3254 *Macromolecules* **2003,** *36,* 3254−3260

Dewetting of Thin Film Blends Containing Block Copolymer: Effects of Nonadsorbing Block Length and Substrate Hydrophobicity

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Received September 19, 2002

ABSTRACT: The effects of block copolymer adhesion promoters on the dewetting of polystyrene, PS, homopolymer films with degree of polymerization, P, ∼300 are investigated using optical microscopy and atomic force microscopy. The copolymers are poly(deuterated styrene-*block*-methyl methacrylate), dPS-*b*-PMMA, having a short anchoring block that is attracted to the substrate and a long nonadsorbing block with a varying degree of polymerization, N_{NA}. Relative to a homopolymer film on silicon oxide, SiO_x, hole growth slows down, and holes stop growing at a diameter of about 100 μm when 1 vol % block copolymer having $N_{NA} < P$ is added. The hole floor is found to exhibit a roughness of 1.5 nm and a uniform array of irregularly shaped ($N_{NA} \sim 2P/3$) and rounder ($N_{NA} \sim P/3$) mounds of polymer. In contrast to this partial dewetting, dewetting is entirely suppressed for $N_{NA} > P$. Moreover, as the substrate is changed from SiO_x to a more hydrophobic and less wettable amino-terminated surface, we observe an improvement in thin film stabilization, and no dewetting is detected. The slowing down of hole growth on SiO_x ($N_{NA} < P$) and the growth suppression on SiO_x ($N_{NA} > P$) and on amine-terminated surface are attributed to the reduction of the interfacial tension between the bulk and the adsorbed chains as the interfacial width between the adsorbed block copolymer and matrix chains increases.

1. Introduction

The stability of polymer thin films on solid substrates is of great technological importance in displays, paints, adhesives, and coatings.[1,2] However, a challenging and fundamental problem is that thin films are particularly unstable to external perturbations, such as thermal fluctuations and impurities, which can induce force gradients into the film. These force gradients may lead to film rupture and eventually, if defects grow, dewetting. Thus, research aimed at slowing down or preventing defect growth is critical.

Many studies of dewetting have focused on films containing one component such as block copolymers[3−6] or homopolymers[6−9] deposited on hard or soft substrates. In these cases, the effect of film thickness and molecular weight on dewetting was investigated by both theory[8,10−13] and experiment.[3−7,14,15] These studies show that film stability can be enhanced by increasing film thickness or molecular weight (i.e., viscosity). However, few studies have investigated the effectiveness of designing block copolymers as additives to promote homopolymer film stability.

Using one-component studies as a springboard,[3−8,14,15] we will investigate the dewetting behavior of polymer blend films containing homopolymer with a minor amount of block copolymer designed to adsorb at the film/substrate interface. As shown in Figure 1, the copolymer is asymmetric with a short block (solid circles) designed to anchor to the substrate and a long block (bold black line) that extends into the matrix.[14,16,17] The matrix chain is represented as a dotted line. The degrees of polymerization are noted in Figure 1. In the present study, we propose new experiments aimed at understanding how the kinetics and mechanism of dewetting depend on the nonadsorbing block length, N_{NA}, and the substrate surface energy. In both cases, the microscopic interfacial properties, such as the interfacial width between adsorbed and matrix chains, are expected to be altered and in turn the macroscopic dewetting behavior. These molecular level properties such as the interfacial excess of copolymer, z^*, and interfacial width, w, will be presented in a future publication.[18]

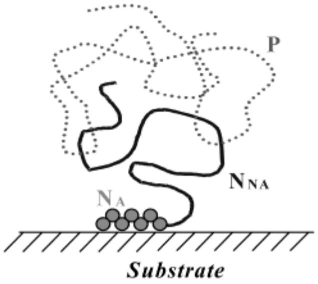

Figure 1. Schematic representation of a block copolymer chain adsorbed from a homopolymer matrix onto a solid substrate. The number of segments of the matrix chain (dotted line), nonadsorbing block (bold solid line), and adsorbing block (filled circles) is denoted as P, N_{NA}, and N_A, respectively.

Depending on the type of long- and short-range intermolecular forces, Sharma et al.[19] identified two main dewetting mechanisms for metastable thin polymer films. In most cases, after annealing above the glass transition temperature, T_g, metastable films begin to dewet near impurities and surface defects, leading to the appearance of holes. These holes nucleate randomly throughout the film. Around holes, material accumulates in circular rims that eventually impinge on neighboring holes and form droplets.[3−7,9,14,15] In addition

10.1021/ma021508k CCC: $25.00

to a nucleation and growth mechanism, a film can rupture by a spinodal mechanism where a bicontinuous pattern is formed as a result of local thickness fluctuations in the film.[3,15] The thin film blends in our experiments dewet by a nucleation and growth mechanism.

