Wetting Behavior of Homopolymer Films on Chemically Similar Block Copolymer Surfaces

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(Received 6 April 1994)

The wetting properties of thin polystyrene (PS) homopolymer films (polymerization index N_H) were studied on the surfaces of polyvinylpyridine-polystyrene (PVP-PS) block copolymer films (polymerization indices N_{PS} and N_{PVP}) oriented into lamellae with the PS block present at the vacuum interface. Autodewetting was observed on the diblock copolymer surface when $N_H/N_{\mathrm{PS}} \geq 5$, with a contact angle independent of N_H, but decreasing with N. The dewetting nucleated at the base of islands on the ordered PVP-PS surfaces. The dewetting processes were explained using mean field theories and Monte Carlo simulations.

PACS numbers: 61.41.+e, 68.45.Gd

Thin uniform polymer films have a large variety of practical applications. Recently it has been demonstrated [1–5] that the wetting properties of polymer molecules can be very different from those of simple liquids. Silberzan and Léger [1] demonstrated, as predicted by Bruinsma [2], that the spreading of a polymer drop on a solid surface occurs via reptation through a precursor layer whose thickness scales as R_g, the radius of gyration of an unperturbed polymer chain in the melt. Reiter [3] studied the effects of chain entanglements on the dynamics of the dewetting process. Zhao *et al.* [4] found that a polymer film can be induced to dewet a surface, which it would otherwise wet, if its thickness becomes smaller than R_g.

The above studies have focused on the properties of the spreading film. In this Letter we concentrate on the role of the molecular architecture of the substrate surface. In particular, if the substrate consists of a "brush" of grafted chains into which the spreading homopolymer cannot penetrate deeply, an interface with corresponding interfacial free energy will be established. In contrast to the case of a simple liquid, which will always spread on a free surface of the same composition, autodewetting of the materials can occur. An entropic barrier can be established when the polymer molecules are confined in specific configurations, i.e., end-grafted to a solid substrate, ordered in lamellae on a block copolymer surface or interconnected in a gel-type matrix. In these cases the entropic gain in free energy associated with interpretation of the homopolymer chains is more than offset by the loss in conformational entropy due to distortion of the substrate chains and a well defined interface is formed. The excess energy associated with this interface can then destabilize the film and induce dewetting.

The conditions for autodewetting were first calculated by Leibler *et al.* [5]. They write the spreading parameter of a homopolymer liquid on a brush surface as $S = \gamma_B - (\gamma_H + \Delta F)$, where γ_B and γ_H are the surface tensions at the vacuum/brush and vacuum/homopolymer interfaces, respectively, $\Delta F = 3/8kT/\lambda a$, is the interfacial tension at the brush/melt interface, k is the Boltzmann constant, a is the polymer statistical segment length [6.7 Å for polystyrene (PS)], and λ is the width of the brush/homopolymer interface. When the brush and homopolymer melt are chemically identical, the difference in surface tensions is due to the fact that distortions of the brush surface involve some stretching of the anchored brush polymers in contrast to homopolymers which may freely translate under surface distortion. In the brush regime, $(\gamma_B - \gamma_H)/\Delta F \sim N^{-1}$, where N is the index of entire diblock ($N = N_A + N_B$), so the surface tension terms can be neglected [5], leaving the spreading parameter $S \cong -\Delta F$ determined entirely by the interpenetration depth. As a result, when λ is finite, partial wetting should occur with an equilibrium contact angle θ given by Young's relation, which for small angle θ reads; $\theta \cong (2\Delta F/\gamma_H)^{1/2}$.

To test these predictions we chose to study via atomic force microscopy (AFM) the dewetting properties of homopolymer films on block copolymer surfaces of the same chemical composition but different polymerization indices. The results were then correlated to the extent of the brush/homopolymer interpenetration as determined by neutron reflectivity (NR) and secondary ion mass spectrometry (SIMS).

The block copolymers used in this study were composed of monodisperse PS or deuterated (*d*) PS and polyvinylpyridine (PVP) blocks anionically polymerized

0031-9007/94/73(3)/440(4)$06.00

[6]. The polymerization indices N_{PS} and N_{PVP} of the copolymers used are listed in Table I. The Flory interaction parameter χ has been measured for this system [6] and for the temperatures discussed here all the block copolymer melts were well below their order-disorder transition (ODT), in the strong segregation regime.

