Orientational Wetting in Hybrid Liquid Crystalline Block Copolymers

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The wetting behavior of hybrid isotropic/smectic block copolymers is examined. For symmetric diblocks, the generic parallel ordering of the lamellae is suppressed, and the copolymer wets the surface with the lamellae perpendicular to the surface. The parallel ordering, however, can be restored in asymmetric lamellar diblocks. We propose an explanation in terms of block-specific interface wetting, and configurational frustration induced by the incommensurability between the smectic spacing and the smectic block size defined by the diblock lamellar period. [S0031-9007(96)01913-8]

Diblock copolymers, which consist of two chemically distinct homopolymer subchains *A* and *B* joined covalently at one end, can self-assemble into spatially periodic bulk phases via an order-disorder transition. The nature of this transition is determined by the total degree of polymerization N, and the *A-B* segment-segment Flory-Huggins interaction parameter χ_{AB}, which is a measure of the component incompatibility. Since the immiscible polymer components are irreversibly tethered at one end, macroscopic phase segregation is not possible. The system will instead separate into microscopic domains, the sizes of which are determined by the competition between entropic losses associated with polymer chain stretching, and enthalpic penalties associated with interface formation. Morphologies consisting of lamellae, cylinders, spheres, or even topologically complex bicontinuous phases can be formed in this process, depending on the volume fractions of the components, Φ_A or Φ_B [1].

The ordering of configurationally complex fluids such as block copolymers, however, can be influenced by the presence of a surface. An isotropic lamellar diblock film usually forms a macromolecular "stack" parallel to the surface, with a period L_0 equal to the thickness of an *ABBA* sequence [2–6]. The thickness of this ordered film must belong to a discrete spectrum of allowed values d_n, where $d_n = (n + 1/2)L_0$, or $d_n = nL_0$, depending on the interfacial segregation behavior of the blocks in the system [3]. If the thickness d of the film is incommensurate with these values, say $d_n < d < d_{n+1}$, then the system will separate into coexisting domains of thicknesses d_n and d_{n+1} [6], in a process which has been compared to 2D topological coarsening [7]. Experimental and theoretical results on isotropic diblocks confined between parallel hard walls have illustrated the effects of frustration between the lamellae period and an externally imposed length scale [8–12]. Side-chain liquid crystal polymers have recently been incorporated into diblock copolymers [13–14], where the smectic ordering of side groups can lead to the competition between two inherently different length scales, and can frustrate generic diblock ordering.

In this Letter, we investigate the influence of this hybrid isotropic-smectic macromolecular architecture on the thin film morphology of lamellar diblock copolymers, using a combination of x-ray specular reflectivity (XSR) and atomic force microscopy (AFM) to gain access to complementary real-space and reciprocal-space information. For symmetric diblocks, we found that the parallel ordering of the lamellae is suppressed, and the copolymer wets the surface with the lamellae perpendicular to the surface. The parallel ordering of lamellae, however, can be restored in asymmetric lamellar diblocks. We provide an explanation for this transition in terms of block-specific interface wetting and the configurational frustration induced by the incommensurability between the smectic spacing and the smectic block size defined by the diblock lamellar period.

The hybrid isotropic/mesogenic diblock copolymer used in this study is PS-PChEMA [Fig. 1(a)], with molecular weights (M_n) ranging from 35 000 g/mol to 71 000 g/mol at a polydispersity of ~ 1.1, and is expected to be in the strong segregation limit ($\chi_{AB}N \gg 10$) [13]. The PChEMA mesogenic block exhibits an interdigitated smectic-A_d phase with a layer spacing of 45 Å and a typical phase sequence of g_{PS}:101 °C:g_{PChEMA}:126 °C: S_A:187 °C:I [13]. Moreover, the direction of smectic layering is orthogonal to the direction of the lamellar microphase segregation in the bulk.