For films containing 5 vol % poly(deuterated styrene-*block*-methyl methacrylate) (dPS-*b*-PMMA) in a polystyrene (PS) matrix, we have investigated how the adsorption of dPS-*b*-PMMA to silicon oxide, SiO_x, depends on the matrix degree of polymerization, P.[16] As P increases, z^* increases rapidly and then becomes constant for $P > 2N_{dPS}$, where N_{dPS} is the dPS, nonadsorbing block length. Moreover, w decreases as P increases before reaching a constant value for $P > 2N_{dPS}$. The behavior of z^* and w is consistent with the entropic repulsion of matrix chains from the adsorbed layer when P is much greater than N_{dPS}. For systems with $N_{dPS} \sim P$ and $N_{dPS} \sim 4P$, hole growth was found to slow down and eventually stop on SiO_x.[14] However, the dPS-*b*-PMMA with the longer dPS block was more effective at slowing down hole growth, suggesting that penetration of the dPS block into the matrix has a large effect on film stability. To systematically investigate the effect of nonadsorbing dPS block length on dewetting, a series of diblocks have been synthesized where N_{dPS} is varied from less than P to far above P ($N_{dPS} \sim P/3$, $2P/3$, $5P/3$, and $4P$), while holding the adsorbing block length nearly constant.

In previous studies,[17] the interfacial excess of dPS-*b*-PMMA adsorbed at the film/SiO_x interface was found to decrease as the bromostyrene mole fraction, y, in a poly(styrene-*ran*-4-bromostyrene) (PBr_yS) matrix was systematically increased. Assuming that matrix chains do not interact with the substrate, self-consistent mean-field calculations predicted an increase in z^* with y, consistent with an increase in unfavorable matrix−dPS interactions. Upon including a small attraction between matrix chains and substrate, z^* was observed to decrease with y in agreement with experimental results. Thus, as y increased, PBr_yS competition for SiO_x counteracted the expected increase in dPS-*b*-PMMA adsorption due to the unfavorable interactions between dPS and PBrS. In the present paper, the matrix−substrate as well as the copolymer−substrate interactions are varied by changing the surface energy of the substrate itself. One surface investigated here, and in prior studies,[14,16,17] is SiO_x, which is a hydrophilic surface. To create a more hydrophobic yet polar surface, a self-assembled monolayer (SAM) terminated with an amino group[20−27] is deposited on SiO_x. Our studies will show that a stronger matrix−substrate interaction is partly responsible for improved film stability on amine-terminated surfaces.

2. Experimental Procedure

2.1. System. The block copolymers were prepared with a nearly constant degree of polymerization for the adsorbing methyl methacrylate block ($N_{PMMA} \sim 40$). To investigate the role of interpenetration between adsorbed and matrix chains, the block length of deuterated styrene (dPS) was varied from $N_{dPS} = 94$ to 933 as listed in Table 1. Note that N_{dPS} varies by 1 order of magnitude. Table 1 also lists the copolymer molar masses and polydispersity indexes (PDI) determined by size exclusion chromatography (SEC) and nuclear magnetic resonance (^{13}C NMR).[28]

The polystyrene, PS, matrix polymer, which represents a nearly neutral environment for the dPS block, has a molecular weight of 30 000 g/mol and a PDI ≤ 1.03 and was purchased from Pressure Chemical. In contrast to prior studies,[14] several of the poly dPS-*b*-PMMA block copolymers have N_{dPS} values less than P, the matrix degree of polymerization. The ratio of N_{dPS} to P is given in Table 1. The PS block is deuterated to allow for contrast in ion beam and neutron reflectivity, NR, experiments to be published.[18]

Table 1. Characteristics of dPS-*b*-PMMA Block Copolymers

M_w (g/mol)	N_{dPS}	N_{dPS}/P	N_{PMMA}	PDI
11 000	94	1/3	10	1.21
22 500	169	2/3	48	1.20
50 000	445	5/3	37	1.21
110 000	933	4	44	1.05

Table 2. Characteristics of the Substrates

substrate	thickness [nm]	θ^{adv} [deg]	θ^{rec} [deg]	θ^{static} [deg]	roughness rms [nm][a]
SiO_x	1.8 ± 0.2	6 ± 2	6 ± 2	0[30]	0.3 ± 0.1
APTES	1.6 ± 0.3	43 ± 3	40 ± 3	50[29]	0.4 ± 0.2

[a] Obtained from 5 μm × 5 μm AFM images using Nanoscope III software.

2.2. Sample Preparation. Two types of substrates were used. To prepare SiO_x films on silicon wafers, the native oxide on the as-received silicon wafers was removed by immersion in a hydrofluoric acid:water solution (1:7) for 3 min. These wafers were placed in a UV ozone cleaner for 10 min to produce a clean SiO_x surface. To prepare amino-terminated surfaces, silicon substrates were oxidized following the procedure described by Tsukruv et al.[29] First, the substrates were immersed in a piranha solution, consisting of sulfuric acid: hydrogen peroxide (2:1) at 75 °C, for approximately 30 min. Then the wafers were removed and immersed in deionized water for about 12 h to oxidize the surface. Finally, the wafers were placed in an ultraviolet ozone cleaner for 10 min to produce a clean SiO_x film. The wafers were then placed in a solution of 0.001 wt % (3-aminopropyl)triethoxysilane (APTES, Gelest Inc.) in hexane for about 2 h. To remove free APTES molecules, the substrate was immersed in both hexane and chloroform and then sonicated in each solvent for about 30 min.

