Surface Reconstruction of an Ordered Fluid: An Analogy with Crystal Surfaces

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The surface structure of a lamellar polystyrene-*block*-polybutadiene-*block*-polymethylmethacrylate (SBM) triblock copolymer forms a complex reconstruction, which breaks the two-dimensional continuous translational symmetry of an ideal (homogeneous) SBM surface. Despite the very different types of matter and order, our findings reveal a remarkable analogy with the well-known phenomenon of surface reconstruction of single crystals, in particular, with the (2 × 1) "buckling row" reconstruction of the Si(100) surface. Similarities and differences between both classes of materials are discussed on the basis of symmetry considerations.

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The identification of analogous behavior of rather different types of matter is an important aspect of science since it can reveal the generality of the underlying concepts of physics. In the present Letter we follow this line and discuss the analogy between the surface structure of a mesoscopically ordered complex fluid and the well-known surface reconstructions of inorganic single crystals. In general, the presence of a surface can alter the equilibrium structure of any (ordered) system by a local rearrangement of matter leading to a state of lower (surface) free energy. As an example, the surface structures of many inorganic crystals differ both in the characteristic spacings as well as in their symmetry from the respective bulk crystal structure. Typical examples are the Si(111)-(7 × 7) [1] and the Si(100)-(2 × 1) "buckling row" reconstructions [2–4].

Block copolymers are long chain molecules composed of two or more blocks of different chemical composition. A frequent incompatibility between the constituent blocks together with their molecular connectivity gives rise to the formation of ordered microdomain structures, which exhibit crystal-like order on mesoscopic length scales [5]. Together with surfactant solutions and liquid crystals, block copolymers belong to the class of ordered complex fluids, which often form regular structures with lamellar and cylindrical microdomains. In recent years, the influence of boundary surfaces on the microdomain structure of block copolymers has received increasing attention, both experimentally [6–11] and theoretically [11–15]. However, a thorough comparison between the phenomena observed at the free surface of an ordered fluid and the well-studied behavior of single crystal surfaces is still lacking. While crystals have point-group symmetry, ordered complex fluids often belong to more general space groups and display higher degrees of symmetry. In this Letter, we show that despite the very different types of matter and order a complex fluid can form a surface reconstruction. This finding extends the analogy between ordered fluids and crystals and reveals common underlying fundamentals.

As a model system, we investigate the *free* surface structure of thin films of a polystyrene-*block*-polybutadiene-*block*-polymethylmethacrylate (SBM) triblock copolymer with almost equal block volume fractions, which exhibits a lamellar microdomain structure in the bulk [16]. When thin films of this material are prepared on a polar substrate like SiO_x, the polymethylmethacrylate (M) end block is expected to accumulate preferentially on the substrate thereby aligning the lamellae parallel to the plane of the film [6,17]. In the absence of specific surface interactions, one would expect the film to be terminated by one of the two lamellar sublayers SBM or MBS, respectively, both leading to a laterally homogeneous, "ideal" surface exhibiting two-dimensional continuous translational symmetry. However, the near-surface region of SBM films exhibits a complex reconstruction, which breaks the symmetry of the ideal surface and exhibits striking similarities with the Si(100)-(2 × 1) surface reconstruction. In the following, we present the experimental data on the block copolymer surfaces, briefly recall the results known for Si(100)-(2 × 1), and finally discuss similarities between both phenomena on the basis of symmetry considerations.

SBM triblock copolymer films with thicknesses in the range 100–1000 nm were prepared on polished Si wafers by dip coating from a 5 wt % polymer solution in chloroform (SBM molecular weight $M_W = 162$ kDa; volume fractions $\Phi_{PS} = 0.33$, $\Phi_{PB} = 0.47$, $\Phi_{PMMA} = 0.20$, where PS is polystyrene, PB is polybutadiene, and PMMA is polymethylmethacrylate [16]). In order to drive the system towards thermodynamic equilibrium, the films were exposed to chloroform vapor at 95% saturation for 1 day and dried subsequently, by reducing the vapor pressure continuously over a period of 10 h. This procedure resembles the preparation used for bulk samples of the same material [16]. The resulting thin film samples were investigated by optical microscopy, TappingMode^{TM} scanning force microscopy (SFM), transmission electron microscopy (TEM), and scanning electron microscopy (SEM).