Thin films of the diblock copolymer were prepared by spin coating toluene solutions onto float glass substrates, which were cleaned in chromic acid for 24 h, then in sulphuric acid for 5 min, and followed by a deionized water rinse. The cast films were dried, and then annealed at 170 °C for 60 h under vacuum. All measurements were performed at room temperature, after the samples had been frozen into their glassy states.

For the XSR measurements [15], the sample is mounted on the inner stage of a two stage oven in a dry N_2 environment. The oven is then coupled to a triple axis diffractometer, with the surface normal of the sample parallel to the z axis of the instrument. For measurements of samples thinner than 700 Å, the incident
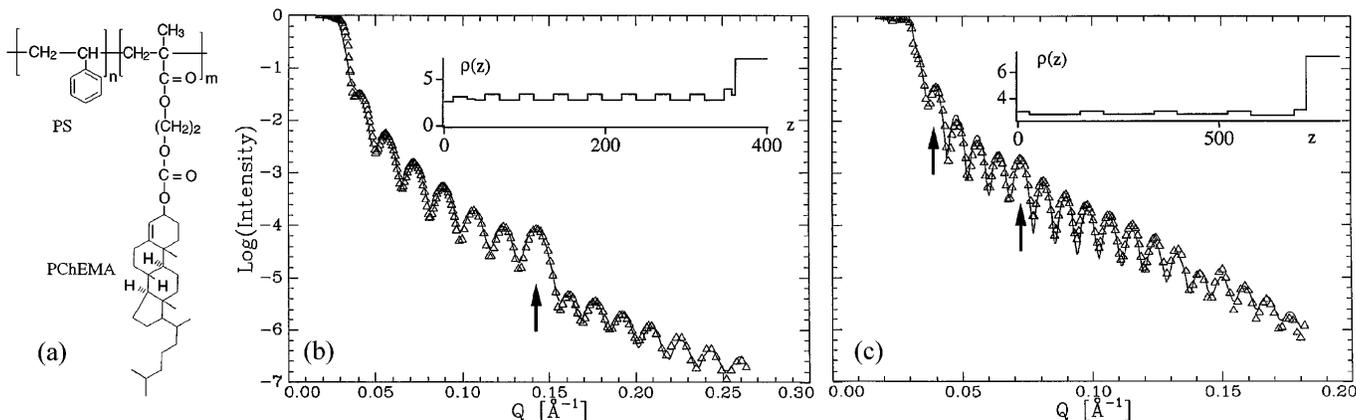
FIG. 1. (a) PS-PChEMA: poly[styrene-block-2-((3-cholesteryloxycarbonyl)oxy)ethylmethacrylate]. (b) The measured and calculated XSR for a 360 Å film of a symmetric PChEMA-PS diblock ($\Phi_{PS} = 0.49, M_n = 57\,000$ g/mol). (c) The measured and calculated XSR for a 720 Å film of an asymmetric PChEMA-PS diblock ($\Phi_{PS} = 0.64, M_n = 36\,000$ g/mol): The low order quasi-Bragg peaks on (b) and (c) are marked with arrows. Electron density profiles $\rho(z)$ used to model the data are shown as insets: z and $\rho(z)$ are expressed in Å's and arbitrary units, respectively.

Cu-$K\alpha$ beam ($k = 2\pi/\lambda = 4.07$ Å^{-1}) is monochromatized and focused using a bent graphite (002) crystal, giving an in-plane resolution of $\Delta q_z = 5.7 \times 10^{-3}$ Å^{-1}, after having been defined by slits. In order to resolve diffraction features from thicker samples, Ge(111) monochromator and analyzer crystals are used nondispersively to select the Cu-$K\alpha_1$ component, which result in a resolution of $\Delta q_z = 7.0 \times 10^{-4}$ Å^{-1}. Further details are described elsewhere [16]. The AFM work was performed with a Nanoscope II commercial AFM operating in the constant force mode at $\sim 2 \times 10^{-8}$ N. The results are independent of the contact forces used in the measurements, and successive scans show no change in the surface topographies.