Table 2 summarizes the substrate characteristics. The ellipsometric thickness values averaged over five samples are similar. The advancing (θ^{adv}) and receding (θ^{rec}) contact angles of water are the average of five measurements on different substrates. These values are consistent with the static contact angle (θ^{static}) values of SiO_x, 0°, and an amine-terminated surface, 50°, found in the literature.[29,30] Using a Digital Instruments Dimension 3000 atomic force microscope (AFM), the root-mean-square (rms) roughness values were obtained from images analyzed with Nanoscope III software. For five samples, the roughness over a 5 μm × 5 μm image was determined. Note that the APTES layer has a roughness similar to SiO_x, suggesting that any change in dewetting can be attributed to a difference in surface composition rather than roughness.

The polymer films were prepared by spin-casting a solution of 1.8 wt % polymer in toluene at 2000 rpm for 60 s. The solutions were filtered prior to spin-casting to remove dust particles. The polymer concentrations corresponded to 1 vol % dPS-*b*-PMMA and 99 vol % PS. This copolymer concentration is far below the critical micelle concentration, cmc, which is 25 vol % for the highest N_{dPS}. Films were dried in a vacuum oven at 110 °C, above the T_g of both polymers, for 12 h to ensure complete solvent removal. The film thickness values ranged from 65 to 72 nm as measured by ellipsometry.

After drying, samples were immediately placed in a Mettler FP90 hot stage preheated to 175 °C and examined by a Leica optical microscope linked to a video camera and a VCR. From the microscope videotape, hole diameter and density were measured as a function of annealing time. In most cases, holes were monodisperse. From the plots of hole diameter, D, vs annealing time, t, the hole growth rate, v, for the four dPS-

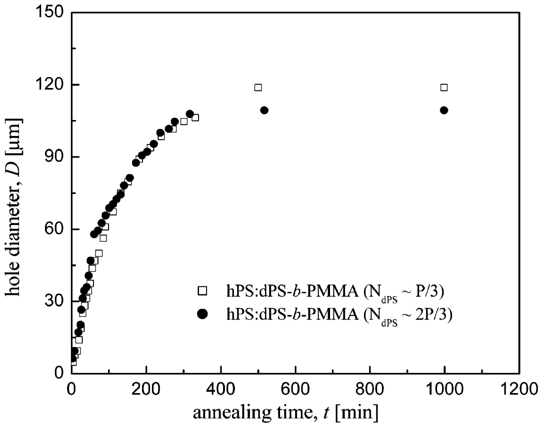

Figure 2. Hole diameter, D, as a function of annealing time, t, for films containing 99 vol % PS and 1 vol % dPS-*b*-PMMA on SiO_x surfaces. The nonadsorbing dPS blocks correspond to $N_{dPS} \sim P/3$ (open squares) and $N_{dPS} \sim 2P/3$ (solid circles). The PS matrix has a molecular weight of 30 000 g/mol.

b-PMMA:PS blend films on SiO_x and APTES was determined. The growth rate was determined at early times when D increased linearly with t. The hole diameter was measured until holes touched each other or reached a constant size. In both cases, AFM was then used to image the hole floors and rims and to determine the roughness and the morphology inside the holes.

In a previous paper,[14] dewetting kinetics was investigated as a function of block copolymer concentration and sample geometry (bilayer vs blend). In that paper, dPS-*b*-PMMA:PS blends with 5 vol % block copolymer were preannealed in a vacuum oven at 175 °C for 5 min to initiate hole growth. After mapping hole distribution, samples were then placed on a hot stage to follow hole growth. In the current studies, the volume percent of block copolymer was reduced from 5 to 1 vol % to facilitate hole formation and therefore avoid the need to preanneal.

3. Results and Discussion

In the first section, the effect of the nonadsorbing block length (N_{NA} or N_{dPS}) on the dewetting kinetics will be analyzed. The size of the nonadsorbing block should play a crucial role in the dewetting behavior because block length affects not only the entanglements across the interface but also the thickness of the adsorbed layer. Second, the effect of polymer−substrate interactions will be examined by varying the surface composition of the substrate. Similar to N_{NA}, substrate hydrophobicity should also affect the thickness of the adsorbed layer and the interfacial width. This section ends with a comparison of dewetting in films with and without dPS-*b*-PMMA.

3.1. Effect of Nonadsorbing Block Length. The dewetting behavior of PS films containing 1 vol % dPS-*b*-PMMA on SiO_x is investigated. The nonabsorbing block length varies such that $N_{dPS} \sim P/3$, $2P/3$, $5P/3$, and $4P$, where P is the matrix degree of polymerization, 288. Except for the copolymer with the shortest dPS block ($P/3$), the PMMA block length is held nearly constant, ∼40. Figure 2 shows D vs t for films containing copolymers with the two shortest N_{dPS}, namely $P/3$ (open squares) and $2P/3$ (solid circles). Initially, D increases linearly with t[6,8] and slows down[31] to $D \sim t^{0.7}$, in agreement with theory[8,32,33] that predicts $D \sim t^{2/3}$ and then reaches a constant value after 7 h. After 16 h, the diameters are 105 and 115 μm for $N_{dPS} \sim P/3$ and $2P/3$, respectively. The initial hole-growth rates are ∼0.8 μm/min for both samples. However, the area densities of holes are ∼100 and ∼ 30 holes/mm^2, respectively, suggesting that hole formation is easier in films containing the shorter nonadsorbing block.

