

Edge Profile of Relief 2D Domains at the Free Surface of Smectic Copolymer Thin Films

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Ultrathin ($\approx 1000 \text{ \AA}$) ordered films of symmetric diblock copolymers deposited on a plane solid substrate exhibit relief domains at their free surface. Their height is equal to the period L of the lamellar stacking ($L = 310 \text{ \AA}$). The thickness profile at the edge of the domains has been investigated using atomic force microscopy. Its shape, independent of the domain size, is close to the theoretical prediction for the free surface of a smectic liquid crystal above a single dislocation. However, its lateral extension appears to be larger than expected by a factor of 20; the effect of the polymer/air surface tension is qualitatively invoked.

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The potentialities of thin symmetric diblock copolymer films in the development of new materials with controlled surface properties are well known. Less common is their use as model systems for quantitative studies of basic two-dimensional (2D) phenomena in physics, such as 2D coarsening processes or 2D phase transitions. These aspects also deserve some attention since well-controlled experimental systems for basic 2D physics are not so numerous.

It has been shown recently [1-3] that ordered symmetric copolymer films of order 1000 \AA thick deposited on a flat solid substrate exhibit relief domains at their free surface. As explained below, the presence of these domains is a direct consequence of the lamellar structure of the organic film which appears spontaneously whenever the temperature T of the sample is between the highest glass temperature T_G of the two species, say A and B , and their mixing transition temperature T_{MST} [4,5]. Here we assume that T_{MST} is high enough so that A and B are strongly segregated.

Since each of the solid and the free surface is selecting the component which yields the lowest surface free energy, the lamellar structure is oriented parallel to the substrate. If the same species is selected at both interfaces, the total thickness of the film has to equal an integer number times the lamellar period L . In the opposite case where A and B are both selected once, the total thickness is an odd number times $L/2$. Experimental examples have been given of the latter case [1]. The present Letter deals on the contrary with a system belonging to the first class. Its thickness in the ordered state must belong to a discrete spectrum of allowed values $d_i = iL$, $i \in \mathbb{N}$. (Actually, the thickness of the first and last layers is different from that of the internal layers, due to the presence of the additional air-polymer and polymer-solid surface tensions in the two external layers.) However, these films can be initially prepared in a disordered state with an arbitrary thickness $d \neq d_i$ and ordered in a second step by changing

the temperature. In that case, the copolymer film, while ordering, demixes in coexistence regions of thicknesses d_n and d_{n+1} with $d_n < d < d_{n+1}$, thereby generating a pattern of (circular) domains of the minority thickness over a continuous film with the majority thickness. The height of the step at the domain edge is always L . Domains can be elevations or depressions, depending on whether the initial thickness d is close to d_n or close to d_{n+1} , respectively. Intermediate situations where $d \approx (d_n + d_{n+1})/2$ are more complicated.

Macroscopic evolution of the domain population with ordering time is a model growth phenomenon in two dimensions, which is currently the subject of both experimental [3] and theoretical [2] investigations. Our first theoretical attempts have been based on several assumptions concerning the copolymer structure and behavior in its smectic state [2]. Among them is the hypothesis that the domain-edge topology is that of a single dislocation located one monolayer below the free surface, whatever the total sample thickness. Experimental probes of the domain edges are therefore crucial for understanding the macroscopic kinetics of the domain-pattern evolution. On the other hand, the deformation of smectic- A layers in the vicinity of a dislocation has been a traditional subject of interest in liquid-crystal physics [6-9]. More specifically, the propagation of such deformation to the free surface of thin liquid-crystal films and its incidence on the surface topology has been theoretically explored [9]. However, no experimental study has been reported to our knowledge where the vicinity of a single dislocation was quantitatively investigated. The molecular scale involved in block copolymers combined with the performance of the recent scanning tunneling microscopy (STM) and atomic force microscopy (AFM) techniques [10-13] has now made such a study tractable. Reporting our first quantitative study of the copolymer domain-edge profile and discussing them in terms of liquid-crystal physics is precisely the aim of the present Letter.

The copolymer sample used in this study is a monodisperse ($I_p = 1.05$) polystyrene/polybutylmethacrylate (PS/PBMA) sample with a total molecular mass of 82000, synthesized using anionic copolymerization. Thin films were prepared by spin coating toluene solutions on silicon wafers cleaned by UV radiation under oxygen atmosphere. The initial thickness of the disordered film was of order 700 Å, leading, after annealing at 150°C for 24 h under vacuum, to ordered domains of height L over a continuous background at $2L$, with $L = 310 \pm 15$ Å. Relief domains were explored using the Nanoscope II commercial AFM (Digital, USA) in the constant-force mode at 2×10^{-8} N after freezing the samples in a glassy state at room temperature. It was checked that the results were independent of the working force in the range $5 \times 10^{-9} - 2 \times 10^{-8}$ N.