In order to align the microdomains parallel to the vacuum surface, thin films of the block copolymers were spun cast out of toluene solution onto polished native oxide covered silicon wafers and annealed at 185 °C for 5 d. The diblock copolymers all had $N_{\mathrm{PVP}} \sim N_{\mathrm{PS}}$, and hence were expected to order into lamellae parallel to the silicon interface. The triblock copolymers were asymmetric, having a PVP volume fraction of 0.25, and hence were expected to order into a single lamellar layer at the silicon interface, followed by hexagonally stacked cylindrical layers [7]. SIMS was used to confirm that the substrate films were well ordered and that the vacuum surface consisted of a pure PS or dPS layer. Film thicknesses corresponding to one to three lamellar height were studied with equivalent results.

Films approximately 100 Å thick of PS homopolymer were spun cast onto glass slides, floated from water on top of the ordered block copolymer films, and reannealed in vacuum at 185 °C. The surface morphology was then studied with a Digital Nanoscope III AFM using a $\mathrm{Si_3N_4}$ tip in the contact mode. Upon dewetting the films coarsened into interconnected patterns or droplets which became visible after annealing for 5 h and reached their equilibrium height after 24 h. The dynamics of the dewetting process was mostly a function of the homopolymer film thickness and will be discussed elsewhere.

Figure 1 shows the surfaces of films obtained after a 24 h anneal. In these cases the block copolymer film thicknesses were chosen to have integral values of n and hence the ordered surfaces were smooth. From the figure we can see that PS film having $N_H \cong 650$ completely wets the surface of the 200–200 diblock copolymer, while it dewets from the surface of the triblock copolymer. A film of PS having $N_H \cong 6700$, on the other hand, is seen to dewet the surface of 200–200 and 510–540 block copolymer, forming large separated droplets. The same film spread on the 800–870 diblock copolymer is seen to roughen but does not break up. The results for other PS homopolymers on the same di- and triblock copolymer surfaces are summarized in Table I, where we designate by "D" the surfaces upon which the films break up into well defined droplets and "W" the surfaces upon which the films remain smooth or simply roughen without breaking up. We can see that the 200–200 and 510–540 diblock copolymer surfaces have a well defined wetting transition around $N_H \geq 5N_{\mathrm{PS}}$ whereas all homopolymer films dewet the triblock copolymer surfaces.

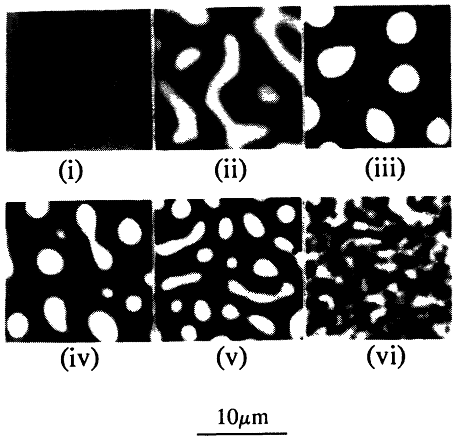

FIG. 1. AFM micrographs of homopolymer films ~100 Å thick annealed for 24 h at 185 °C on ordered block copolymer films. (i) $N_H = 650$, 200–200; (ii) $N_H = 650$, 91–590–91; (iii) $N_H = 2200$, 200–200; (iv) $N_H = 6700$, 200–200; (v) $N_H = 6700$, 510–540; (vi) $N_H = 6700$, 800–870.

TABLE I. Molecular weight dependence of dewetting (W denotes wet and D denotes dewet).

PVP-PS copolymer	PS homopolymer (N_H)					
Index	220	650	1040	2200	6700	10000
200–200	W	W	W	D	D	D
510–540	W	W	W	D	D	D
800–870	W	W	W	W	W	W
44–286–44	W	D	D	D	D	D
91–590–91	D	D	D	D	D	D

Figure 2 shows the NR spectra for a $N_H = 5500$ homopolymer film of 710 Å on top of an ordered 200–200 block copolymer surface, plotted as $\log(Rk_z^4)$ vs k_z, where R is the reflectivity and k_z is the neutron wave vector normal to the surface. The upper curve corresponds to the unannealed bilayer while the lower curve corresponds to the sample following 5 h anneal at 172 °C. The annealing time was optimized so that it was sufficient for the interface to reach equilibrium and for the thin films of Fig. 1 to dewet the block copolymer surfaces. On the other hand, the time was too short for the thicker film (710 Å) used in the NR experiment to dewet the surface. The solid line corresponds to a fit using a layered model with a Gaussian interfacial profile. Prior to annealing the interfacial width was $\lambda = 10$ Å which is similar to the roughness at the vacuum interface, $\sigma = 12$ Å. After annealing, the homopolymer interface broadens to $\lambda = 71$ Å, while σ increases slightly to 15 Å. Similar experiments were also conducted for this homopolymer on the 510–540 and 800–870 block copolymer surfaces. In these cases the interfacial widths, after annealing became 120 and 145 Å, respectively, sufficiently broad such that they could also be observed with SIMS.