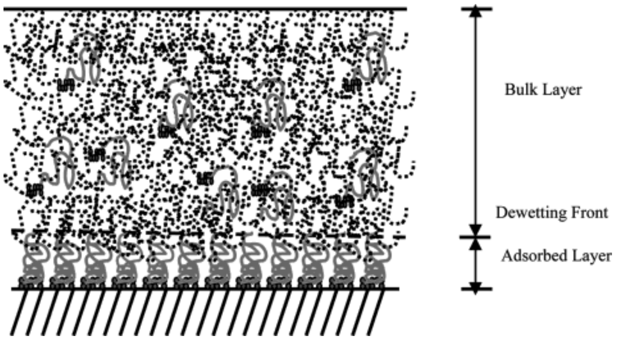

Figure 3. Schematic representation of a polymer blend film of PS (black dotted lines) and dPS-*b*-PMMA (bold solid lines with filled circles attached to one end) on a substrate. Some block copolymer chains are adsorbed at the substrate and form a “soft” adsorbed layer with a characteristic thickness. This adsorbed layer is covered by a bulk layer that contains mainly matrix chains, although some free block copolymer chains are also present. The dewetting front occurs at the contact line or interface between the bulk and adsorbed layers as denoted in the figure. Across this interface the adsorbed block copolymer chains interpenetrate with the matrix chains as defined by a characteristic width.

In contrast to the two systems with the shortest dPS block lengths, films containing 1 vol % dPS-*b*-PMMA at either $N_{dPS} \sim 5P/3$ or $N_{dPS} \sim 4P$ are stable for annealing times up to 16 h. Thus, for $N_{dPS} > P$, dewetting is suppressed and hole formation inhibited. These experimental observations are in good agreement with previous results[14] where hole growth was slowed by the addition of 5 vol % dPS-*b*-PMMA with $N_{dPS} \sim P$ and $N_{dPS} \sim 4P$. Although these copolymers had similar values of z^*, the dPS-*b*-PMMA with the longest nonadsorbing block length, $4P$, was more effective at slowing down hole growth, suggesting that the penetration of the dPS block into the matrix chains (i.e., interfacial broadening) has a large effect on dewetting kinetics. For copolymers with $N_{dPS} \sim P/3$ and $N_{dPS} \sim 2P/3$, hole growth effectively stops after 6 h as previously reported for homopolymer films containing block copolymers with a strong adsorbing block.[14] However, for homopolymer films without additives, holes grow continuously until they touch each other and form droplets.[4,8]

For pure homopolymer films, the viscosity of the melt has been reported to influence the dewetting kinetics.[34] Here, the local viscous dissipation is attributed to slip at the solid substrate and flow in the viscous bulk film.[6,35,36] Thus, the dewetting velocity depends on the viscosity at the substrate. For films with block copolymer additives, the viscosity near the substrate can be altered by the adsorbed block copolymer.[16] Therefore, dewetting in a homopolymer:block copolymer blend film is similar to spreading a bulk layer of PS matrix and free copolymer on a “soft” layer of adsorbed block copolymer. Replacing a rigid solid substrate with this “soft” bottom layer shifts the position of the dewetting front to the interface between the bulk and adsorbed layers. During dewetting, the extent of local deformation or local viscous dissipation taking place at this new contact line will then depend on the magnitude of the interfacial tension between the two layers, which is directly related to the interfacial broadening. Figure 3 represents the distribution of chains found in the bulk and adsorbed layers. For clarity, the homopolymer and

