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Confinement of Block Copolymers on Patterned Surfaces

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ABSTRACT: Smectic ordered films of the copolymer PS-P2VP were studied on periodic silicon surfaces (surface gratings). The modulation of the film surface with respect to that of the underlying substrate was found to be either in phase (conformal) or—surprisingly—out of phase (anticonformal). The critical height of the surface grating which is defined by the transition from conformal behavior to the anticonformal conformation of the films was found to be proportional to the lamellar height of the diblock copolymers. This has been quantitatively understood within a mean field theory as a result of balancing the deformation and interfacial energies. Furthermore, diblock copolymer films propagate the substrate roughness by significantly larger distances than observed for amorphous homopolymers.

1. Introduction

The properties of copolymers on flat surfaces have been extensively studied.[1] But a systematic experimental study of the morphologies of copolymer thin films on rough surfaces has not been performed. It is well-known that A−B symmetric diblock copolymers can be induced to form lamellar layers ordered parallel to the substrate surface. Islands or holes can be formed if the film thickness is not an exact multiple of the period, which is defined by the lamellar height, L. The motivation of the present work was given by Turner and Joanny,[2] who have studied theoretically the ordering of symmetric diblock copolymers on a sinusoidal surface under the condition that the amplitude, h_0 (referred to as "the roughness" throughout this paper[3]), of the sinusoidal surface is *small* compared to the lamellar height, L. They found that when the lateral period of the surface, d, is large compared to L, the roughness of the film surface is *in phase* with the roughness of the substrate. On the other hand, when $d/L \ll 1$, the result that the roughness on the copolymer surface is anticonformal, i.e., completely *out of phase*, to the substrate was derived. In the first part of this paper we show that such unexpected anticonformal configurations in diblock copolymer films can also result from the internal structure of the block copolymer. In the present case the condition $d/L \ll 1$ is relaxed and we show both, experimentally and theoretically, that the conformal/anticonformal transition happens as a function of the ratio h_0/L when the roughness amplitude h_0 is *not small* compared to the lammellar height L.

A related topic which is of great interest in thin film physics is the propagation of interfacial roughness in the direction perpendicular to the solid substrate. This phenomenon has been studied in thin films of small molecules[4,5] and homopolymer liquids.[6,7] It has been shown that the degree of roughness propagation is a result of balancing the surface tension of the liquid film against the surface confinement of the liquid molecules. For small molecule liquids, the confinement is simply the van der Waals interaction between the liquid and the solid. Consequently, the healing length a, which is a measure of the propagation of the roughness through the adsorbed film, never exceeds 100 Å and scales as $a = [A_{\mathrm{eff}}/(2\pi\gamma)]^{1/2}$ where A_{eff} is the effective Hamaker constant and γ is the surface tension of the film.[4] For small molecule organic liquids wetting silicon surfaces, a is typically on the order of 10 Å.[5] Polymer liquid films have been shown to be confined much more strongly due to the size of the polymer chains. Confinement of the polymer chains can change the amorphous polymer liquid into a gel or solidlike structure over a distance corresponding to several polymer radii of gyration ($\approx 10^2−10^3$ Å) near a solid interface.[8] This effect has been shown to significantly increase the healing length.[6,7] In

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Table 1. Summary of the Conformations Obtained for the Triblock (Column 2) and the Diblock (Columns 3−5) Copolymer Films with Lamellar Heights, *L*, on Top of Si Gratings with Spacing, $d = 1\ \mu$m, and Different Heights, h_0[a]

	$N_{P2VP} - N_{PS} - N_{P2VP}$ 90−560−90 $L = 210$ Å	$N_{PS} - N_{P2VP}$ 200−200 $L = 310$ Å	$N_{PS} - N_{P2VP}$ 510−540 $L = 550$ Å	$N_{PS} - N_{P2VP}$ 1000−1000 $L = 720$ Å
$h_0 = 40$ Å	conf	conf	conf	
$h_0 = 120$ Å	anticonf	conf	conf	conf
$h_0 = 170$ Å		anticonf	anticonf	conf
$h_0 = 250$ Å	anticonf	anticonf	anticonf	conf
$h_0 = 440$ Å		anticonf	anticonf	anticonf

the case of block copolymer films, it is known that the surface induced smectic ordering can propagate for several thousand angstroms into the film.[1] An important question addressed in the second part of this paper is whether this ordering also makes copolymer films more efficient in propagating surface roughness.

The third issue addressed in this paper deals with the contours of islands of block copolymers on rough surfaces. On planar surfaces it was found that the contour of the island boundaries was well fit with the theory of Turner et al.[9,10] In this paper we will also investigate whether this fact remains unchanged on rough surfaces.

We have studied the conformation of di- and triblock copolymers on trapezoidal shaped-Si grating surfaces, acting as model roughness with only a few enhanced Fourier components of the roughness spectrum, using atomic force microscopy (AFM), to detect directly the surface morphology, secondary ion mass spectrometry (SIMS) for depth profiling, and transmission electron microscopy (TEM) for obtaining detailed in-plane information. Additionally X-ray scattering experiments were performed which will be discussed in detail in a forthcoming paper.[11]

The paper is organized as follows: After the Introduction a description of the samples and the experiments follows. In section 3 we show that a conformal to anticonformal transition happens as a function of the grating and lamellar heights and is found to be connected to the edge confinement of the lamellar islands. This new phenomenon will be discussed in terms of a mean field theory approach in section 4, which is formulated in the thick film (continuum) limit. There it will be shown that this transition can be explained by a balancing of the interfacial tension and the bending energy across the grating (sections 4.1 and 4.2). Also an analytic expression for the vertical roughness propagation is found and will be compared in section 4.3 with the experimental data. Finally, in section 5 we summarize our results.

2. Experimental Section

The Si grating substrates were produced using holographic methods and subsequent chemical etching techniques.[12] X-ray scattering and AFM investigations of bare surface gratings and gratings covered with homopolymer films have revealed that both probes yield equal results for the surface parameters. The deviation in the z-direction perpendicular to the surface is less than 5 Å.[7,13] The spacing of the gratings used in this paper was $d = 1\ \mu$m, and the heights varied in the range $40 \leq h_0 \leq 440$ Å (see Table 1). Figure 1 shows an example of the structure of a bare grating obtained with the AFM.

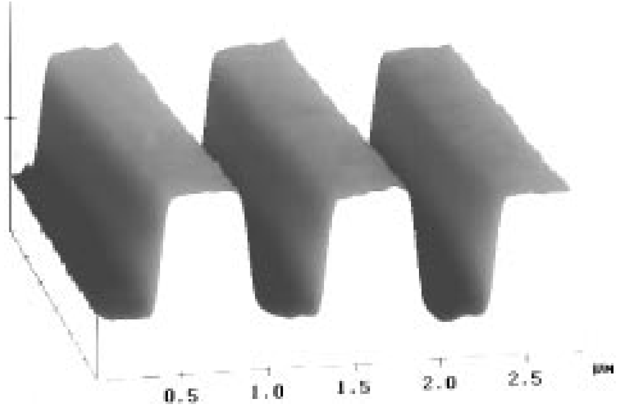

Figure 1. AFM image of a Si surface grating with periodicity $d = 1\ \mu$m and height $h_0 = 250$ Å.