XSR is sensitive to the modulations of the average electron density $\rho(z)$ along the surface normal, and measurements for representative PS-PChEMA symmetric diblock films ($\Phi_{PS} = 0.49, M_n = 57\,000$ g/mol) are shown in Fig. 1(b). The data have been background subtracted, and the standard geometrical correction for the beam "footprint" have been applied. The FWHM of a typical transverse "rocking" scan across the specular reflectivity is $\sim 0.045°$. Fits to the data have been calculated with an iterative matrix solution of the Fresnel equations for the reflectivity of the multilayer system, using periodic "slab" profiles of electron densities separated by interfaces with Gaussian roughness [16,17]. A schematic of the model electron density profile is also included. The higher electron density at the center of a smectic layer is attributed to the more efficient packing of the interdigitated PChEMA side groups. The thickness of the PS-PChEMA film obtained from the fit is 360 Å. No evidence of quasi-Bragg peaks that correspond to the lamellar spacing of ~ 300 Å is evidenced. However, a developing quasi-Bragg peak can be observed, with an associated periodicity of 42 Å, which corresponds closely to the bulk smectic spacing of the PChEMA homopolymer, and implies that the smectic layers are parallel to the surface, with the mesogenic side

groups anchoring homeotropically, perpendicular to the surface [18]. We observed the same homeotropic anchoring behavior in XSR measurements of PChEMA homopolymer thin films.

The surface topography of a representative sample of the same compound prepared under identical conditions has been measured with AFM [Fig. 2(a)]. The average thickness of the sample is ~ 330 Å, and two terraces with an average height difference of 50 Å can be observed, which is comparable to the thickness of a smectic layer. This is consistent with the previous x-ray observation, and confirms that the smectic layers formed from the mesogenic side groups are parallel to the surface. The serpentine corrugations on the terraces have an average in-plane spatial period of $\sim 320 \pm 40$ Å, which is essentially L_0, the ABBA lamellar period. The combination of XSR and AFM results unambiguously indicates that the generic ordering found in isotropic symmetric diblock films, where the lamellae are parallel to the surface, has been suppressed in these hybrid diblock films [Fig. 2(b)]. The anchoring of the mesogenic groups dominates the wetting, and the hybrid diblock lamellae order in a direction perpendicular to the surface. Similar results are obtained from other nearly symmetric diblocks ($\Phi_{PS} = 0.43$) with a lower molecular weight of $M_n = 35\,000$ g/mol.