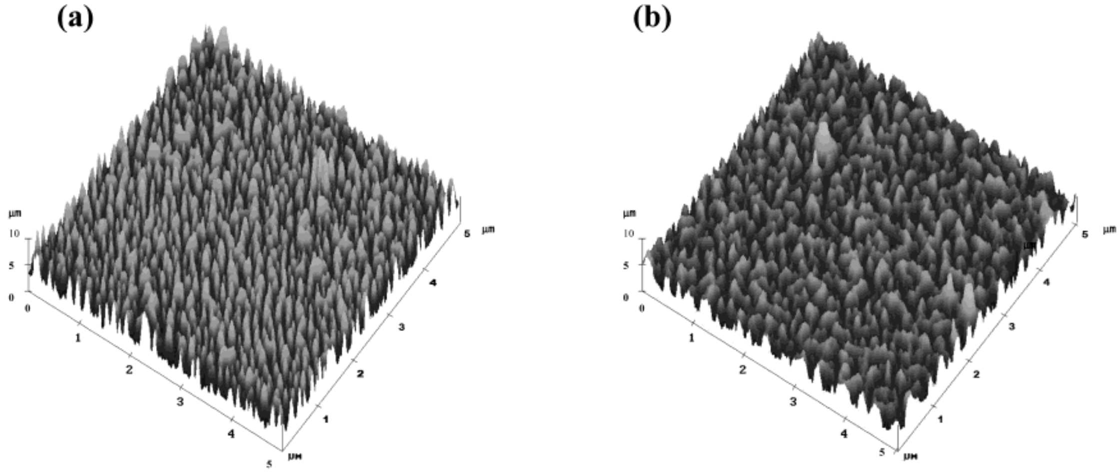

Figure 4. AFM surface images of the hole floor morphology for films on SiO$_x$ that contain block copolymers with (a) $N_{\mathrm{dPS}} \sim P/3$ and (b) $N_{\mathrm{dPS}} \sim 2P/3$. Samples were annealed for 16 h at 175 °C to produce hole diameters of 105 and 115 μm, respectively. The images are taken near the center region of the hole and did not depend on time.

free chains that penetrate the adsorbed layer are minimized. Thus, the key effect of the adsorbed layer is to move the dewetting front, where viscous dissipation occurs, to the interface between the bulk and adsorbed layers.

This concept of a dewetting front at the interface between the bulk and adsorbed layers can be used to explain why dewetting was not observed in films containing block copolymers with $N_{\mathrm{dPS}} > P$. Forward recoil spectrometry (FRES) and NR experiments[18] show that as N_{dPS} increases, the adsorbed block copolymer layer swells and extends into the matrix, resulting in a broader interfacial width, w. This result is consistent with the previously observed crossover from a stretched to a collapsed conformation at $P \sim 2N_{\mathrm{dPS}}$.[16] Correspondingly, the interfacial tension, γ, between the matrix and the adsorbed copolymer film is reduced as N_{dPS} decreases. The capillary driving force responsible for hole growth is given by $\gamma\theta^2$, where θ is the dynamic contact angle.[14] Therefore, as N_{dPS} increases, the driving force for dewetting is reduced. Interfacial broadening and interfacial tension were also invoked by Akpalu et al.[7] to explain thin film stability.

Analysis of the hole floor can provide clues about whether the dewetting front is located at the film−solid interface or at the matrix−adsorbed layer interface as shown in Figure 3. Parts a and b of Figure 4 show surface images of the hole floor morphology for systems containing 1 vol % dPS-*b*-PMMA with $N_{\mathrm{dPS}} \sim P/3$ and $N_{\mathrm{dPS}} \sim 2P/3$, respectively. Over a 5 μm × 5 μm area, the rms roughness values are similar, 1.6 and 1.5 nm, respectively. These values are about 5 times larger than those of bare SiO$_x$ (see Table 2), suggesting that the hole floors in the blend films contain mounds of polymer. This observation is consistent with autophobic dewetting[5,6] of a PS film from a substrate with a high graft density of similar chains. Although difficult to prove, these mounds may also contain block copolymer chains that are detached from the oxide surface as the rim moves over the adsorbed layer. In summary, the hole floor morphology is consistent with viscous dissipation taking place at the interface between the bulk and adsorbed layers as illustrated in Figure 3.

Figure 5 shows top-view images (top) and cross-sectional analysis (bottom) of the hole floor in the systems containing $N_{\mathrm{dPS}} \sim P/3$ (left) and $N_{\mathrm{dPS}} \sim 2P/3$ (right). The 5 μm × 5 μm top-view images, as well as the 3-D surface images in Figure 4a,b, are characteristic of three or more holes for each system. For $N_{\mathrm{dPS}} \sim P/3$ (Figure 5a), the hole floor is covered with discrete patches (bright), whereas for $N_{\mathrm{dPS}} \sim 2P/3$, the patches are more irregularly shaped and more interconnected (Figure 5b). In phase contrast mode, the bright and dark regions have similar phase angles, suggesting similar moduli. However, it is difficult to determine whether the dark, interconnected regions are a thin layer of polymer or bare SiO$_x$. To quantify feature size, line scans (diagonal lines in Figure 5a,b) are analyzed and shown in Figure 5c,d, respectively. Although their heights are similar, the features have significantly different widths, 190 vs 300 nm, respectively.

A previous study[14] shows that polymer patches form at the contact line between the wall of the rim and the hole floor. The larger patches for $N_{\mathrm{dPS}} \sim 2P/3$ suggests that disentanglement between PS chains and adsorbed block copolymer is more strongly hindered than for $P/3$. If these patches contain mainly adsorbed “stretched” block copolymer, the increase in lateral size is consistent with an increase in N_{dPS}. The model depicted by Figure 3 assumes that the dewetting front is located at the interface between the bulk and adsorbed layers. As this front uncovers the adsorbed layer, the matrix and copolymer chains at the interface may untangle, leaving behind an adsorbed layer containing unperturbed and/or stretched copolymer. This combination could lead to the patchy surface observed by AFM, although pull-out of block copolymer should not be ruled out. Although one results from viscous dissipation and the other is an interfacial characteristic, we note that the hole floor rms roughness of ∼1.5 nm for both systems is similar to the interfacial width values determined from NR, 1.8 and 2.2 nm, for $P/3$ and $2P/3$, respectively.[18] Given the similar length scales, these values suggest that dewetting is indeed dictated by the interfacial width between matrix and adsorbed layers.