The block copolymer system chosen was that of polystyrene−poly(2-vinylpyridine) (PS−P2VP) for which the Flory−Huggins parameter $\tilde{\chi}$, was previously measured to be, $\tilde{\chi} = -0.033 + 63/T$.[14] Consequently, for the annealing temperature $T \sim 180$ °C used in this study, $\tilde{\chi} \sim 0.1$, and all the copolymers listed in Table 1 are strongly microphase segregated. The anionic synthesis and the ^{13}C characterization procedure of the block copolymers is described in ref 15. The polymerization indices of the copolymers used and their lamellar heights, L, are summarized in Table 1. The lamellar heights were determined for each copolymer by spinning layers approximately 1000−3000 Å thick, on flat polished Si surfaces, and annealing for 5 days at 185° C and 10^{-4} Torr. The lamellar height was then measured using dynamic SIMS (DSIMS). As described previously, this procedure causes the symmetric block copolymers to order in lamellae parallel to the Si substrate with PS and P2VP layers always present at the vacuum and Si interfaces, respectively.[9]

The triblock copolymers (P2VP−PS−P2VP) used in this study have also been shown to order in layers consisting of cylinders lying parallel to the Si interface. The cylinders have P2VP cores and PS coronas, and the lamellar height listed in Table 1, $L = 210$ Å, is the measured core−core spacing perpendicular to the surface between cylinders in adjacent layers (for details see ref 16).

If the initial film thickness of the block copolymer films is not an integer multiple of L, island or hole morphologies form on the surface.[17,18] The height of these islands or holes, as determined by AFM, provided another measure of L. Since the DSIMS and AFM results agree within 20 Å, the average of the two determinations is listed in Table 1.

Due to the corrugation it is not possible to obtain uniform films by spin casting directly on the grating surfaces. The samples were therefore prepared by first spin casting the copolymer from toluene solution on float glass plates and then floating from the surface of deionized water onto the Si gratings. Afterward the samples were annealed until the films reach equilibrium. At 185 °C, 10^{-4} Torr the annealing time was 2 days for the diblock and 3 days for triblock copolymers. Control samples were also generated by floating some of the films on polished flat native oxide covered Si substrates. The total film thickness H was measured on the float substrates using ellipsometry. Note that in section 3 we always give as film thickness H the value determined by ellipsometry on a flat surface and before annealing. The actual thicknesses on the surface gratings may be different from these values. However X-ray scattering measurements have shown that the thicknesses H determined on the flat glass substrates are about 10%−15% larger than those determined on the gratings after annealing.[11] The morphologies of the surfaces were then scanned with a Digital Instrument Nanoscope III AFM.

The films were built up either layer by layer or by floating directly on the grating surface a layer of thickness H. In the

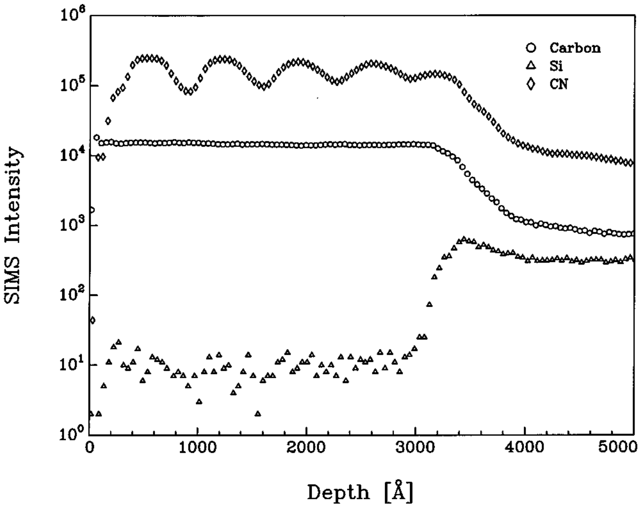

Figure 2. SIMS profiles of CN, C, and Si perpendicular to the surface from a $H = 3200$ Å thick $N_{PS} - N_{P2VP} = 1000 - 1000$ film on a Si grating with height $h_0 = 250$ Å.

first case, a thin layer, approximately L in thickness, was first floated on top of the bare grating, annealed and analyzed with the AFM. The second layer, also approximately L in thickness, was floated on top of the first, annealed again, and analyzed. In this manner, a layer consisting $H \leq 6L$ was generated (for most of the experiments $H \leq 4L$). No difference in the final surface structure was observed between the two methods for a given final film thickness.

In order to determine the ordering on the grating DSIMS experiments were carried out. Several samples were covered with a sacrificial deuterated PS layer,[19] and the concentration profiles of CN− (proportional to P2VP content), CH− (proportional to the PS content), CD−, and D− (proportional to dPS) were obtained. The DSIMS experiments were performed on an Atomika 6000 instrument at 30 nA with a 2 keV beam as described in ref 19. The spatial resolution in this configuration is approximately 80 Å, although the accuracy of the peak position determination is far better (~15 Å).

Figure 2 shows the SIMS spectra obtained from an $N_{PS} - N_{P2VP} = 1000-1000$ film of $H = 3200$ Å on a grating having $h_0 = 250$ Å. The CN ion trace is proportional to the P2VP concentration profile, while the Si profile indicates the grating interface. The carbon trace monitors the sputtering rate, which appears constant from layer to layer. From the well-defined oscillations in the CN profile, the lamellar height was found to be $L = (720 \pm 20)$ Å, in good agreement with previous measurements on flat silicon. Similar SIMS measurements were done on all block copolymer samples to prove independently that the lamellar structure of the films on the gratings was still present.

The TEM samples were imaged with a Philips CM12-T microscope using a 120 keV electron beam. The preparation was done by floating films approximately one lamellar height on the grating and annealing them at 180 °C. The films were then floated off the grating onto SiO-covered TEM grids through a 5% KOH/water solution at 80 °C. The KOH removes the polymer film by reacting with the underlying native silicon oxide. Afterwards the KOH residue was removed by rinsing the samples in destilled and deionized water after floating. The samples were then stained in I_2 vapor which segregates only into the P2VP regions and yields an enhanced contrast between the P2VP and PS blocks. The phase separation in the diblock copolymer films can then be resolved in addition to height variations.

3. Results and Discussion

3.1. Conformality of Smectic Copolymer Films. The phases of the surface modulations of the films compared to those of the substrate were obtained with the AFM by scanning a region which shows both, the bare grating *and* a region covered by the copolymer film. Using this technique, in phase or complete out of phase configurations were found for various samples. Figure 3a shows a typical *conformal* configuration of a diblock copolymer film ($N_{PS} - N_{P2VPS} = 200-200$) of total thickness $H = 440$ Å on a grating with $h_0 = 120$ Å. It can be seen that the depths of the holes are exactly one lamellar height, $L = 310$ Å, which indicates that the lamellar structure is unperturbed and the same as that measured on flat silicon. The only difference is that the shapes of the holes which are normally circular on flat Si are now rectangular where the long edges of the holes follow the grooves of the grating.

The contour of the thin film as measured by AFM reveals a sinusoidal shape, indicating that the higher harmonics of the substrate are rapidly damped and only the $n = 1$ component survives. This attenuation is similar to that previously reported for homopolymer films.[7,13] It is interesting to note that the contours *inside* the holes are also roughly sinusoidal i.e. they do not correspond to the bare grating (see sectional scan in Figure 3a).

The difference between the film thickness, $H = 440$ Å, and the depth of the holes, $L = 310$ Å, corresponds to the thickness of a conformal P2VP layer which always formed at the grating surface due to the strong interaction of P2VP with the SiO surface.[9] This layer occurs for all structures (lamellar, cylindrical, conformal, and nonconformal) on the gratings or flat Si, and the thickness never exceeds $L/2$.

A typical *anticonformal* configuration is demonstrated in Figure 3b, and shown schematically in Figure 4, where we show the edge of a $N_{PS} - N_{P2VP} = 1000-1000$ diblock copolymer film of nominal thickness $H = 710$ Å on a grating with $h_0 = 440$ Å.[20] The left part of the grating is covered with polymer while the right half is the bare grating. It can clearly be seen across the film boundary that the higher parts of the film lie in the depressions of the bare grating. These high sections are composed of islands of height 720 Å or exactly one lamellar layer. This was determined from an AFM cross-sectional scan running parallel to the grooves. In contrast to the holes in Figure 3a, these islands (and small holes) fit neatly into the grooves. A cross section of the surface contour shows it to be sinusoidal, indicating again that the $n = 1$ Fourier component is predominantly propagated in the anticonformal configuration as well.