Figure 1(a) presents a large-scale view of the domain population obtained at the free surface of the copolymer film when its average thickness $\langle d \rangle$ is slightly larger than $2L$. Comparable patterns (not shown here) have been obtained with holes instead of islands for $\langle d \rangle$ slightly smaller than $3L$. Note the circular shape of the domains and their size polydispersity. Figure 1(b) shows the thickness profile associated with one of these domains, with a diameter of order 4 μm. The slight depression at the center of the island surface has been observed on all domains of some samples, and is totally absent on all domains of others. Its origin is not understood. Figure 1(c) is a schematic representation of the internal structure of the smectic layers at the domain edge inferred in Ref. [2], and adapted to the present boundary conditions. It satisfies the following requirements: (i) The species with the lowest surface tension in the melt state, say A (here for PBMA), is selected at the free surface; (ii) layers of polymer A are those to be interrupted in the defect topology, because A is also expected to have the lowest cohesion energy; (iii) the dislocation is as close as possible to the free surface within constraints (i) and (ii), since the latter is supposed to be attractive for any defect [9]. Note that the schematic model of Fig. 1(c) intends to describe the topology of the defect, not the detailed shape of the core.

Figure 2 now presents the actual thickness profiles at the edge of different domains with respective diameters of 7, 5, and 4 μm, after an annealing time of 24 h. The existence of larger domains would require longer annealing times while smaller domains show overlapping effects of opposite edges, to be studied separately.

The profiles shown are rough data extracted from the nanoscope images in the direction Y normal to the main scan X , so that they can be directly compared with each other without wondering about the respective calibrations of the X and Y piezoelectric displacements of the sample holder. Absolute values shown on the X and Y axes are to be taken within an uncertainty of order 5%. The three profiles (A-C) are very similar. Their shape does not de-

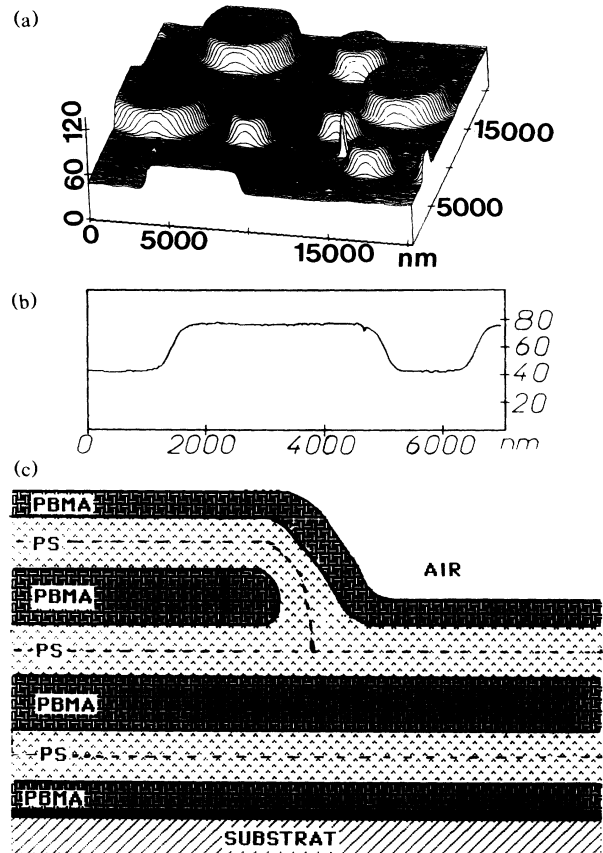


FIG. 1. (a) AFM image of relief domains at the free surface of a PS/PBMA diblock copolymer film. The height of the circular elevations is 310 Å independent of their diameter. (b) Section of one domain with a diameter of 4 μm. The slight depression at the center of the island surface is not understood. (c) Assumed domain-edge structure. The dark and white regions correspond to PBMA and PS, respectively. The dark lines represent PS/PBMA interfaces, while dotted lines are fictive PS-PS or PBMA-PBMA separations.

pend on the domain size in the narrow range investigated. Since the sample was frozen from an out-of-equilibrium state in which the growth rate of domains is a function of their size [2], this similitude suggests that the profiles are not strongly affected by dynamic effects. When looking at the Y and Z scales (Z is normal to the surface), it exhibits a very surprising feature: The height of the step is 310 Å, while its lateral extension is larger by more than an order of magnitude. The maximum slope of the profile is therefore of order 0.1. On the technical side, this ensures that convolution effects with the tip shape are negligible for standard tip radii of curvature (≈ 100 Å). On the physical side, it shows that the deformation of lamellae extends much further than expected from Fig. 1(c).