The wetting behavior of an asymmetric lamellar diblock with an increased PS content ($\Phi_{PS} = 0.64$) at a molecular weight of $M_n = 36\,000$ g/mol, however, is quite different. Figure 1(c) contains an XSR measurement from a 720 Å thick sample. The characteristic quasi-Bragg feature of the mesogenic ordering has disappeared, and has been replaced by a new set of quasi-Bragg features that correspond to the block copolymer lamellar periodicity of $L_0 = 154$ Å. In order to model the data, the electron densities for PS and PChEMA have been calibrated by independent reflectivity measurements of homopolymer thin films. These data also indicate that the component which wets both the
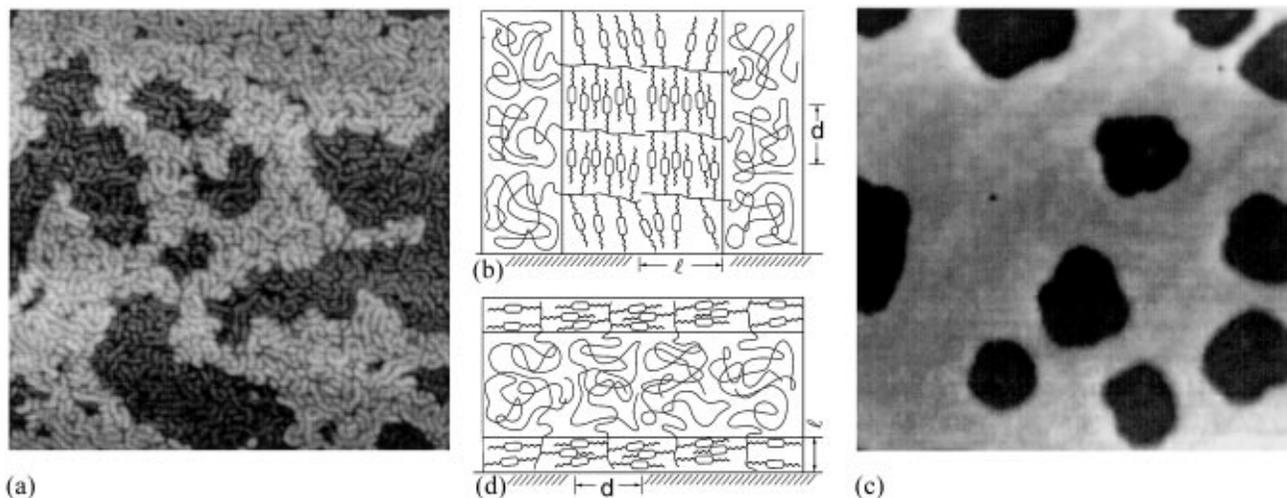
FIG. 2. (a) Perpendicular wetting of the hybrid lamellae in a symmetric ($\Phi_{PS} = 0.49, M_n = 57\,000$ g/mol) PS-PChEMA diblock film, as observed by AFM (2.0×2.0 μm^2 viewing area): The in-plane corrugation period is $\sim 320 \pm 40$ Å, which is essentially L_0. (b) A schematic representation of perpendicular wetting: Note relative sizes of the smectic spacing d and the interfacial block size ℓ: $\ell > d$ and $\ell \neq Nd$, where N is a positive integer. (c) Generic parallel wetting of the hybrid lamellae in an asymmetric ($\Phi_{PS} = 0.64, M_n = 36\,000$ g/mol) diblock film, as observed by AFM (4.0×4.0 μm^2 viewing area): The height difference between the two domains is $\sim 150 \pm 15$ Å, which is equal to L_0 for this diblock. (d) A schematic representation of parallel wetting: $d > \ell$.

air-copolymer interface and the copolymer-glass interface is PChEMA.

A representative 330 Å thick sample of the same compound prepared under identical conditions has been measured with AFM [Fig. 2(c)]. Generic ordering found in isotropic lamellar diblock films has been restored: The system has formed coexisting domains of PS-PChEMA macromolecular "stacks" parallel to the surface. The average height difference ($d_{n+1} - d_n$) between the majority and minority domains is 150 ± 15 Å, which is essentially L_0, and is consistent with XSR measurements. The smectic layers of PChEMA are now perpendicular to the surface and the block lamellae [Fig. 2(d)].

In order to understand the orientational wetting behavior of these hybrid block copolymers, we consider first the corresponding behavior in isotropic block copolymers. At equilibrium, wetting layers with the lamellae perpendicular to the surface have never been experimentally observed in films of diblocks with two isotropic components; a macromolecular stack is always formed parallel to the surface. This orientational behavior of a symmetric diblock film at equilibrium has received extensive theoretical attention [11,19]. The work per unit area Δ required to change from perpendicular to parallel wetting of the lamellae can be written as [19]

$$\Delta = \frac{a}{V} \left(-c_w V^1 - c_e V^{1/9} + c_n V^{1/3} \right).$$

V is the volume occupied by a chain, a is a monomer length, and c_w, c_e, and c_n are constants. The first term describes the differential contact interaction and usually dominates the wetting: If either component is preferentially adsorbed at one or both of the interfaces, then the system will favor a parallel ordering of the lamellae and their inter-