Figure 3c shows the anticonformal configuration formed by a triblock ($N_{P2VP} - N_{PS} - N_{P2VP} = 90-560-90$) copolymer film of nominal thickness $H = 400$ Å on a grating with $h_0 = 120$ Å. The height of the ordered cylindrical layer in this case was previously measured[16] to be $L = 210$ Å or the same as the height of the islands observed in the grooves. A conformal layer adjacent to the silicon grating is also observed. This layer was previously found on flat silicon and neutron reflection showed that its conformation is lamellar.[16] It is interesting to note that the island contours appear much more “square” in this figure than those shown for diblock copolymers in parts a and b of Figure 3. Apparently, the higher Fourier components can be more efficiently propagated in both the conformal and anticonformal layers of triblock copolymer films. This phenomena may be related to the fact that the triblock copolymer forms an interconnected micelle network with fewer defects than the diblock copolymer films.[9,16]

The formation of an anticonformal layer can then be described as follows: When the film thickness is less

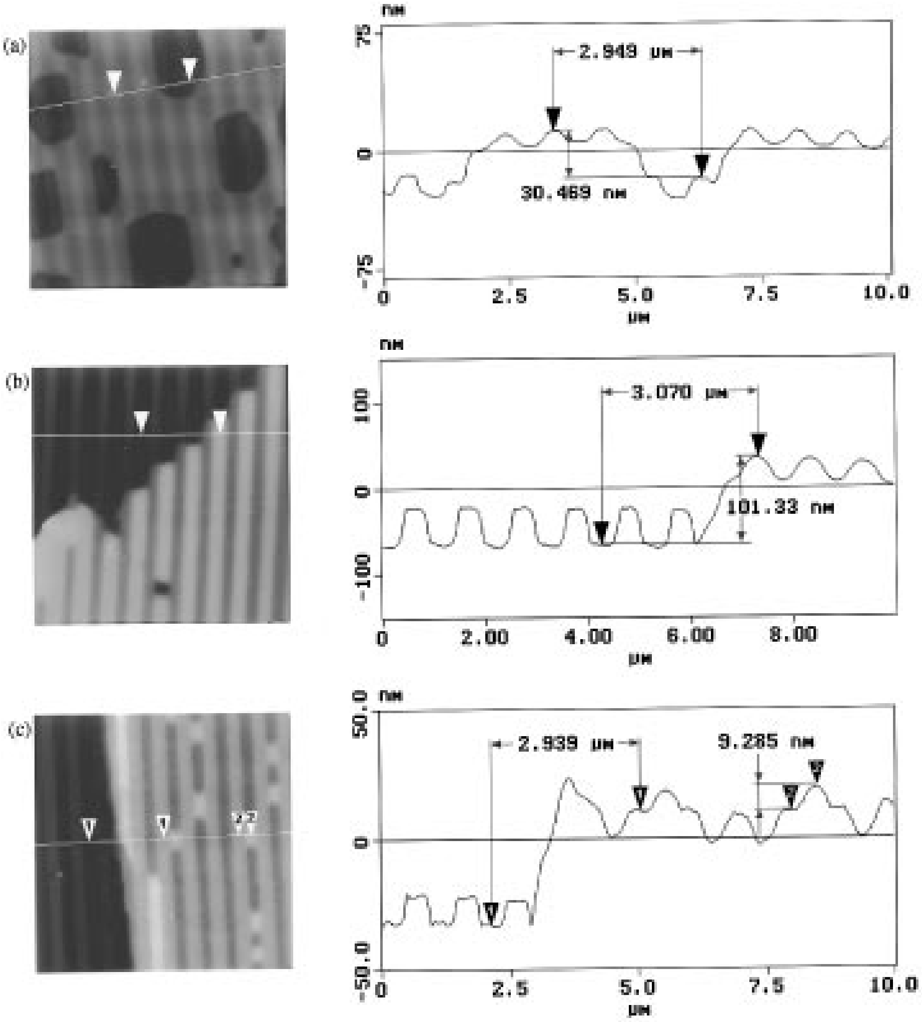

Figure 3. (a) Conformal configuration of a $N_{PS} - N_{P2VP} = 200-200$ PS−P2VP diblock copolymer film of total thickness $H = 440$ Å on grating with height $h_0 = 120$ Å. (b) Anticonformal configuration of a $N_{PS} - N_{P2VP} = 1000-1000$ film with a thickness of $H = 710$ Å $\approx L$ on a grating with $h_0 = 440$ Å. (c) Anticonformal configuration of a $N_{P2VP} - N_{PS} - N_{P2VP} = 90-560-90$ triblock copolymer film of total thickness $H = 400$ Å on a grating with $h_0 = 120$ Å. The associated cross-sectional AFM scans are shown above all pictures.

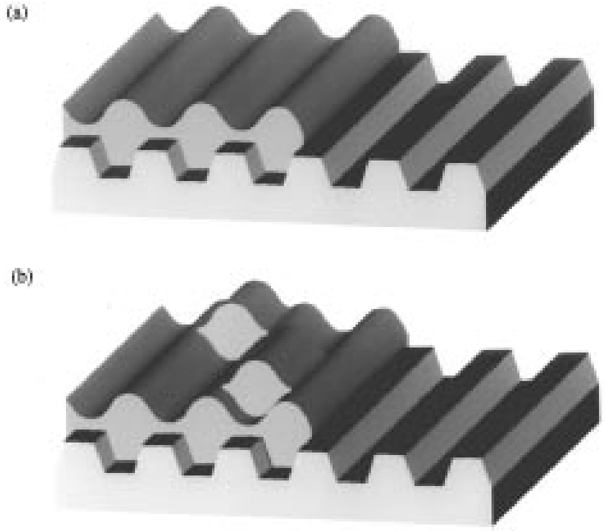

Figure 4. Schematic drawing of the anticonformal arrangement of block-copolymer films on a grating as observed by AFM in parts b and c of Figure 3.

than an integral multiple of L, the excess material forms islands or holes confined only in the grooves. The islands grow till the grooves are completely filled. Upon the completion of the one layer, another layer begins to grow in the grooves of the previous layer. In this manner alternating anticonformal and conformal layers to the substrate grating are formed. This process is illustrated in Figure 5 which shows an anticonformal structure of a $N_{PS} - N_{P2VP} = 200-200$ film of thickness $H = 660$ Å on a grating having $h_0 = 250$ Å. Even though this film is probably in a nonequilibrium state, it nevertheless provides a good snapshot of the layer formation process. In the figure it can be seen how new layers are formed in the grooves of previous underlying ones, forming alternating anticonformal/conformal/anticonformal structures with respect to the grating.

The proposed underlying morphologies of the block copolymer in the conformal and anticonformal configurations are illustrated schematically in Figure 6. The trapezoidal structure of the bare grating is shown in Figure 6a. In both conformal and anticonformal structures, the bare grating is first covered by a conformal brush layer of maximum height $L/2$ (the height of this layer is somewhat larger than L/2 for the triblock copolymer, since the in-plane structure of subsequent layers changes from lamellar to cylindrical). This cover layer is shown in Figure 6b−d. The P2VP and PS layers are drawn as shaded and clear, respectively. Strong hydrogen bonding with silanol groups always assures that the P2VP layer is present at the grating interface,

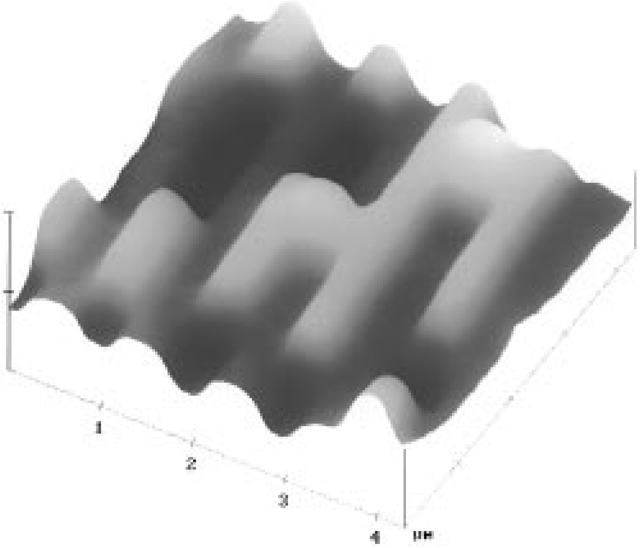

Figure 5. Three-dimensional AFM image of a $N_{PS} - N_{P2VP} =$ 200−200 diblock copolymer film of thickness $H = 660$ Å on a Si grating with $h_0 = 250$ Å. Several layers are visible which form alternating conformal and anticonformal structures relative to the grating.

