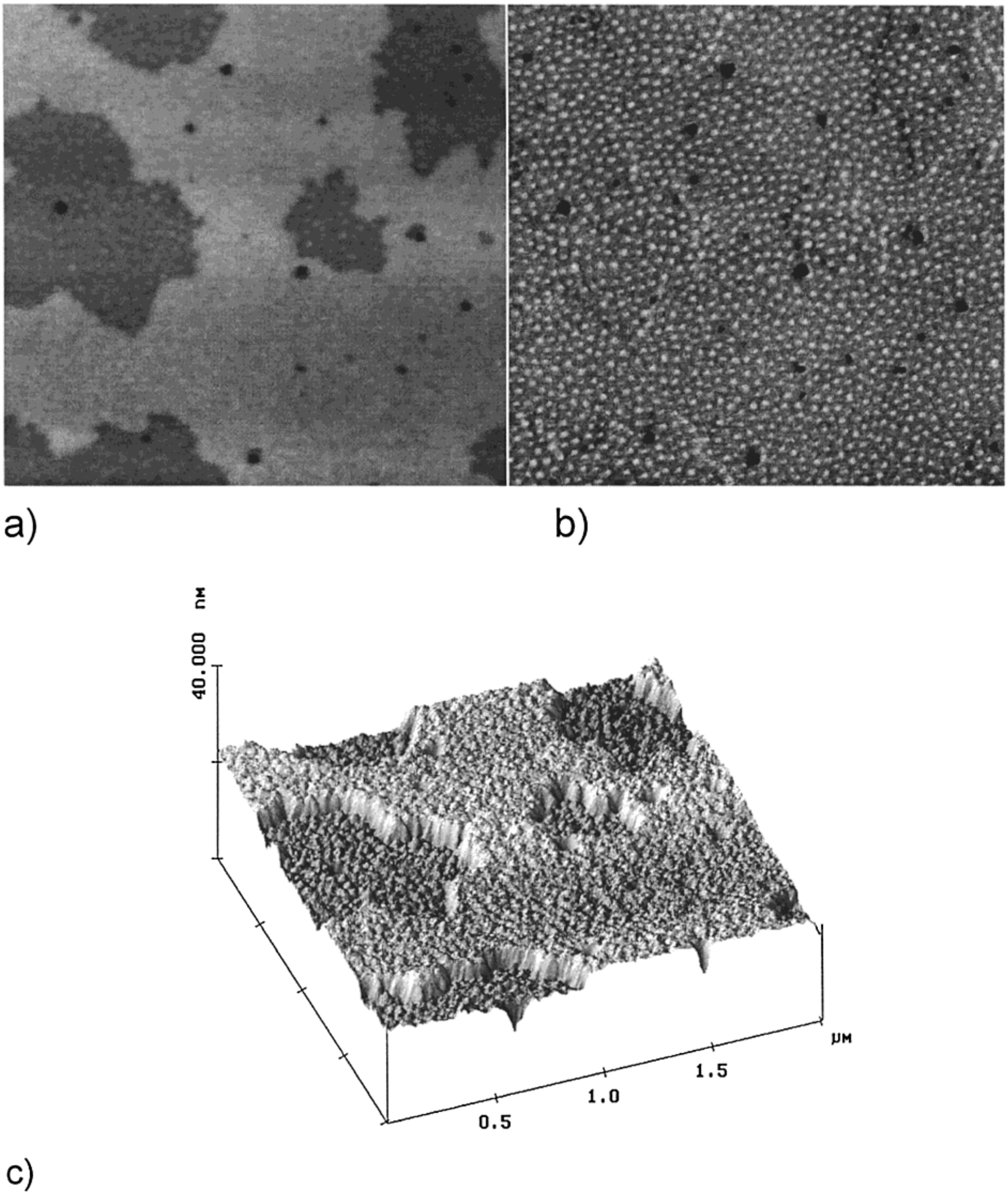

Figure 6. Representative (a) height, (b) phase, and (c) three-dimensional height images obtained by AFM in tapping mode of a $2 \times 2\ \mu m^2$ area of a smectic (SMB) block copolymer film prepared on Si and annealed for 86 h at 105 °C in the smectic mesophase. The height image shows film dewetting and the step height corresponding to the first smectic layer, whereas the phase image provides evidence for PS cylinders oriented normal to the film surface.

Smectic Block Copolymer Films on Si. To ascertain the influence of specific mesogen−substrate interactions, thin films of the SMB block copolymer have been prepared on Si wafers and subjected to the same annealing protocol used in the previous sections. Since the films could not be removed without damage from the surface (due to strong polar interactions between the SMB mesogens and the oxidized surface of the Si wafer), only the surface morphology has been examined here. In contrast to the SMB films prepared on NaCl, no morphological transition is observed. After 6 h of annealing at 105 °C, the initially disordered morphology fully transforms to a morphology composed of perpendicular cylinders. This morphology remains stable for annealing times up to 86 h. Figure 6 shows the height and phase images, as well as the three-dimensional representation of the height image, acquired from AFM in tapping mode of a film annealed for 86 h. The arrangement and order of the PS cylinders are reminiscent of the morphology observed after short annealing times in films cast on NaCl. The height image in Figure 6 clearly shows large areas that are depleted of the first smectic surface layer. It should be recognized that the step height in Figure 6c is equal to the thickness of one smectic layer as measured by X-ray scattering and reflectivity. In addition, several small holes are visible in the height and phase images in Figure 6. Recall that similar holes are observed in phase images of the SMB films produced on NaCl (see Figure 4) and are attributed to film dewetting.