Using a parabolic mean filed potential, several groups [8,9] have calculated the interpenetration length, λ, between a Gaussian polymer chain and a block copolymer lamellar surface of the same chemical composition. The results show that even though the block copolymers are

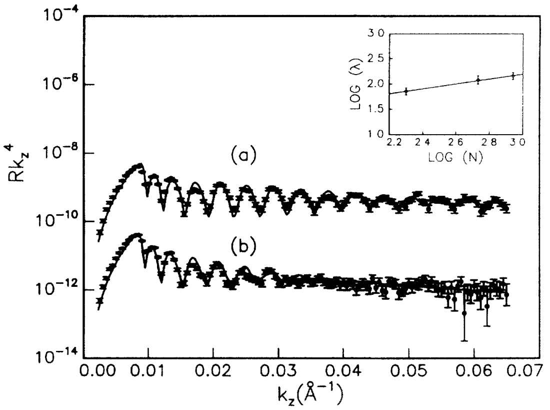

FIG. 2. Neutron reflectivity data plotted as $\log(Rk_z^4)$ vs k_z (Å^{-1}) for a *d*PS ($N_H = 5500$) film, 710 Å thick, on the top of a ordered 200–200 diblock copolymer film, 720 Å thick; (a) unannealed (b) after annealing for 5 h at 172 °C. Inset: $\log(\lambda)$ vs $\log(N)$ for homopolymer films of $N_H = 5500$ and 6700, on the ordered block copolymer surfaces.

in the strong segregation regime, i.e., $40 \le \chi N \le 167$, for the copolymers used in this paper [6], L scales as $N^{0.6}$ [9], indicating that the chains in the brush are only moderately extended and are therefore easily penetrated by the homopolymer. In this case, the calculations [9] give, $\lambda \sim a\chi^{-1/18}N^{4/9}$, independent of N_H. For our system, $\lambda \cong 7.6N^{4/9}$, or nearly equal to $L/4$, the entire outer layer thickness of the surface-active block in a symmetric lamellar structure. The log of λ, as measured by NR and SIMS is plotted in the inset of Fig. 2 as a function of $\log N$. The slope and the intercept values 0.49(3) and 0.72(8) are in reasonable agreement with mean field predictions [9]. Substituting λ in the expressions of the spreading parameter S and the contact angle θ, we obtain $S \cong -0.0074N^{-4/9}$ (kT/Å), and $\theta \cong 0.56N^{-2/9}$. The contact angle $\theta = 3.4° \pm 0.5°$ measured by AFM, for a PS droplet with $N_H = 2200$ on the 200–200 block copolymer surface, is smaller than the value $\theta = 8.6°$ calculated from the expression above. In contrast to a solid surface, a brush surface can deform at the droplet contact line in response to the vertical component of the surface tension, $\gamma \sin\theta$. The equilibrium contact angle will then be found by balancing the energy gained in minimizing the interfacial area with the energy penalty incurred in stretching the brush. This effect is not considered in the calculation of θ and can easily reduce the contact angle [5]. On the other hand, the decrease of θ with increasing N predicted by Ref. [5] is consistent with our data. It can be seen that the contact angle of homopolymer with $N_H \ge 2200$ is decreased to less than 2° on the 800–870 block copolymer surface. Such a small value is difficult to measure accurately and causes the film to appear rough, rather than as large isolated droplets.