3.2. Effect of Substrate Hydrophobicity. By changing the substrate from wettable SiO$_x$ to a moderately hydrophobic amine-terminated surface, dewetting behavior can be investigated as a function of the interaction strength between S and MMA segments and the substrate. Using the same four block copolymer systems as before (Table 1), films containing 1 vol % dPS-*b*-PMMA added to matrix PS (30 000 g/mol) are prepared on amine-terminated surfaces. Similar to films on SiO$_x$,

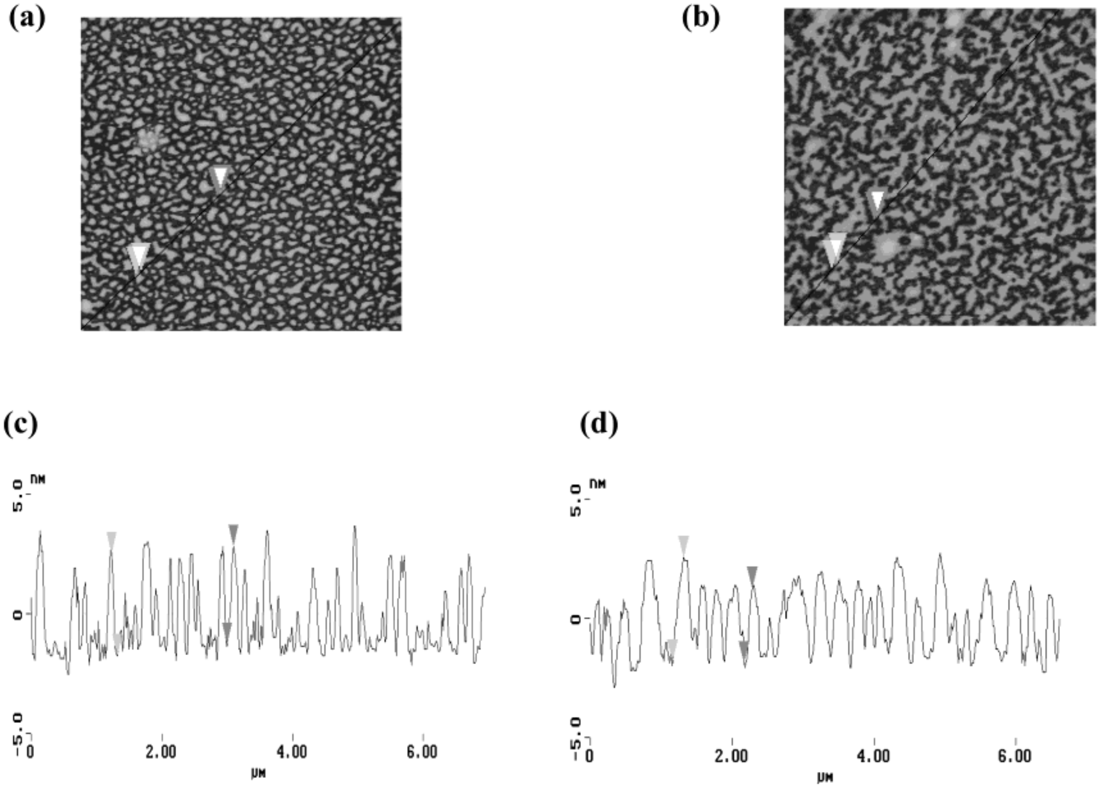

Figure 5. AFM top-view (a, b) and cross-section images (c, d) of the hole floor for films corresponding to (a, c) $N_{dPS} \sim P/3$ and (b, d) $N_{dPS} \sim 2P/3$. The top-view area is 5 μm × 5 μm. The substrate is SiO_x. The cross-section profiles are taken from the diagonal lines in the top-view images. The cross-section and top-view images show patches of polymer (white) across the hole floor for both systems. Details are given in the text.

blends containing copolymer with the two longest blocks do not dewet. In contrast to the films on SiO_x, no dewetting is detected on amine-terminated surfaces when the copolymers with the two shortest dPS blocks, $N_{dPS} < P$, are added.

The copolymer adsorbs to SiO_x and amine-terminated surfaces via the PMMA anchoring block.[14,16,17] Previous studies[20] have shown that MMA segments are expected to act as a Lewis base and be more attracted to acidic surfaces such as SiO_x than to amino-terminated surfaces. If this is the case, the anchoring of the short MMA block is stronger on SiO_x, and therefore the change in MMA−substrate interaction cannot explain the improved film stability on amine-terminated surfaces.

To explain the absence of dewetting on amine-terminated surfaces, PS matrix chain interactions with the amine-terminated surface should also be considered. If PS chains are attracted to the substrate, matrix chains and dPS-*b*-PMMA copolymers will compete for surface sites, as previously described.[17] Experimental evidence suggests that the interaction between S segments and amine surface is stronger than the one between S segments and SiO_x. Using FRES, z^* for each dPS-*b*-PMMA (Table 1) is larger on SiO_x than on the amine-terminated surface, consistent with a weaker matrix−SiO_x interaction.[18] Because dewetting is observed on SiO_x but not on the amine-terminated surface, z^* by itself should not be used to predict film stability.