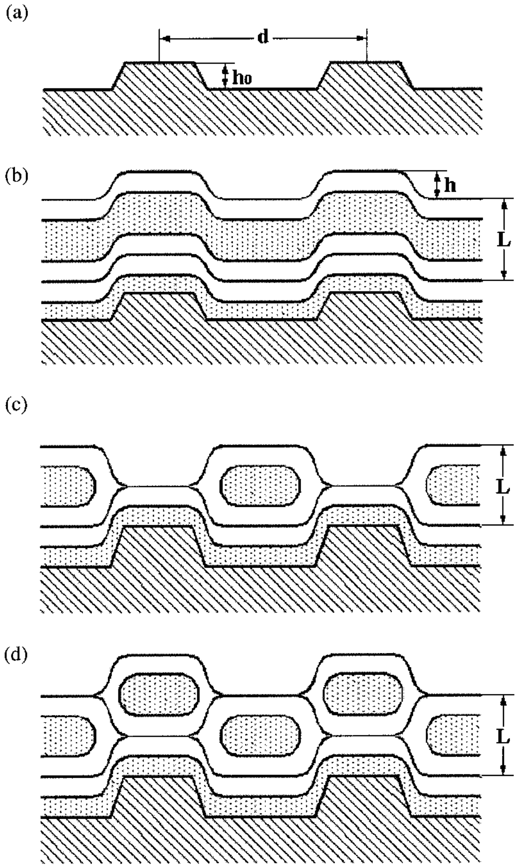

Figure 6. Schematic cross section of the configurations: (a) bare Si grating, (b) conformal arrangement of a diblock copolymer lamellar on a grating with $h_0 < h_c$; (c) anticonformal configuration of a copolymer film on a grating with $h > h_c$; (d) arrangement of different layers in the anticonformal case. This drawing is based on the TEM image shown in Figure 8c. Note that the uppermost two layers are anticonformal to each other.

while the lower surface energy of PS[21] requires a PS layer at the vacuum interface. Figure 6b shows the conformation of block copolymer layers in the conformal configuration, while Figure 6c shows the configuration of the same block copolymer on a higher grating where the ordering becomes nonconformal to the grating interface. In Figure 6d a sketch of a layer system of an anticonformal sample is shown. Note that our TEM data reveals that the P2VP cores of the different layers are *not* connected (see below) so that each single layer is anticonformal with respect to the underlying interface. The structures of the triblock copolymer are similar, except that the in-plane ordering of the cylinders could lie either parallel or perpendicular to the grating grooves.

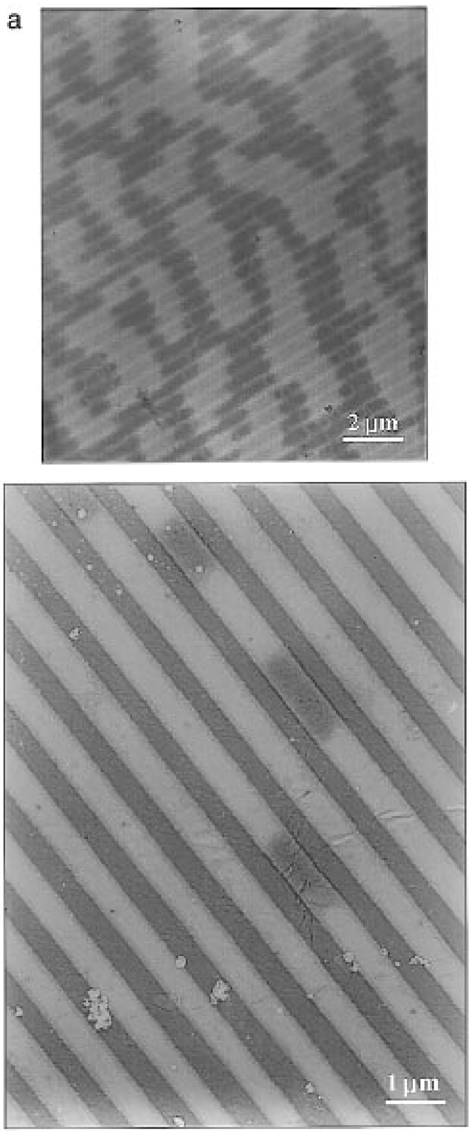

Figure 7. TEM plan view of an $N_{PS} - N_{P2VP} = 1000-1000$ film of thickness H ≈ 710 Å on (a) a grating of $h_0 = 173$ Å, $d = 0.5$ μm, which is conformal to the grating surface and (b) a grating of $h_0 = 440$ Å, $d = 1$ μm, which is anticonformal to the grating surface.

Parts a and b of Figure 7 are TEM micrographs of films having both $N_{PS} - N_{P2VP} = 1000-1000$ and a thickness of $H = 710$ Å but lying on gratings with heights $h_0 = 173$ Å and $h_0 = 440$ Å with conformal and anticonformal structures, respectively. In both figures, the P2VP phase is stained with I_2 to enhance the electron transmission contrast between the P2VP and PS phases. The electron density contrast which results from imperfect flattening of the grating structure when the film is floated on a flat grid is significantly smaller than that due to staining.[22]

Figure 7 is in qualitative agreement with Figure 6. The major difference in a plan view TEM image between