Discussion

To employ theoretical arguments for thin films of isotropic block copolymers, we must first examine the stability of parallel and perpendicular morphologies in LC/i block copolymers by assessing the free energy (F) difference, viz.,

$$F_p - F_v = \Delta E_d - \Delta E_s + \Delta E_{LC,e} - \Delta E_{LC,s} \qquad (1)$$

where the subscripts p and v correspond to parallel and vertical (perpendicular) microdomain orientation. The first two terms have been introduced for isotropic block copolymers and analytically expressed in terms of structural parameters by Suh et al.[5] The term ΔE_d represents the energy difference due to the difference between the lattice period (d) of a block copolymer adopting a parallel orientation and d_0. In the case of the vertical orientation, it is assumed that the equilibrium period is the same as d_0. Last, ΔE_s designates the extra free surface energy of the vertical orientation relative to the parallel orientation. For hybrid LC/i block copolymers, we add the last two phenomenological terms, where $\Delta E_{LC,e}$ is the difference in the elastic free energy of the LC mesophase and $\Delta E_{LC,s}$ denotes the difference in the free surface energies of orientational wetting (homeotropic vs homogeneous) of the vertical orientation relative to the parallel orientation. Note that a free energy difference due to orientational wetting at internal microdomain interfaces does not appear in eq 1. As previously demonstrated for the CNB and SMB block copolymers in ref 9 and Figure 5, respectively, anchoring at internal interfaces is homogeneous for both the parallel and vertical orientations.

First, we discuss the CNB block copolymer. Over the course of the entire annealing period (within the nematic mesophase), only the parallel cylindrical orientation is observed. This morphology increases substantially in its degree of order with increasing annealing time. The film thickness allows for only one layer of PS cylinders positioned between surface layers of PS at the substrate/film and film/air interfaces. The TEM images displayed in Figure 2 reveal a large equilibrium distance in the film, with $d \sim 1.35d_0$. An important question to address at this juncture is whether the concomitant increase in microdomain energy (ΔE_d) can be compensated by the relatively small gain in surface energy (ΔE_s) due to migration of PS to the surface. By applying the stability criterion of Suh et al.[5] for parallel and vertical microdomain orientations in thin films of isotropic block copolymers and by using (i) measured interfacial energies at the film/air interface, (ii) an estimated negligible interfacial energy difference at the NaCl interface, and (iii) an estimated intermicrodomain interfacial energy, it is reasonable to expect that the vertical orientation is the most stable.

The observed parallel orientation of the PS cylinders in films of the CNB copolymer must therefore be a consequence of a difference in either the elastic interactions ($\Delta E_{LC,e}$) or orientational interfacial interactions ($\Delta E_{LC,s}$) associated with the nematic mesophase. Since we assume homogeneous anchoring of the mesogens at the surfaces of the PS cylinders, there is no reason to account for an elastic free energy difference between the parallel and vertical orientations of the CNB block copolymer, i.e., $\Delta E_{LC,e} = 0$. On the other hand, we expect a difference between parallel and vertical orientational wetting. As a consequence of the parallel orientation of both the PS cylinders and the nematic director (due to homogeneous mesogen anchoring at internal interfaces), the orientational wetting at the external film interfaces will be homogeneous (if the cylinders adopt a parallel orientation) and homeotropic (if the cylinders adopt a vertical orientation). The external surfaces on both sides of the film consist of PS. Since homogeneous mesogen anchoring at these interfaces must also be ensured, the system gains additional free orientational surface energy (i.e., $\Delta E_{LC,s} > 0$) for orienting the PS cylinders parallel to the substrate. In other words, the specific interfacial interaction of the isotropic block is enhanced by the homogeneous orientational wetting of the LC block and is therefore able to balance the relatively large stretching energy associated with the parallel cylindrical orientation.