The bottommost curve (D) in Fig. 2 has been obtained from the theoretical model of Pershan [9]. The agree-

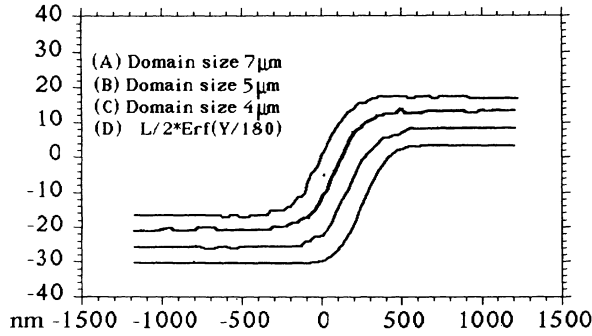


FIG. 2. The thickness profiles obtained for an annealing time of 24 h at the edge of different domains with respective diameters of 7, 5, and 4 μm . Curve D (bottommost curve) presents Pershan's theoretical profile for comparison.

ment with experimental shapes is qualitatively good. However, a slight dissymmetry of the experimental profiles with respect to the inflection point is almost always observed. At this stage, this dissymmetry cannot be exploited since it has to be extracted from a statistical study on a large number of profiles before being claimed as significant. This averaging requires very careful tests with respect to the necessary flattening corrections. This dissymmetry would be the mark of a preferential sign in the curvature of the lamellae. Its origin could be either in the surface tension of the polymer/air interface or due to slight differences in chain lengths or A and B densities.

The agreement between experimental profile and theoretical model for smectic A is almost surprising since one of the major hypotheses of the model is clearly not fulfilled. It concerns the distance between the free surface and the dislocation core, supposed in the theory to be large when compared to the lamellar period (continuum medium approximation). However, since no better theory is available, we go further into the comparison [14]. The theoretical dependence of the height Z of the top surface with Y obeys, from Ref. [9],

$$Z(Y) = (L/2) \operatorname{erf} Y/2(\lambda h)^{1/2}, \quad (1)$$

where the origins for Z and Y have been chosen at the inflection point. The length λ is the "penetration depth" [15] defined from Young's elasticity coefficient B [15] for compression of the layers and the Franck-Oosen splay elastic constant K_1 [16] by $\lambda = (K_1/B)^{1/2}$. The height h is the distance between the free surface and the core of the defect. Within the continuum medium approximation, it becomes $h = L/2$. This thickness profile differs only by a factor of 2 on the Z amplitude from the shape of the distorted lamellae in a semi-infinite medium at a distance h from the dislocation, calculated previously by de Gennes [17]. Pershan's model explicitly assumes that surface-tension effects are negligible. These contributions to the free energy of our system will be taken into account in a

forthcoming theoretical work [18].

The best fit of experimental data with expression (1) is obtained for $L/2 = 155 \text{ \AA}$ and $\lambda = 5200 \text{ \AA}$. The half period $L/2$ is 10% below, and therefore comparable to, previous optical estimations.

For comparison, the parameter λ is derived independently from the usual expression of the free energy per chain of the lamellar copolymer system. It is written [19,20] as

$$F_c = \alpha^{3/2} k_B T (L^2/Na)^2 + \gamma_{AB} (Na^3/L),$$

where k_B , T , N , a , and γ_{AB} stand for the Boltzmann constant, the absolute temperature, the chain length in monomer units, the length of statistical segments, and the A - B surface tension, respectively. α is a numerical constant close to 1 [19,20]. This expression leads in a second-order approximation [18] to $B = \alpha(9k_B T/4Na^3)L^2/Na^2$ and $K_1 = \alpha 13k_B T_L \sqrt{8Na^3Na^2}$, from which we get $\lambda = L\sqrt{13/18}$.

The experimental value of the profile width $\sqrt{\lambda h}$ is therefore larger than its theoretical evaluation by a factor of 20. Several effects can be thought of to explain this discrepancy.