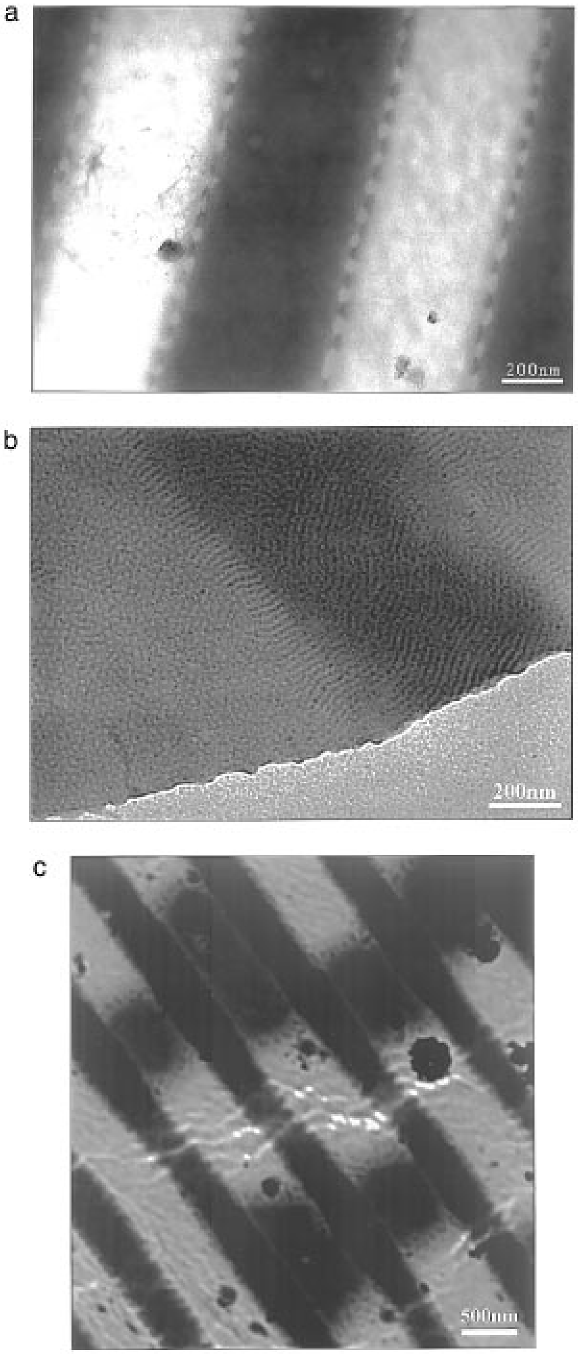

Figure 8. (a) Magnified section of the boundary at the island formed in the grating grooves shown in Figure 7b. Note the defects decorating the island boundary. (b) Ordering of cylinders in a triblock copolymer of P2VP−PS−P2VP on a grating with $h_0 = 90$ Å. The structure is anticonformal. (c) Plan view of a thicker edge of the film shown in Figure 7b. A third layer is seen to form in the grooves of the second. Defects decorate the boundaries of all islands.

the proposed structures in parts b and c of Figure 6 for a lamellar phase is that only the anticonformal structure would show significant in-plane contrast. Figure 8a is a magnified section of the anticonformal film in Figure 7b. The defects observed around the dark P2VP rich sections further confirm that they are the borders of islands confined in the grooves. Similar structures were also found by Liu et al.[9] to decorate island boundaries on flat silicon. They were interpreted as local order−disorder transitions which occur to minimize chain stretching when the islands are confined between two high energy surfaces.[23,24]

Figure 8b shows a slightly thicker film than the one in Figure 8a. The excess material is seen to form the beginning of a third layer in the grooves of the second. It is clear from the plan view shown that the P2VP part of the second and third layers are arranged as shown in parts c and d of Figure 6, respectively. The same defect structure decorates the islands of the third layer, and we would like to emphasize again that it is not connected to the underlying second layer.

Figure 8c shows the edges of the island structure of an anticonformal triblock copolymer film in the grooves of a grating of height $h_0 = 90$ Å. The diameter of the cylinders is approximately 210 Å, as previously observed on flat Si.[9] It is interesting to note that in contrast to the diblock copolymer films, which are disordered at the island boundary, the in-plane ordering of the cylinders is strongest at the island boundaries. Furthermore, the ordering at the boundary orients the cylinders in a direction roughly perpendicular to the grating grooves. This result is not understood as yet, since it seems to maximize rather than minimize the bending of the cylinders by the grating.

The observed conformalities of the smectic copolymer films with different lamellar heights L as a function of h_0 are listed in Table 1. The lamellar heights for all copolymers are consistent with previous investigations.[16] From the table we can summarize as follows: (a) For a given lamellar height L the grating height h_0 is the key parameter that determines whether the conformation of the copolymer is conformal or anticonformal. On gratings with lower heights conformal configurations are prefered whereas higher gratings always yield anticonformal configurations. (b) We may define a *critical* grating height h_c by the condition that for $h_0 < h_c$ the surface of the copolymer film and the substrate are conformal and for $h_0 > h_c$ the film surface and the substrate are anticonformal. The data in Table 1 suggest that h_c increases linearly with the lamellar height, L, and we may roughly estimate the relationship $h_c \approx L/3$.

A qualitative explanation for this conformal/anticonformal transition is that as h_0 increases, the energy penalty of bending the lamellae around the edges of the grating increases, too. When h_0 becomes larger than a critical value h_c the bending energy becomes too large for the lamellar layer to form the conformal configuration. The lamellae then break down to form flat islands in the grooves with an energy cost of increasing the interfacial energy between the PS and P2VP blocks. The energeticly favorable state is a result of balancing the elastic and interfacial energies. This will be discussed further and compared with mean field theory estimates in section 4.

3.2. Roughness Propagation. The second topic which is of importance in connection with diblock or triblock copolymer films is their ability of roughness propagation over rather large vertical distances. This is demonstrated in Figures 9 and 10 where the roughness attenuation $\chi = h/h_0$, h being the roughness of the topmost surface, is shown for different systems as a function of the overall thickness H of the adsorbed films. In Figure 9 the dots are the theoretical prediction for simple liquids,[4] and the dot dashed line shows the result for a homopolymer (PS) with large (M_W = 1.03 M) molecular weight (for details see refs 6, 7, and 13). The curves for the copolymers in the anticonformal configuration are given by the other symbols. The data of the conformal and anticonformal cases corresponds to a

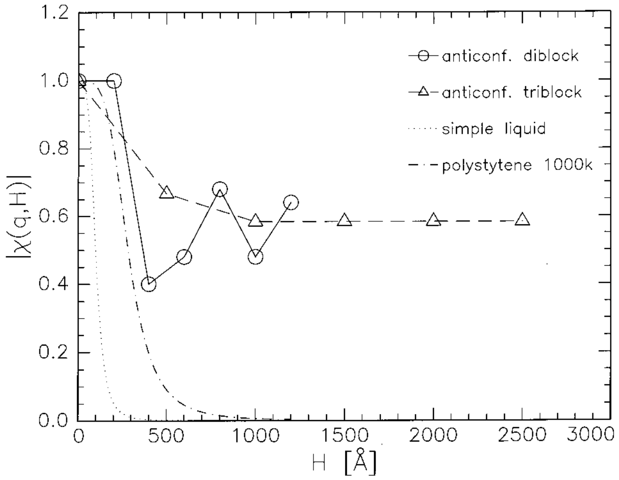

Figure 9. Roughness attenuation $|\chi(q,H)| = h/h_0$ as a function of the total film thickness H for different systems: small molecule liquid (dots); homopolymer liquid (broken line); diblock copolymer anticonformal case (open circles); triblock copolymer anticonformal case (open triangles). The solid and broken lines for the block copolymer films are just lines drawn to connect the points for clarity. They are not given by the theory.

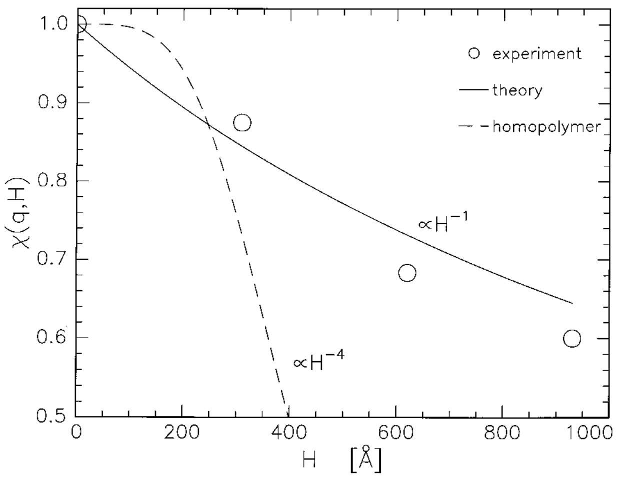

Figure 10. Measured roughness attenuation (open circles) and calculation (solid line) with the model presented in the text. The broken line is the calculation for a homopolymer liquid.

series of $N_{PS} - N_{P2VP} = 200-200$ diblock copolymer films on gratings with heights $h_0 = 120$ and 250 Å, respectively.