In marked contrast to the morphology development in thin films of the CNB copolymer, the PS cylinders in the SMB block copolymer are found to orient perpendicular to the film surface in films prepared on NaCl and annealed for intermediate times in the smectic mesophase. Since the mesogens remain homogeneously anchored at internal surfaces, orientational interactions at internal interfaces are the same as in the case of the CNB copolymer. A comparable parallel orientation of the SMB copolymer with one layer of PS cylinders residing in the center of the film is not possible by virtue of the film thickness (55 nm), the equilibrium cylinder distance (48 nm), and the corresponding high-energy penalty. It is likewise improbable that PS layers can form at both film surfaces with vertically oriented smectic layers lying between the PS surface layers. On the basis of these issues, a vertical cylindrical orientation is expected on the basis of both the microdomain free energy (ΔE_d) and the surface energy (ΔE_s). If one considers the parallel anchoring of mesogens at the cylinder surfaces, then vertical cylindrical orientation implies homeotropic anchoring of the mesogens at the film interfaces (i.e., parallel orientational wetting of the exterior interfaces by the smectic layers). In fact, such anchoring on free or neutral surfaces is typical for side-chain polymer LCs having side groups that terminate with an aliphatic moiety.[27] According to Scheme 1, the mesogen in the SMB copolymer satisfies this requirement. Thus, the perpendicular cylindrical orientation receives an additional energy gain due to the free energy associated with the orientational wetting of the LC block ($\Delta E_{LC,s} < 0$). The elastic free energy of the director field is also apparently minimized in this situation ($\Delta E_{LC,e} = 0$).

Despite the relaxed conformational energy and favorable interfacial interactions of the mesogens in the case of the vertical cylindrical orientation, a very small difference in surface tension between PS and SMB apparently induces reorganization of the PS microdomains, forcing them to orient parallel to the surface at the film/air interface after lengthy annealing times. This morphological reorganization is accompanied by fluctuation of the smectic layer normals, as demonstrated by the increase in birefringence. It is assumed that the undulation amplitudes are enhanced across the film proceeding from the substrate/film to the film/air interface driven by the parallel arrangement of the cylinders at the film/air interface. Such reorientation of the PS cylinders and the smectic director does not occur in films prepared on Si. Stronger homeotropic anchoring of the mesogens on the Si surface (due to hydrogen bonds) is apparently responsible for the stability of the vertical orientation. The long-range nature of mesogenic anchoring is crucial for an understanding of the stability of the vertical orientation, since the elastic forces exerted by the smectic layers prevent bending of the PS cylinders in the vicinity of the surface. The parallel orientation of the smectic layers may extend as far as 100 nm into the bulk copolymer.[27] The only degrees of freedom remaining that can permit reorientation of the cylinders arise from sliding of the smectic layers or the motion of cylinders within the layers. Both processes are hindered by high viscosity or elastic forces due to the triblock nature of the copolymer. Rearrangement of the PS microdomains is facilitated if a component of motion exists in the vertical direction. Such motion can be realized if one assumes that the smectic layers undulate due to weak mesogen anchoring at the substrate, as in the case of NaCl. Recently, Auernhammer et al.[28] have demonstrated that such undulations constitute a prestage of instabilities in layered systems under shear. Only slight fluctuations of the smectic layers in the vicinity of the substrate propagate at distances removed from the substrate/film interface. With this in mind, it immediately follows that the rearrangement of perpendicular cylinders to parallel cylinders and stringlike elements at the film/air interface in SMB copolymer films are most likely induced by a combination of (i) minimization of the surface free energy of the PS block and (ii) subtle undulations of the smectic layers. The results presented here suggest that a lower surface tension of the isotropic block may not be sufficient to induce a transformation from vertical to parallel cylindrical orientation in a smectic block copolymer if the homeotropic mesogen anchoring at the substrate is strong (as in the case of the Si wafer).

Conclusions

The present morphological study of thin films composed of hybrid LC/i block copolymers exhibiting the cylindrical morphology has demonstrated that mesogenic anchoring at internal microdomain interfaces and at external film interfaces plays a key role in elucidating the mechanism of microdomain ordering. Homogeneous mesogen anchoring at microdomain interfaces strongly couples the alignment of the cylinder axis to the LC director in copolymers possessing nematic and smectic blocks. The ordering of isotropic cylinders with respect to external surfaces therefore depends on the orientational wetting of the LC block on the film surfaces. The nature of the film surface depends sensitively on the surface energies of the blocks relative to the substrate and to air. If, on one hand, the isotropic block interacts preferentially with the surface (as in the case of the CNB copolymer examined here), the block will form layers at the surface, which favors parallel alignment of the nematic director and, consequently, the cylinders with respect to the film surfaces. If, on the other hand, a strong chemical interaction exists between the substrate and the LC block (as in the case of the SMB copolymer on Si), the director of the smectic mesophase is anticipated to lie perpendicular to the substrate, thereby compelling the isotropic cylinders to orient in the same direction. Through elastic forces induced by the smectic field, this orientation is stabilized even though the free energy at the film/air surface is not minimized. When the LC/substrate interaction is reduced (as in the case of the SMB copolymer on NaCl), fluctuations in the smectic director permit reorganization of the surface morphology due to surface energy considerations originating from the film/air interface. Because of the homogeneous coupling of the mesogens to the microdomains, reorientation of the smectic director is accompanied by reorientation of the isotropic cylinders in close proximity to the film/air interface. In the present case, this process is very slow due to the high molecular weight of the SMB block copolymer, and the morphology observed at long annealing times (86 h) is probably not the equilibrium morphology. How far the reorganization would go in thin films composed of a lower molecular weight copolymer (or in a diblock copolymer) and would complete reorientation of the smectic director and cylindrical microdomains be possible remain open questions at the present time.

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