Competition between matrix and dPS-*b*-PMMA chains for the substrate will not only lower z^* but it can also alter the interpenetration between the free matrix chains and the adsorbed copolymer layer. Because PMMA is strongly attracted to SiO_x,[16,23,37] adsorption of dPS-*b*-PMMA chains is much stronger than PS matrix chains. Thus, on SiO_x, the layer adjacent to the substrate should be primarily composed of the block copolymer chains. However, if PS matrix chains have a stronger affinity for the amine surface than the SiO_x, matrix chains will tend to "wet" the brush layer, leading to fewer dPS-*b*-PMMA chains in the adsorbed layer. Thus, the adsorption of PS matrix chains on the amine surface is consistent with the smaller z^* observed for amine surfaces. These adsorbed PS matrix chains may also crowd the adsorbed dPS-*b*-PMMA chains, causing them to stretch into the matrix. This interfacial broadening would be accompanied by a reduction in the interfacial tension between the bulk and adsorbed layers. Because of a lower interfacial tension, the driving force for dewetting will be reduced consistent with better film stability on amine-terminated surfaces.

To test this hypothesis, dewetting studies were performed on PS films deposited on SiO_x and on amine-terminated surfaces. To mimic the homopolymer:copolymer blend system, the PS:PS blend films were prepared using the same PS matrix chains as before (30 000 g/mol) plus 1 vol % of PS (200 000 g/mol). Figure 6 shows how the hole diameter increases with time for films on SiO_x (open squares) and on amine-terminated surface (solid circles). Initially, D increases linearly with annealing time, t, before slowing down. On SiO_x, linear growth resumes at later times although at a slower rate. No explanation for this behavior is given due to the rapid dewetting times involved. For films on SiO_x and amine surface, holes impinge after 13 and 19 min as denoted by crosses in Figure 6. The diameters prior to impingement correspond to 254 and 183 μm, respectively. After impingement, the rims coalesce into droplets on both substrates as previously reported.[6−8] Rela-

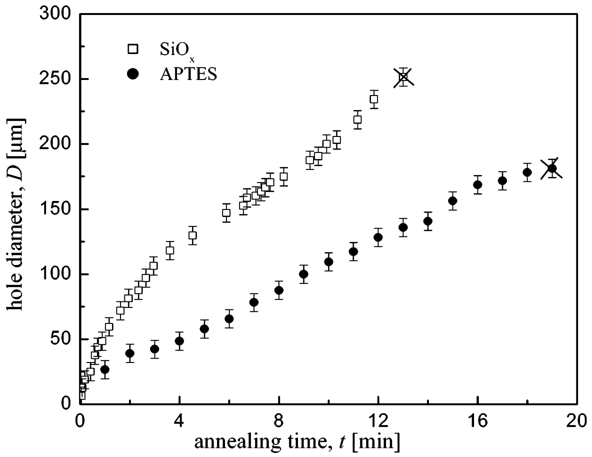

Figure 6. Hole diameter, D, as a function of annealing time, t, for a homopolymer blend of 99 vol % PS (30 000 g/mol) and 1 vol % PS (200 000 g/mol) on SiO$_x$ (open squares) and on amine surfaces (solid circles). The error bars (±5 μm) are estimated from the microscope calibration ruler with line spacing of 10 μm. The crosses represent D and t values at which holes impinge.

tive to the copolymer blends, dewetting occurs very rapidly on SiO$_x$ and on amine substrates with initial hole growth rates of 25 and 10 μm/min, respectively. For both surfaces, the hole area densities are similar, ∼40 holes/mm^2. The significantly faster dewetting rate on SiO$_x$ suggests a stronger attraction between the PS molecules and the amine-terminated surface. This preferable attraction of PS matrix chains for the amine surface may partly explain the greater stability observed for both systems, the PS:PS and PS:copolymer blend films, on amine surfaces. These studies also demonstrate that the prevention of dewetting in homopolymer films containing the 50 000 and 110 000 g/mol copolymer additives is not due to an increase in viscosity, but rather due to the adsorption of the block copolymer.

AFM images (5 μm × 5 μm) of the PS:PS blend on both surfaces are examined. For each sample, the images are acquired between droplets that form after holes coalesce and inside the holes before impingement. The rms roughness values were approximately 0.2 and 0.5 nm for the SiO$_x$ and amine surfaces, respectively, both between droplets and inside holes. Comparison of these results with those from the bare SiO$_x$ and amine substrates (Table 2) suggests that the substrates do not contain residual polymer. Thus, autophobic dewetting[5,6] has probably not occurred in these systems. These results suggest that the dewetting front for the homopolymer films is formed at the interface between the rigid solid substrate and the polymer film.