We start our discussion with the “bulk structure” of the films as revealed from cross sectional TEM experiments. The films were floated off the SiO_x covered Si substrates onto aqueous KOH solution, picked up onto a TEM grid, embedded into epoxy, and subsequently cut into ~50 nm thick slices. TEM images taken after an OsO_4 stain (Fig. 1) clearly show a lamellar microdomain structure, which is aligned parallel to the boundary surfaces. The lamellar spacing is comparable to that of the bulk structure. An assignment of the different blocks is straightforward, as the B-microdomains appear dark due to selective staining, while the M-microdomains typically appear thinner than the S-microdomains due to electron beam damage of the acrylate sidegroups [19]. In regions of laterally varying film thickness, the SBM film surface exhibits terraces separated by steps of well-defined height (Fig. 2a), reflecting the layered morphology of the underlying film. So far, the results resemble the well-known alignment of lamellae found, e.g., in thin films of SM (polystyrene-*block*-polymethylmethacrylate) diblock copolymers [6,17,18,20,21].

Closer inspection of the surface, however, reveals a well-defined lateral structure within each terrace. This can be seen in Figs. 2a and 2b. While the height image (Fig. 2a) clearly shows the stepped nature of the film surface, the phase image (Fig. 2b) reveals the existence of two distinctly different types of terrace structures, referred to as S_{PL} and M_{PL} in the following. Terrace S_{PL} is characterized by a dotted structure in the SFM phase image with a typical lateral repeat distance of some 60 ± 3 nm between neighboring dots. Terrace M_{PL} exhibits some lateral structure as well; however, no further details can be extracted from Fig. 2b. The surface structure alternates between the two types as one moves along the surface; i.e., every other terrace exhibits qualitatively the same surface morphology. It is interesting to note that along with the changing terrace structures, the shape of the steps varies systematically, too, and changes between a “dotted” and a “continuous” appearance. The height difference between like terraces (80 ± 10 nm on average) is somewhat smaller than the bulk lamellar spacing (110 nm) possibly due to shrinkage during the drying process [22]. We conclude at this point that the block copolymer forms a layered structure aligned parallel to the substrate and two different terminations of the layers are observed at the free surface of the films.

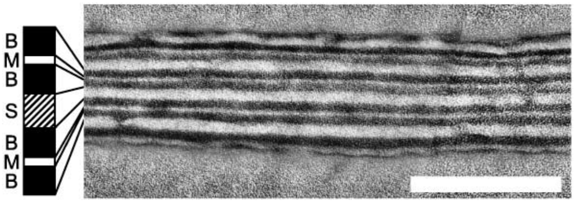

FIG. 1. TEM image of a cross section (stained with OsO_4) of a chloroform-vapor-annealed SBM film floated off from a Si substrate. The scale bar corresponds to 250 nm.

To get further insight into the near-surface morphologies responsible for the observed surface structures, we have exposed our samples to a reactive plasma (1 mbar air, 60 W at 13.56 MHz, 45 sec). This procedure removes about the topmost 14 nm of the polymeric material. In Figs. 2c and 2d height images of the same area of the sample (white box in Fig. 2a) are shown prior to and after plasma etching, respectively. The isolated protrusions visible on terrace S_{PL} (Fig. 2c) are turned in isolated depressions after the plasma treatment. Accordingly, the rather featureless surface of terrace M_{PL} exhibits isolated protrusions after the etch. Given the different etching rates of the three polymers (~10 nm/min for PS and ~20 nm/min for both PB and PMMA), we conclude that terrace S_{PL} consists of a PS matrix, whereas in terrace M_{PL} isolated PS microdomains