faces by enforcing a maximal wetting of that component. The second term accounts for an entropic bonus associated with the parallel orientation. Each free chain end lowers the free energy of the copolymer-wall interface by $\sim kT$. Since the density of chain ends is significantly higher at the mid plane (*A-A* or *B-B*) interfaces [20], a parallel ordering of the lamellae will maximize this entropy gain. Finally, the chains are more easily stretched along a wall than they are in the bulk, because of the effective nematic interaction that the hard wall exerts to limit the conformations of the polymer segments near it. This favors the perpendicular orientation and is described by the third term. The main chain of bulk PChEMA, however, is already partially confined to the interstices between the smectic layers, so this effect cannot explain our observations.

Since PChEMA readily wets both the quartz and air interfaces, and since PS is usually repelled from hydrophilic substrates, intuition informed by theoretical descriptions of isotropic diblocks suggests that the contact interaction should dominate and lead to parallel wetting of the lamellae, with homeotropic PChEMA at both interfaces. For PS-PChEMA, however, homeotropic anchoring of the PChEMA side groups is inherently antagonistic to parallel wetting, because it necessarily generates defects and extra unfavorable segment-segment contact near PS-PChEMA interfaces. More important, the equilibrium bulk lamellar period L_0 defines a thickness ℓ for the PChEMA block at the interface, which is in general not commensurate with the thickness of an integral number of homeotropic smectic layers. The value of ℓ calculated from L_0 and Φ_{PS} for the samples used in Figs. 1(b) and 2(a) is 76 Å, which is between one and two bulk smectic layers thick (~ 45 Å). This incommensuration between smectic ordering and ℓ

exist in all of our samples which exhibit perpendicular wetting. The frustration from both effects, however, can be avoided in perpendicular wetting of the lamellae, where homeotropic anchoring is maintained without layer incommensuration, but at the cost of some unfavorable PS wetting at the substrate.

As the volume fraction Φ_{PS} increases for a PS-PChEMA diblock at a fixed total molecular weight, however, the area of unfavorable PS wetting must increase at the expense of the area of favorable PChEMA wetting, and contribute to a destabilization of the perpendicular lamellae arrangement. Furthermore, confinement effects become important as the size of the PChEMA block decreases. For the samples described by Figs. 1(c) and 2(c), the size of the PChEMA block wetting the substrate is 28 Å, which is less than the bulk smectic spacing. One may expect the smectic phase to be destabilized as its lateral extent is reduced to the order of a smectic spacing. Moreover, it is clear that homeotropic anchoring can no longer be maintained within this confined volume in parallel wetting. Since the effects favoring perpendicular wetting are contingent on homeotropic anchoring, which is no longer possible, generic parallel wetting of the lamellae is restored. By comparison, thick films of asymmetric PS-PChEMA diblocks at a similar volume fraction ($\Phi_{PS} = 0.68$) but larger molecular weight ($M_n = 71\,000$ g/mol), which have similar contact interactions but no confinement of the mesogenic block, roughens irreversibly with annealing. This suggests that the contact interaction alone cannot account for the observations, and that mesogenic block confinement is necessary to obtain the parallel ordering generic to isotropic diblocks.

In summary, hybrid isotropic-smectic diblock copolymers can wet a surface with its lamellae parallel or perpendicular to the surface. We propose an explanation in terms of block-specific interface wetting and the configurational frustration induced by the incommensurability between the system's two internal length scales. Moreover, with a propitious choice of hybrid liquid crystalline diblock, this result may have applications in nanolithography.

[1] See, for example, F. S. Bates and G. H. Frederickson, Annu. Rev. Phys. Chem. **41**, 525 (1990), and references therein.

[2] K. R. Shull, Macromolecules **25**, 2122 (1992).