From $S \cong -0.0074N^{-4/9}$ and Fig. 2 we can see that $S < 0$, i.e., autodewetting is predicted on a block copolymer surface even though the brush is not significantly stretched and the homopolymer penetrates the entire surface layer, i.e., the brush is always "wet." The measured critical values for dewetting observed in Table I are therefore different from those discussed in Ref. [5] which describe a "wet" to "dry" brush transition for permanently grafted chains. For a realistic binding energy, it is possible to dissolve the block copolymer chains into the homopolymer layer, thereby eliminating the interface. As a result, the values we measured are better understood in terms of the block copolymer–homopolymer phase diagram. It is well known [10,11] that homopolymers having $N_H \sim N_{\text{PS}}$ can be incorporated into ordered diblock copolymer structures. For $N_H/N_{\text{PS}} \ll 1$, the degree of solubility, ϕ_H, can be sufficiently high so as to induce a wide range of nonlamellar morphologies [11,12]. For $N_H/N_{\text{PS}} \ge 1$, ϕ_H decreases and the homopolymer, say of type A, is localized between the copolymer brushes in the corresponding lamellar domains. This localization induces an expansion of the A domain and a corresponding compression of the B domain [10]. As N_H continues to increase, the energy penalty for distorting the compressed domain becomes larger than that required to produce a macrophase separated system [13] and the homopolymer is not only excluded from the brush but also from the domains between the brushes. In this case, regions of pure homopolymer are shown to coexist with ordered block copolymer domains, with the lamellar spacing the same as that in the pure block copolymer melt [10,13]. The crossover molecular weight for which the brush-brush interaction becomes attractive has been shown via Monte Carlo simulations [13] to occur at approximately $N_H \sim 5N_{\text{PS}}$. For $N_H \le 5N_{\text{PS}}$, the homopolymer layer can diffuse into the ordered block copolymer structure and become localized in the PS domains. As a result, λ is no longer well defined. This can be seen in Figs. 3(a) and 3(b) which shows the SIMS profiles of bilayer samples composed of *d*PS with $N_H = 270$ (3a) or $N_H = 1040$ (3b) allowed to diffuse into an ordered 200–200, PS-PVP block copolymer layer for 5 h at 172 °C. From the deuterium volume fraction in Fig. 3(a) we can see that the ordered lamellar structure is not preserved for $N_H/N_{\text{PS}} \approx 1$. For $N_H/N_{\text{PS}} \approx 5$ the film is still lamellar but the *d*PS has penetrated the structure and is now localized in the PS domains, increasing the lamellar spacing from 300 to 370 Å. This is the same result as that obtained by Mayes *et al.* [10] for a thin film spun cast from a homopolymer–block copolymer melt. The similarity between the two results highlights the fact that the diffusion of homopolymer perpendicular to the ordering direction is not severely hindered [14]. The most probable mechanism for the diffusion process is via penetration of the homopolymer through defects in the lamellar structure. As a result, thin films having $N_H < 5N_{\text{PS}}$ diffuse readily into the block copolymer and the surface appears wet. When $N_H > 5N_{\text{PS}}$, the homopolymer can no longer penetrate between brushes and hence diffusion through defects no longer occurs. The phase separated bilayer is now the equilibrium condition for both single and multilayer block copolymer substrates as shown in Fig. 2, where homopoly-

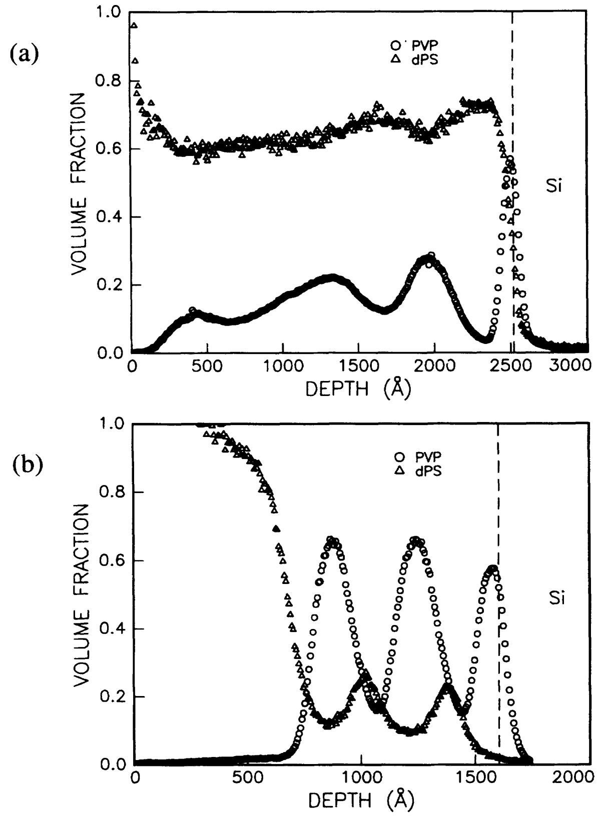

FIG. 3. The volume fraction vs depth profile as measured by SIMS of *d*PS homopolymer films (△) after annealing for 5 h at 172 °C on a previously ordered 200–200 block copolymer substrate (PVP volume fraction designated by (○); (a) N_H = 270, (b) N_H = 1040.

mer of $N_H = 5500$ is seen to form a stable interface with the 200–200 block copolymer and no *d*PS penetration past the first layer occurs.

In contrast to the diblock copolymer films, triblock copolymer films were shown [7] to form ordered cylindrical micelle gels with very few defects. Because of the interconnected structure of penetration the homopolymer into the network was shown to be severely hindered even for $N_H \sim N_{\mathrm{PS}}$. As a result the condition for dewetting the triblock copolymer surface is more severe and occurs for $N_H \geq N_{\mathrm{PS}}$.