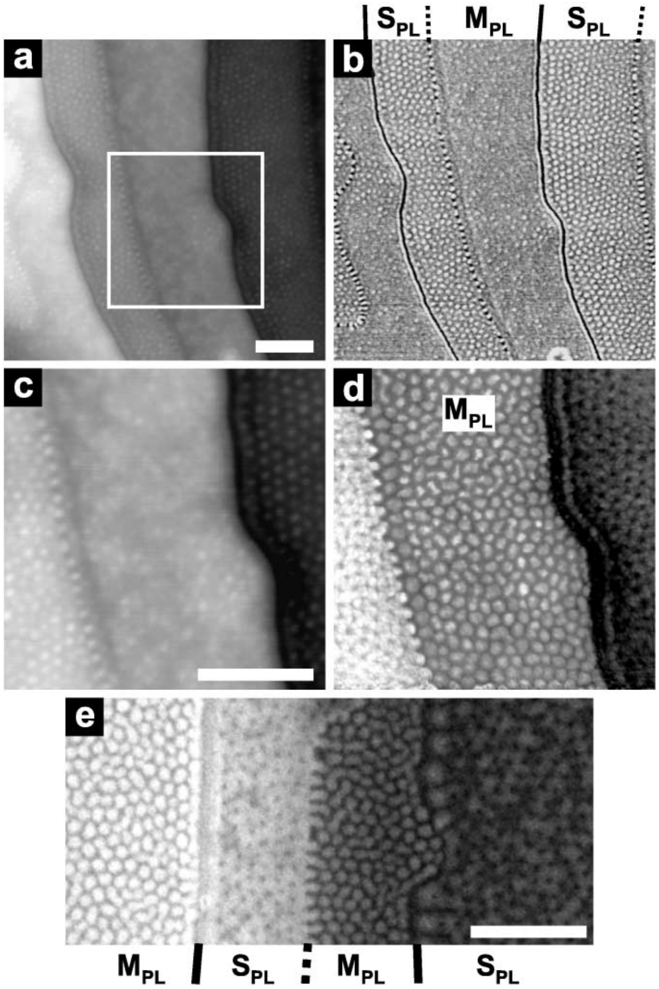

FIG. 2. SFM height (a) and phase (b) image of an SBM film (~160 nm thick) on a Si substrate after annealing in chloroform vapor. Height image before (c) and after (d) plasma etching. (e) SEM image of SBM surface (stained with RuO_4; SEM operated at 1 kV resulting in ~15 nm sampling depth). Scale bars correspond to 500 nm in all cases.

are found. To further corroborate this assignment, we have imaged the samples with a field emission source scanning electron microscope (SEM, Fig. 2e). The sample was stained with RuO_4 prior to imaging. Again, two distinct types of terraces are observed ending with two distinctly different types of steps. Terrace S_{PL} is characterized by isolated dark spots in the SEM image, while terrace M_{PL} exhibits an array of isolated bright microdomains. Since RuO_4 is known to preferentially stain both the PS and the PB blocks, they are expected to appear bright in the SEM image. Therefore, we find isolated PMMA domains on terrace S_{PL} while a continuous PMMA matrix can be attributed to terrace M_{PL}. The SEM images therefore confirm and complement the SFM results discussed above. Quantitative measurements of the tip indentation during SFM experiments [23] reveal that the surface is covered by a continuous (rubbery) PB layer.

We note that surfaces of thicker films (1 μm, not shown here) show the same type of surface reconstruction thereby excluding significant substrate or confinement effects on the observed microdomain structures. Moreover, experiments with a lower molecular weight SBM copolymer reveal the same type of terraces, surface structures, and steps, however, with smaller length scales corresponding to the smaller length of blocks.

If we combine the results presented so far, the following picture evolves: Terrace S_{PL} is characterized by isolated PMMA microdomains in a continuous PS matrix, while isolated PS microdomains in a continuous PMMA matrix are observed on terrace M_{PL}. As a working hypothesis, we may explain the experimental observations by a model as depicted in Fig. 3. The lamellar structure of the block copolymer is preserved in the bulk of the thin film and aligned with respect to the substrate surface. As a result, quantized thicknesses are observed in agreement with earlier work on symmetric diblock copolymers [6]. However, the near-surface structure deviates from the lamellar morphology. This *surface reconstruction* is driven by the fact that an ideal surface termination does not expose the lowest surface energy butadiene block to the surface and therefore is energetically unfavorable. An exposure of the B middle block may be accomplished by some backfolding of either PS or PMMA chains allowing the free surface to be covered by PB. This picture is in qualitative agreement with earlier 2D computer simulations on the structure of triblock copolymer thin films with symmetric boundary conditions [12]. In contrast, in the case of SBM the topmost polymer layer is facing asymmetric boundary conditions: The middle block is attracted by the free surface and one of the end blocks is attracted to the termination of the underlying (bulk) lamellar structure. As the underlying lamellae can be terminated by either S or M, two different surface structures are formed. These structures may best be described as isolated microdomains of the backfolding species embedded in a perforated lamella of the respective other end block, which leads us to the nomenclature S_{PL} and M_{PL}, respectively.

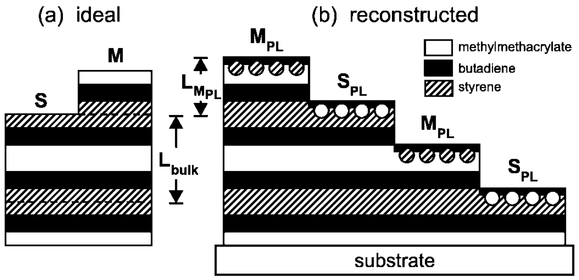

FIG. 3. Schematic model of the (a) ideal and (b) reconstructed surface of SBM block copolymers with lamellar microdomain structure in the bulk. For a corresponding model of Si(100)-(2 × 1) see, e.g., Fig. 1 in Ref. [4].