From these figures it can be seen that the copolymers are much more efficient in the propagation of the roughness than homopolymers or simple liquid films. Figure 6d indicates that for the anticonformal configuration the roughness of the next layer is simply given by a subtraction of the roughness of the present layer from the lamellar height; i.e., the roughness should oscillate under ideal conditions between $h \approx L - h_0$ and $h \approx h_0$. Oscillations in h/h_0 can be seen for the anticonformal configuration of the diblock copolymer sample.[25]

For the film thicknesses studied, i.e. $H \leq 6L$ we observe that when $h_0 \sim L/2$ then $h \sim h_0$ in all layers and the roughness remains nearly constant (see triangles in Figure 9). Similarly if $h_0 < L/2$, then $h > h_0$, and amplification of the grating roughness occurs in alternate layers. This was observed with the triblock copolymer film value $L = 210$ Å. On a grating surface with $h_0 = 90$ Å an amplified roughness of $h = 120$ Å was found whereas on a grating with $h_0 = 100$ Å a roughly constant value of $h \approx (105 \pm 5)$ Å was measured. A similar amplification was also observed with a $N_{PS} - N_{P2VP} = 1000-1000$ diblock copolymer film on a grating with $h_0 = 280$ Å and maximum $h \approx 440$ Å. An amplification of the roughness is always present if a strongly ordered copolymer of appropriate lamellar height L is chosen. Anticonformal copolymer films, which are very easy to produce, are therefore well suited for applications of nanocontact printing.[26]

4. Theory

The theory of Turner and Joanny,[2] which we mentioned in the introduction, assumes $h_0 \ll L$ and predicts a conformal/anticonformal transition as a function of the lateral spacing, d, and the lamellar height, L. Since we always work in the region $h_0 \sim L$, this theory is not applicable to explain our data.

In this section we will give a theoretical explanation for both major experimental findings—the conformal/anticonformal transition and the very effective roughness propagation of smectic diblock copolymer films. This theory also works in the case $h_0 \sim L$ but is only rigorously true in the thick film limit; i.e., $H/L \gg 1$. Note that experimentally we always work in the limit of only a few layers $H \leq 4L$ (for diblock copolymer films) so that deviations between our results presented in Table 1 and the calculations shown below in sections 4.1 and 4.2 are not unexpected. However, we will see that the theory is able to yield the experimentally determined relationship between h_c and L quite well. For this purpose we first have to calculate the free energy of a smectic film on a periodic surface.

4.1. Free Energy of Copolymer Films on Periodic Surfaces.

A free energy analysis of a conformal layer stack of diblock copolymer films on periodic surfaces can be carried out using a mean field theory ansatz. The smectic-A phase has rotational symmetry around the layer normal (the z-direction) and symmetry in the $x-y$ plane. Since we have a smectic film of thickness H on a grating with very long parallel grooves we assume translational symmetry in the y-direction. Deformation away form the average (flat) layer position may conveniently be expressed by a continuous scalar displacement field $u(\mathbf{r})$ which represents the normal displacement of the layers in the z-direction. Such a description has been shown to lead to the so called Landau de-Gennes[27,28] free energy per unit length in the y-direction

$$F = \frac{B}{2} \int [(\partial_z u)^2 + \xi^2 (\partial_x u)^2]\, \mathrm{d}x\, \mathrm{d}z \qquad (1)$$

where ξ is a length characteristic of the smectic defined by

$$\xi = \sqrt{K/B} \qquad (2)$$

and B and K are the compressional and bending moduli of the smectic and may be estimated from appropriate microscopic theories.[10] The length ξ is predicted[10,27] to be on the order of the lamellar period L. The Landau de-Gennes free energy represents the leading order term in an expansion in powers (and derivatives) of $u(\mathbf{r})$ and is accurate for slowly varying deformations.[27,28] Minimization of F and subsequent calculations are most easily performed in Fourier space where, anticipating periodicity in x, the Fourier transform of $u(\mathbf{r})$ is defined by the series

$$u(x, z) = \frac{1}{\sqrt{2\pi}} \sum_{n=-\infty}^{\infty} \tilde{u}_n(z) \exp(inqx) \qquad (3)$$

where $q = 2\pi/d$. Apart from the periodicity of the problem the following calculation follows closely that of ref 10. Minimizing the free energy F gives the deformation field which minimizes the bulk deformation energy

$$\tilde{u}_n(z) = \alpha_n \exp(\xi n^2 q^2 z) + \beta_n \exp(-\xi n^2 q^2 z) \qquad (4)$$

where the integration constants α_n and β_n are determined by the boundary conditions at the substrate and the free surface of the film, i.e. at $z = 0$ and $z = H$, finally yielding

$$\tilde{u}_n(z) = (\tilde{u}_n(H) - \tilde{u}_n(0) \exp\{-\xi n^2 q^2 H\}) \frac{\sinh(\xi n^2 q^2 z)}{\sinh(\xi n^2 q^2 H)} + \tilde{u}_n(0) \exp\{-\xi n^2 q^2 z\} \qquad (5)$$

A surface term must now be added to eq 1 in order to include the work done in deforming the free surface of the smectic film against the surface tension γ. This term is an energy density of the form

$$F_{\text{surf}} = \frac{\gamma}{2}(\partial_x u)^2\, \delta(z - H) \qquad (6)$$

which leads to the following energy per unit area of the surface

$$F = \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} \left[\frac{\gamma}{2} n^2 q^2 \tilde{u}_n(H) \tilde{u}_{-n}(H) + \frac{B}{2} \int_0^H (\partial_z \tilde{u}_n(z) \partial_z \tilde{u}_{-n}(z) + \xi^2 n^4 q^4 \tilde{u}_n(z) \tilde{u}_{-n}(z))\right] \mathrm{d}z \qquad (7)$$

Minimization of eq 7 with respect to the shape of the free surface, specifically $\tilde{u}_n(H)$, gives

$$\tilde{u}_n(z) = \tilde{u}_n(0) \frac{\cosh\{\xi n^2 q^2 (H - z)\} + \Gamma \sinh\{\xi n^2 q^2 (H - z)\}}{\cosh(\xi n^2 q^2 H) + \Gamma \sinh(\xi n^2 q^2 H)} \qquad (8)$$

where $\Gamma = \gamma/(\mathrm{KB})^{1/2}$ is assumed to be much larger than unity in what follows. This is a quite reasonable assumption for diblock copolymer films where $(\mathrm{KB})^{1/2} \approx \gamma_{\mathrm{AB}}$, the interfacial tension acting at the interface between the two copolymer blocks. Substitution of the result (eq 8) into eq 7 yields

$$F = \sum_{n=-\infty}^{\infty} \frac{\sqrt{KB}}{4\pi} n^2 q^2 \tilde{u}_n(0) \tilde{u}_{-n}(0)\, \Lambda_n \qquad (9)$$

with

$$\Lambda_n = \frac{\Lambda + \tanh(n^2/{n_c}^2)}{1 + \Lambda \tanh(n^2/n_c 2)} \qquad (10)$$

where we have introduced $n_c = 1/(q\sqrt{\xi H})$. We model the deformation of the substrate by a periodic step function of peak to peak amplitude h_0 (the grating height)

$$u(x,0) = \pm h_0/2 \qquad (11)$$

where the plus sign has to be chosen for $md < x < md + d/2$ and the minus sign for $md - d/2 < x < md$, respectively, and m is an integer. Calculating the Fourier coefficients and inserting the respective $\tilde{u}_n(0)$ into eq 9 finally leads to

$$F = \sum_{n=1;\text{odd}}^{n^*} \frac{\sqrt{KB}}{\pi^2} {h_0}^2 q^2\, \Lambda_n \qquad (12)$$

where we have introduced $n^* = c_1/(q(\xi \mathrm{L})^{1/2} = c_1 n_c(\mathrm{H}/\mathrm{L})^{1/2}$ as a high wavelength cutoff in order for F to converge. Here c_1 is a positive constant of order unity which depends on the precise choice of the small wavelength cutoff. The physical origin of this cutoff is the failure of the continuum smectic theory to correctly account for modes with wavelengths smaller than the lamellar period. The length $(\xi \mathrm{L})^{1/2} \sim L$ appears in the definition only for notational convenience. Our estimate of F neglects the energy of deformation, or local phase changes, on length scales smaller than L. Clearly the energy F can be calculated numerically for arbitrary parameter values, but in order to develop an understanding of the physics involved, it is convenient to assume separation of length scales according to $n^* \gg n_c$. Such separation is valid provided that the film has several layers $H/L \gg 1$. In this case Λ_n has the following asymptotic behavior

$$\Lambda_n \approx \begin{cases} \dfrac{\Gamma}{1 + \Gamma n^2/{n_c}^2} & \text{for } n \ll n_c \\ 1 & \text{for } n \gg n_c \end{cases} \qquad (13)$$