(i) The residual amount of homopolymer in the copolymer sample, after synthesis and purification, is of order 2%. It could concentrate in the defect region in order to relax the local stresses, acting as a lignactant (the two-dimensional analog of a surfactant). This explanation has been eliminated by intentionally adding 3% of polystyrene homopolymer, with the same molecular mass as the polystyrene block in the copolymer molecules, to the sample. It was checked that it had no appreciable effect on the profile width. Significant distortions were only obtained for homopolymer weight fractions of 10% and above.

(ii) The h value itself could be larger than $L/2$ if the dislocation was located further away from the free surface. However, the maximum h value compatible with the total film thickness is $5L/2$, which is not large enough to solve the discrepancy.

(iii) The surface tension γ of the air/polymer interface tends to minimize the total free surface of the film and opposes large curvatures in the surface profile. Therefore, γ , like K_1 , acts against B in broadening the profile width. We believe this surface-tension effect to be responsible for the observed anomalous width. A complete understanding of the effect of γ on the profile extension would require, on one hand, inclusion of the surface terms in the smectic film free energy [18,21], and, on the other hand, development of the theory of the smectics distortion at the vicinity of a dislocation beyond the continuous medium approximation. Indeed, one can infer that the core structure itself, the topology of which is shown in Fig. 1(c), is strongly flattened in the dislocation region. The theoretical calculation of the exact core shape should, in principle, be tractable in that particular case

since the molecular scale itself can be treated using a continuum theory, due to the polymeric nature of the smectic molecules.

In conclusion, this first experimental study of the free surface of a smectic film has shown that the shape of the thickness profile above a dislocation was compatible with the results of the continuum medium approximation, but that its extension could not be explained within this frame. It demonstrates the need for new theoretical developments, in which surface-tension effects and exact core shapes will be taken into account. On the other hand, lamellar copolymers turn out to be very promising systems for quantitative studies on liquid-crystal physics. Indeed, they are one-component smectic-*A* systems with a large lamellar period (macrosmectics) and they can still be treated as continuous media at a molecular scale.

Similar studies using the STM technique after metal deposition have been performed. They give qualitatively the same results, but with a slightly poorer resolution. Finally, it should be mentioned that, when interpreting the thickness domains as coexisting 2D phases in the out-of-equilibrium copolymer film, the present results provide the order-parameter distribution in the interlignal (2D analog of interfacial) region.

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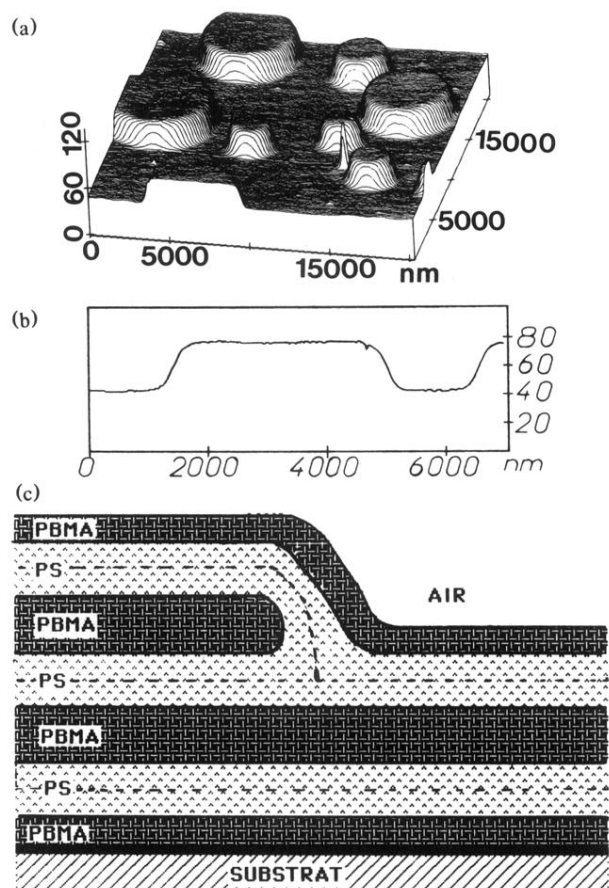


FIG. 1. (a) AFM image of relief domains at the free surface of a PS/PBMA diblock copolymer film. The height of the circular elevations is 310 \AA independent of their diameter. (b) Section of one domain with a diameter of $4 \mu\text{m}$. The slight depression at the center of the island surface is not understood. (c) Assumed domain-edge structure. The dark and white regions correspond to PBMA and PS, respectively. The dark lines represent PS/PBMA interfaces, while dotted lines are fictive PS-PS or PBMA-PBMA separations.