Finally, we note the role of the curvature of block copolymer surfaces on the wetting process. An AFM 3D micrograph (Fig. 4) of a $N_H = 6700$ film on an island formed surface of 510–540 diblock copolymer shows that the homopolymer avoids the edge and base of the island, and favors the flat region near the upper edge. This phenomena can be ascribed qualitatively to the additional perturbations of the brush structure due to the curvature of the surface (inset). Around the upper edge of the island the curvature is convex, separating the grafting points and lowering the deformation energy with respect to the flat brush [15]. A similar situation also exists around the top of the holes. At the base of the island the curvature is concave, increasing the grafting density and the deformation energy of the brush. As a result the interfacial free energy of the brush/homopolymer interface is expected to be lower in the convex regions and higher in the concave regions, resulting in the wetting and dewetting regions observed.

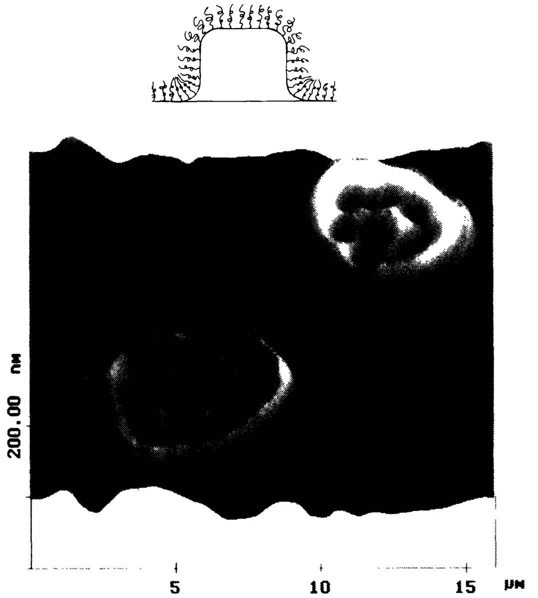

FIG. 4. AFM micrograph of the dewetting structure of a *h*PS film, N_H = 6700, around islands on the surface of a 510–540 ordered diblock copolymer layer. Inset: schematic of the brush surface around the periphery of an island.

We thank M. Rubinstein and A. Balasz for many helpful discussions. Support from NSF (DMR-8921556) and DOE (DE-F602-90-ER) is gratefully acknowledged.

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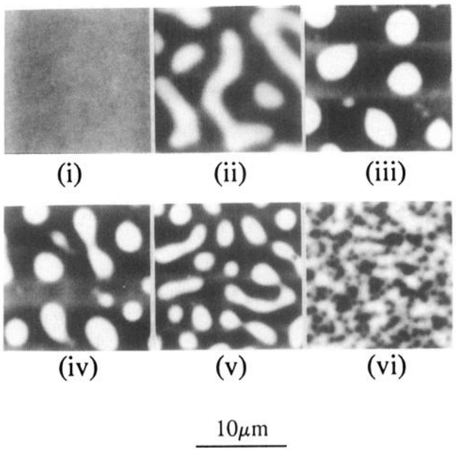
(i) (ii) (iii)

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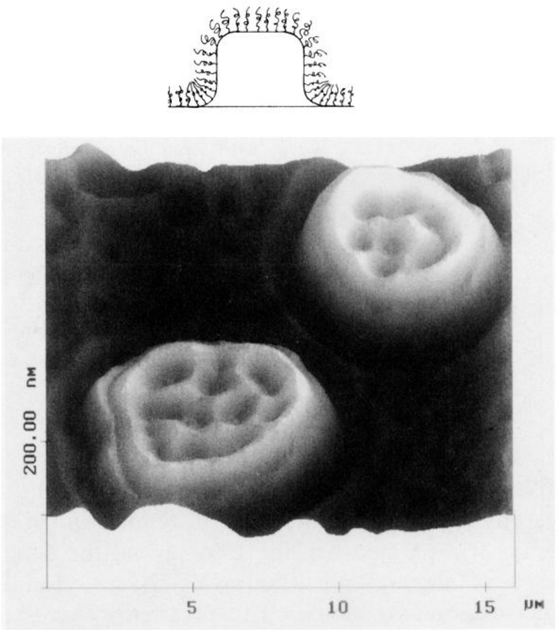

FIG. 4. AFM micrograph of the dewetting structure of a *h*PS film, $N_H = 6700$, around islands on the surface of a 510–540 ordered diblock copolymer layer. Inset: schematic of the brush surface around the periphery of an island.