With the further assumption ${n_c}^2 \gg \Gamma$, i.e., that the grating repeat period d is large enough, we find to leading order

$$F \approx \frac{q}{2\pi} {h_0}^2 \frac{\sqrt{KB}}{\pi\sqrt{\xi L}} \left(\frac{\pi}{2}\sqrt{\Lambda\, L/H} + c_1\right) \qquad (14)$$

where we recall that c_1 is an undetermined positive constant of order unity which depends on the precise choice of the small wavelength cutoff. The factor $q/(2\pi)$ in eq 14 must be present in the $q \to 0$ limit and simply means that the energy is linear with the number of grooves per unit length in x-direction.

Before estimating the critical height with eq 14 we would like to recapitulate the assumptions made to obtain this result.

(i) We have worked in the thick film limit. The calculation described in this section is formulated in the continuum limit which is appropriate for $H/L \gg 1$. We extrapolate our results to the thin films studied experimentally here with the warning that our theory is starting to break down for films with only one or two layers.

(ii) The calculation is valid only for strongly segregated copolymers and the lamellar phase. It is valid neither for the hexagonal phase nor for the anticonformal array shown in parts c and d of Figure 6.

(iii) There was the assumption that we have $d \gg H$, L, ξ. This assumption is not crucial, and at least we would be able to calculate the sum given by eq 12 numerically for arbitrary configurations. Furthermore we have calculated eq 14 for a periodic step function grating rather than for the trapezoidal shape of our substrates. Since the deviation from a periodic step function is small we expect that this effect on the final result is negligible.

Points (i) and (ii) mean that our theory may only be expected to give an estimate for the critical height h_c. A completely different, discretized theory may be able to be more quantitative. However, in the following section we will see that our simple result given by eq 14 is able to explain the experimentally observed connection between h_c and L quite well.

4.2. Estimate for the Critical Height. So far we have merely derived the energy of a conformal film on a general, but periodic, substrate. The problem which we are primarily interested in here is predicting under what conditions the upper free film surface is caused to undulate out of phase with the substrate. This kind of arrangement will be produced whenever defects occur consisting of stripes of material inside the grooves of the grating.

The energy F_{conf} of the conformal arrangement of the smectic film on the periodic substrate is simply given by eq 14. To calculate the energy F_{anti} of the anticonformal case we have to bear in mind that in the thick film limit $H/L \gg 1$ the P2VP cores may be connected and only the layer next to the substrate consists of defects, so that also for the anticonformal arrangement a bending energy $F_{\mathrm{bend}} \approx F_{\mathrm{anti}}$ according to eq 14 has to be taken into account but with $L - h_0$ instead of h_0. Balancing both energies, i.e. solving $F_{\mathrm{conf}} = F_{\mathrm{anti}}$, would simply yield for the critical height $h_c = L/2$.

However, since our experiments were done in the region of only a few layers and we found experimentally that the structure can be described by parts c and d of Figure 6, i.e., by defects throughout the *whole* sample, this result is not applicable to explain our data.

The main contribution to the free energy in the anticonformal case of only a few layers stems from the creation of new interfaces between PS and P2VP. This interfacial energy F_{int} is obviously proportional to the height of the lamellar and the number of stripes so that we may assume

$$F_{\mathrm{anti}} \approx F_{\mathrm{int}} = c_2 \frac{q}{2\pi} L \sqrt{KB} \tag{15}$$

where c_2 is another positive constant which magnitude can be crudely estimated from a calculation given by Semenov.[29] Solving $F_{\mathrm{conf}} = F_{\mathrm{anti}}$ is again the condition for the critical height h_c leading to ($\xi \approx L$)

$$h_c = \left(\frac{2c_2}{\sqrt{\Lambda L/H} + 2c_1/\pi} \right)^{1/2} L \tag{16}$$

Since H is always on the order of L in our experiments, eq 16 yields a linear increase of the critical height h_c with the lamellar height L of the polymer with a prefactor which is on the order of $\Gamma^{-1/4} \approx 0.4$ for our copolymers in good agreement with the experiment (see Table 1, section 3.1, and note ref 30).

The question whether for thick films, i.e., films with $H/L \gg 1$, the structures of the anticonformal arrangement are also given by parts c and d of Figure 6, or whether anticonformal *connected* P2VP layers plus only one defect layer exist cannot be solved by our study. We may only estimate from which total film thickness H_c one may expect to see such a configuration by the following consideration. The energy cost of creating defect stripes throughout the sample is merely given by $F_{\mathrm{int}}H/L$ for more than one layer. If this energy is compared with the total deformation energy F_{conf}, the maximum value of H_c occurs for $h_0 \approx L/2$ for which we find ($\Gamma = 30$ in our study)

$$H_c \sim L\Gamma^{1/3} \approx 3L \tag{17}$$

Since almost all data for the diblock copolymer samples were taken for three layers or less we have worked in the regime $H \leq H_c$. For thicker anticonformal films we may expect to see a single layer of defect stripes and alternate connected P2VP and PS layers.

4.3. Roughness Propagation in Copolymer Films. For a conformal smectic film with thickness H the attenuation function $\chi(nq, H) = \tilde{u}_n(H)/\tilde{u}_n(0)$ of the Fourier components with wave vector nq can simply be calculated using eq 8. The result is the explict expression

$$\chi(nq, H) = \frac{1}{\cosh(\xi n^2 q^2 H) + \Gamma \sinh(\xi n^2 q^2 H)} \tag{18}$$

for the roughness propagation. The function χ is for the first harmonics, i.e., $n = 1$, equivalent to h/h_0 with h being the depth of the grooves for a film of total thickness H. If we chose the values for the $N_{\mathrm{PS}} - N_{\mathrm{P2VP}} = 200-200$ diblock copolymer sample used, we are able to explain very well our data obtained with a $h_0 = 120$ Å grating. This is demonstrated in Figure 10 by the line which represents the theory. Note that this line is close to the data points without having any free adjustable parameters.

For $\xi q^2 H n^2 \ll 1$ (i.e. $n_c^2 \gg n^2$) we may expand eq 18

$$\chi(nq, H) = \frac{1}{1 + \Gamma\, n^2/n_c^2} \tag{19}$$

yielding a rapid decay according to $1/n^2$ for the higher harmonics as observed in our experiments. Using the definition $b = 1/(\Gamma\xi)$, eq 19 may be rewritten as

$$\chi(nq, H) = \frac{1}{1 + n^2 q^2 b^{-1} H} \sim H^{-1} \tag{20}$$

For small molecule liquids and homopolymers χ is given by[4,6,7]

$$\chi(nq, H) = \frac{1}{1 + n^2 q^2 a^{-2} H^4} \sim H^{-4} \tag{21}$$

with the healing length a which is on the order of 10 Å for simple liquids and on the order of 100 Å for long chain homopoloymers. The broken line in Figure 10 represents this function which can not be adjusted to our data points. Equations 20 and 21 show that vertical roughness propagation in thin diblock copolymer films is much more efficient ($h/h_0 \propto H^{-1}$) than in homopolymer films even with much higher molecular weight ($h/h_0 \propto H^{-4}$).