To critically test the role of the surface energy differences between the respective blocks, we have studied another block copolymer of similar molecular weight and volume fractions, however, with a different succession of the blocks, i.e., BSM instead of SBM. Here, the lowest surface energy component (B) is an end block and an ideal surface terminating with the B end block should be energetically favorable. Indeed, BSM films prepared in the same way form terraces with well-defined film thicknesses, too. In contrast, however, no lateral structure whatsoever is observed on the terrace surfaces. Details of these experiments are beyond the scope of this Letter, but we do note that our findings on BSM thin films closely resemble the situation of *diblock* copolymer thin films with asymmetric wetting conditions [17].

Despite being totally different types of matter and order, our observations on SBM surfaces display remarkable similarities with the surface reconstructions of single crystal surfaces, in particular, with the (2 × 1) buckling row reconstruction of Si(100) [3,4]. Indeed, the latter also exhibits two different terrace terminations, characterized by a characteristic 90° rotation of the buckled rows between successive terraces on stepped surfaces. In addition, two different types of steps are observed, depending on the relative orientation of the buckled dimer rows and the steps (see, e.g., Fig. 2 in Ref. [4]).

For a thorough discussion of the similarities between ordered complex fluids and "classical" crystals, we first consider the symmetry of the respective structures. The structure of a classical crystal is described by the periodic spatial arrangement of electron density and pointlike nuclei. Therefore its symmetry belongs to the class of *point groups*. The microdomain structure of a block copolymer on the other hand is described by the density of its components (S, B, and M in the case of SBM) and a region with an increased density of one component is called a microdomain. Microdomains can form spheres, cylinders, lamellae, or more complex shapes which self-assemble into regular periodic structures resembling crystal-like order. However, since cylinders and lamellae exhibit (partial) continuous translational symmetry, the corresponding bulk microdomain structures belong to the more general class of *space groups*. (Smectic and columnar phases of liquid crystals exhibit a similar symmetry.) The bulk structures of silicon and SBM can both be described as an alternating stack of two nonequivalent layers. In the case of Si, successive (100) planes of the diamond lattice differ in terms of the bond directions to the neighboring atomic layer. The two lamellar subunits SBM and MBS of a lamellar structure, on the other hand, differ in the orientation of blocks. In both cases, the introduction of a surface causes a local rearrangement of matter which leads to a state of lower free energy. In the case of the Si(100)-(2×1) buckling row reconstruction atomic nuclei and electron density are rearranged in order to decrease the number of dangling bonds and thereby lower the surface free energy of the system. The same is achieved in the case of SBM by rearranging the microdomain structure in the topmost layer such that the low surface energy *B* block is exposed to the surface (Fig. 3). Since the bulk structure can be terminated by either one of the nonequivalent layers, two nonequivalent surface structures are observed both on Si(100) and on SBM.

The lateral order within the layers of the bulk structure is different for the two materials: Si is a classical crystal with 2D lattice symmetry within its (100) plane, while the SBM bulk structure is lamellar with continuous two-dimensional translational symmetry (Euclidian symmetry) within the lamellae. In both cases the symmetry of the reconstructed surface is lowered with respect to the ideal surface, however, in very different ways. In the case of the Si(100) surface the size of the unit cell of the 2D surface lattice doubles. In the case of SBM, the Euclidian symmetry is broken. We emphasize the fact that in both cases a boundary condition imposed in the direction *perpendicular* to the layer breaks the *in-plane* symmetry of the ideal surfaces. This indicates that all three spatial coordinates are coupled on an underlying microscopic scale. This coupling is due to the three-dimensional nature of the underlying elements (atoms in one case and polymer molecules in the other). The same phenomenon is found in other fields of physics (e.g., high energy physics), where the type of symmetry breaking can reveal properties of underlying (invisible) microscopic particles and processes. An important consequence for block copolymer physics is that the assumption that bulk symmetry is preserved in thin films and at surfaces, which is often made for reasons of simplicity in computer simulations of thin block copolymer films [11,12,15], is not necessarily justified. Therefore, truly three-dimensional calculations without any symmetry constraints [13,14] are required for an unbiased prediction of thin film and surface structures of block copolymers.

In conclusion, we have shown that the surface structure of a mesoscopically ordered block copolymer exhibits a remarkable analogy to the well-studied surface reconstructions of classical crystals. Both systems differ significantly in the type of matter and order. Common to both is only the presence of a surface, a bulk structure with two nonequivalent alternating layers along the surface normal, and a three-dimensional structure of the underlying elements. Nevertheless, in both cases the presence of a surface leads to a surface reconstruction with (1) a spontaneous breaking of lateral symmetry of the ideal surface, (2) two types of alternating terraces, and (3) two types of alternating steps. Given the wealth and complexity of ordered bulk structures of block copolymers and surfactant based complex fluids, the study of their surface behavior is expected to become a rewarding field of science.

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