[3] G. Coulon, T. P. Russell, V. R. Deline, and P. F. Green, Macromolecules **22**, 2581 (1989); T. P. Russell, G. Coulon, V. R. Deline, and D. C. Miller, Macromolecules **22**, 4600 (1989).

[4] S. H. Anastasiadis, T. P. Russell, S. K. Satija, and C. F. Majkrzak, Phys. Rev. Lett. **62**, 1852 (1989); S. H. Anastasiadis, T. P. Russell, S. K. Satija, and C. F. Majkrzak, J. Chem. Phys. **92**, 5677 (1990).

[5] M. D. Foster, M. Sikka, N. Singh, F. S. Bates, S. K. Satija, and C. F. Majkrzak, J. Chem. Phys. **96**, 8605 (1992).

[6] G. Coulon, B. Collin, D. Ausserre, D. Chatenay, and T. P. Russell, J. Phys. (Paris) **51**, 2801 (1990); M. Maaloum, D. Ausserre, D. Chatenay, G. Coulon, and Y. Gallot, Phys. Rev. Lett. **68**, 1575 (1992).

[7] P. Bassereau, D. Brodbeck, H. R. Brown, and T. P. Russell, Phys. Rev. Lett. **71**, 1716 (1993); G. Coulon, B. Collin, D. Chatenay, and Y. Gallot, J. Phys. II (Paris) **3**, 697 (1993); D. Aussere, D. Chatenay, G. Coulon, and B. Collin, J. Phys. (Paris) **51**, 2571 (1990).

[8] P. Lambooy, T. P. Russell, G. J. Kellogg, A. M. Mayes, P. D. Gallagher, and S. K. Satija, Phys. Rev. Lett. **72**, 2899 (1994).

[9] G. J. Kellog, D. G. Walton, A. M. Mayes, P. Lambooy, T. P. Russell, P. D. Gallagher, and S. K. Satija, Phys. Rev. Lett. **76**, 2503 (1996).

[10] M. S. Turner, Phys. Rev. Lett. **69**, 1788 (1992).

[11] M. S. Turner, A. Johner, and J.-F. Joanny, J. Phys. I (Paris) **5**, 917 (1995).

[12] D. G. Walton, G. J. Kellog, A. M. Mayes, P. Lambooy, and T. P. Russell, Macromolecules **27**, 6225 (1994).

[13] H. Fischer, S. Poser, and M. Arnold, Liq. Cryst. **18**, 503 (1995); H. Fischer, S. Poser, and M. Arnold, Macromolecules **27**, 7133 (1994).

[14] J. Adams and W. Gronski, Macromolek. Chem. Rap. Commun. **10**, 553 (1989); R. Bohnert and H. Finkelmann, Macromol. Chem. Phys. **195**, 689 (1994); I. E. Serhatti, G. Galli, Y. Yagci, and E. Chiellini, Pol. Bull. **34**, 539 (1995); M. Yamada, T. Iguchi, A. Hirao, S. Nakahama, and J. Watanabe, Macromolecules **28**, 50 (1995).

[15] T. P. Russell, Mater. Sci. Rep. **5**, 171 (1990).

[16] E. A. Mol, J. D. Shindler, A. N. Shalanginov, and W. H. de Jeu, Phys. Rev. E **54**, 536 (1996).

[17] Reflectivity analysis program SPEEDO, M. Knewtson, R. M. Suter, and J. D. Shindler. See also L. G. Parratt, Phys. Rev. **95**, 359 (1954).

[18] For a review of anchoring, see, for example, B. Jerome, Rep. Prog. Phys. **54**, 391 (1991); B. Jerome, J. Commandeur, and W. H. de Jeu (to be published).

[19] G. T. Pickett, T. A. Witten, and S. R. Nagel, Macromolecules **26**, 3194 (1993).

[20] However, the localization of the chain ends is not likely to be as strong as that assumed by [19]. See, for example, M. W. Matsen and F. S. Bates, Macromolecules **28**, 8884 (1995), and references therein.