Since the theory of section 4.1 does not work for the anticonformal arrangements of the thin films shown in Figures 6c and 6d, we cannot make a quantitative comparison with the data which we obtained for the roughness propagation in this case. However, we may do a crude qualitative discussion. Figure 6d and the discussion in section 3.2 suggest that $\chi(q, H)$ may be written as (m is an integer)

$$\chi(q, H = mL) \approx \begin{cases} -\dfrac{L - h_0}{h_0} & \text{for } m \text{ odd} \\ +1 & \text{for } m \text{ even} \end{cases} \tag{22}$$

because alternate anticonformal/conformal configurations with respect to the grating are present. The minus sign in front of the first case indicates that this layer is anticonformal (the Fourier components are negative compared to those of the grating!). Note that eq 22 does not contain a q-dependence, which means that all Fourier components are transferred with the same strength. Since the experiments reveal that higher harmonics are rapidly damped in the anticonformal case too, we have to bear in mind that this is an oversimplified picture. In the limit of very thick films, where the surface induced ordering is attenuated,[25] one would expect a similar attenuation function χ as in the conformal case.

For the $N_{PS} - N_{P2VP} = 200-200$ diblock copolymer films with $L = 310$ Å on a grating with height $h_0 = 250$ Å, according to eq 22, we would expect an oscillation of χ between the values $\chi(m_{odd}) = -0.24$ and $\chi(m_{even}) = 1$, respectively. In Figure 9 the measured absolute values of χ for the diblock copolymer films are given by the open circles. The oscillation is clearly visible but the amplitude is smaller than that calculated from eq 22. A possible reason for this is the always present conformal P2VP layer next to the Si surface which has to be treated in a different way.

Equation 22 also suggests that if $L \sim 2h_0$ the attenuation function $|\chi(q, H)|$ should remain constant as discussed in section 3.2. This behavior is confirmed by the measurement with the $L = 210$ Å triblock copolymer film on the grating with height $h_0 = 120$ Å $\sim L/2$. The roughness remains constant but a lower value than the ideal value 1 given by eq 22 is found. The reason may again be the thin always present conformal P2VP layer which leads to a certain amount of roughness attenuation before the χ function given by eq 22 can start to work.

5. Conclusions

Ordered copolymers form conformal and anticonformal roughness configurations on patterned substrates and have a high efficiency to propagate the roughness over long vertical distances. This particular behavior of diblock and triblock copolymer films on grating surfaces is described by a simple mean field theory. It is shown that this theory is able to explain the data both the confromal−anticonformal transition and the roughness attenuation. The reason for the transition from conformal to anticonformal behavior is found to be the edge confinement of the lamellar islands. The theory has confirmed the experimental finding that the critical grating height for the transition is proportional to the lamellar height of the used copolymer. Furthermore we have shown that block-copolymer films are much more efficient in roughness propagation than homopolymer or liquid films.

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References and Notes

(1) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *Phys. Rev. Lett.* **1989**, *62*, 1852.
(2) Turner, M. S.; Joanny, J.-F. *Macromolecules* **1992**, *25*, 6681.
(3) We neglect throughout this paper the statistical high freqency roughness of the substrate and copolymer films. This roughness is always on the order of 5 Å and is therefore negligible.
(4) Andelmann, D.; Joanny, J.-F.; Robbins, M. O. *Europhys. Lett.* **1988**, *7*, 731.
(5) Tidswell, I. M.; Rabedeau, T. A.; Pershan, P. S.; Kosowsky, S. D. *Phys. Rev. Lett.* **1991**, *66*, 2108.
(6) Li, Z.; Tolan, M.; Höhr, T.; Sokolov, J.; Rafailovich, M. H.; Lorenz, H.; Kotthaus, J. P.; Wang, J.; Sinha, S. K. *Macromolecules*, submitted for publication.
(7) Tolan, M.; Vacca, G.; Wang, J.; Sinha, S. K.; Li, Z.; Rafailovich, M.; Sokolov, J.; Gibaud, A.; Lorenz, H.; Kotthaus, J. P. *Phys. B* **1996**, *221*, 53.
(8) Hu, H. W.; Granick, S. *Science* **1992**, *258*, 1339.
(9) Liu, Y.; Rafailovich, M. H.; Sokolov, J.; Schwarz, S. A.; Zhong, X.; Eisenberg, A.; Kramer, E. J.; Sauer; B. B. *Phys. Rev. Lett.* **1994**, *73*, 440.
(10) Turner, M. S.; Maaloum, M.; Ausseré, D.; Joanny, J.-F.; Kunz; M. *J. Phys. II* **1994**, *4*, 689.
(11) Tolan, M.; Li, Z.; Rafailovich, M. H.; Sokolov, J.; Lorenz, II.; Kotthaus; J. P. To be published.
(12) Hansen, W.; Kotthaus, J. P.; Merkt, U. *Semiconductors and Semimetals 35*; *Nanostructured Systems*; Academic Press, Inc.: New York, 1992, p 279.
(13) Tolan, M.; Vacca, G.; Sinha, S. K.; Li, Z.; Rafailovich, M. H.; Sokolov, J.; Lorenz, II.; Kotthaus, J. P. *Phys. D: Appl. Phys.* **1995**, *28*, A231.
(14) Dai, K. H.; Kramer, E. J. *Polymer* **1994**, *35*, 151.
(15) O'Malley, J. J.; Crystal, R. G.; Erhardt, P. F. *Polym. Prepr.* **1969**, *10*, 796.
(16) Liu, Y.; Zhao, W.; Zheng, X.; King, A.; Singh, A.; Rafailovich, M. H.; Sokolov, J.; Dai, K. H.; Kramer, E. J.; Schwarz, S. A.; Gebizlioglu, O.; Sinha, S. K. *Macromolecules* **1994**, *27*, 4000.
(17) Coulon, G.; Russell, T. P.; Deline, V. R.; Green, P. F. *Macromolecules* **1989**, *22*, 2581.
(18) Maaloum, M.; Ausseré, D.; Chatenvay, D.; Coulon, G. *Phys. Rev. Lett.* **1992**, *68*, 1575.
(19) Schwarz, S. A.; Wilkens, B. J.; Pudensi, M. A. A.; Rafailovich, M. H.; Sokolov, J.; Zhao, X.; Zhao, W.; Zheng, X.; Russell, T. P.; Jones, R. A. L. *Mol. Phys.* **1992**, *76*, 937.
(20) Independently from the AFM pictures we did X-ray scattering measurements to confirm the anticonformal structures. From the particular phases of the intensity oscillations measured along the rods in reciprocal space, which are given by the lateral periodicity, we can rule out a conformal arrangement for the films shown in parts b and c of Figure 3 (see ref 11).
(21) Sauer, B. B. Private communication.
(22) This point was verified further by obtaining images of the same film with and without I_2 staining.
(23) Carvalho, B. L.; Thomas, E. L. *Phys. Rev. Lett.* **1991**, *73*, 3321.
(24) Walton, D. G.; Kellogg, G. J.; Mayes, A. M.; Lambooy, P.; Russell, T. P. *Macromolecules* **1994**, *27*, 6225.
(25) For very large film thicknesses, the degree of orientation of the lamellae parallel to the surface diminishes. In this case island formation is not that efficient and the roughness is attenuated as strong as in the conformal case.
(26) Kim, E.; Whitesides, G. M.; Lee, L. K.; Smith, S. P.; Prentiss, M. *Adv. Mater.* **1996**. *8*, 139.
(27) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(28) de Gennes, P. G. *J. Phys. Suppl. C4* **1989**, *30*, 65.
(29) Semenov; A. N. *Sov. Phys.-JETP (Engl. Transl.)* **1985**, *61*, 733.
(30) From Table 1, we estimate $h_c \sim L/3$. However, the accuracy of the data rules out neither the value $h_c \sim 0.4L$ nor the thick film limit result $h_c \sim L/2$.

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