3.3. Comparison and the Effect of Block Copolymer. In this section, the dewetting behavior of films with and without block copolymers is compared. Previous experiments show that the morphology of the hole floor depends on whether block copolymers are added to the film.[14] Consistent with these studies, patches of polymer are found inside holes for films with block copolymers as shown in Figure 5a,b. In contrast, homopolymer films that dewet from SiO$_x$ and amine surfaces display a smooth hole floor with rms roughness values similar to those of bare surfaces. Another important difference in the dewetting behavior of films with and without block copolymers is that holes in homopolymer films grow continuously until rims eventually impinge.[9] This kind of behavior is not observed for systems with 1 vol % block copolymer, where holes stop growing after 6 h of annealing. Moreover, for homopolymer films on both surfaces, hole growth is much faster and dewetting is completed in less than 20 min of annealing. In contrast, for blends with block copolymer, annealing times up to 400 min are reached before holes stop growing. Thus, the time scale for observing hole growth is about 2 orders of magnitude longer for blends containing block copolymer.

4. Conclusions

In this paper, the addition of block copolymer that adsorbs to the homopolymer/substrate interface is shown to stabilize thin films against dewetting. In particular, for nonadsorbing block lengths less than the matrix chain length (i.e., $N_{\mathrm{dPS}} < P$), holes grow more slowly on SiO$_x$ than pure homopolymer films. Moreover, holes reach a constant size and the hole floor displays mounds of polymer, suggesting that the dewetting front is located at the interface between the matrix chains and the adsorbed copolymer layer. Dewetting is found to be completely arrested for long nonadsorbing block lengths where $N_{\mathrm{dPS}} > P$. The substrate type is also varied from SiO$_x$ to silicon oxide grafted with an amine-terminated SAM. For all values of N_{dPS}, homopolymer:copolymer blend films deposited on the amine surface remained stable. Hole growth of PS films is found to occur more slowly on the amine surface compared to SiO$_x$. This result suggests that the improved adhesion is related to a stronger attraction between the PS matrix chains and the amine surface. Similar to the SiO$_x$ case for $N_{\mathrm{dPS}} > P$, the matrix affinity for the substrate can broaden the interface and reduce the interfacial tension between the bulk and adsorbed layers, leading to an improvement in thin film stability. The composition of the mounds covering the hole floor remains unknown. This information would be very useful to test the mechanism of dewetting proposed in this study. A technique with great potential for this task is scanning transmission electron microscopy combined with local electron energy-loss spectroscopy.[38,39]

Acknowledgment. We gratefully acknowledge support from ACS/PRF 34081, NSF/polymer program (DMR99-74366 and INT99-75486), NSF/MRSEC program (DMR00-79909) for facility support, and a collaboration grant from the U.S.−Czech Republic Science and Technology Program, Grant 203/01/0513.

References and Notes

(1) Budkowski, A.; Steiner, U.; Klein, J.; Fetters, L. J. *Europhys. Lett.* **1992**, *20*, 499−504.
(2) Jones, R. A. L.; Norton, L. J.; Shull, K. R.; Kramer, E. J.; Felcher, G. P.; Karim, A.; Fetters, L. J. *Macromolecules* **1992**, *25*, 2359−2368.
(3) Segalman, R. A.; Green, P. F. *Macromolecules* **1999**, *32*, 801−807.
(4) Green, P. F.; Limary, R. *Adv. Colloid Interface Sci.* **2001**, *94*, 53−81.
(5) Hamley, I. W.; Hiscutt, E. L.; Yang, Y. W.; Booth, C. *J. Colloid Interface Sci.* **1999**, *209*, 255−260.
(6) Limary, R.; Green, P. F. *Langmuir* **1999**, *15*, 5617−5622.
(7) Akpalu, Y. A.; Karim, A.; Satija, S. K.; Balsara, N. P. *Macromolecules* **2001**, *34*, 1720−1729.
(8) Brochard-Wyart, F.; Gay, C.; de Gennes, P. G. *Macromolecules* **1996**, *29*, 377−382.
(9) Reiter, G. *Phys. Rev. Lett.* **1992**, *68*, 75−78.
(10) Martin, J. I.; Wang, Z.-G.; Schick, M. *Langmuir* **1996**, *12*, 4950−4959.
(11) Long, D.; Ajdari, A.; Leibler, L. *Langmuir* **1996**, *12*, 1675−1680.

(12) Milchev, A.; Binder, K. *J. Chem. Phys.* **1997**, *106*, 1978−1989.

(13) Kargupta, K.; Sharma, A. *J. Chem. Phys.* **2002**, *116*, 3042−3051.

(14) Oslanec, R.; Costa, A. C.; Composto, R. J.; Vlcek, P. *Macromolecules* **2000**, *33*, 5505−5512.

(15) Renger, C.; Muller-Buschbaum, P.; Stamm, M.; Hinrichsen, G. *Macromolecules* **2000**, *22*, 8388−8398.

(16) Oslanec, R.; Vlcek, P.; Hamilton, W. A.; Composto, R. J. *Phys. Rev. E* **1997**, *56*, 2383−2386.

(17) Oslanec, R.; Composto, R. J.; Vlcek, P. *Macromolecules* **2000**, *33*, 2200−2205.

(18) Costa, A. C.; Composto, R. J.; Geoghegan, M.; Vlček, P., to be submitted to *Macromolecules*.

(19) Sharma, A.; Khanna, R. *Phys. Rev. Lett.* **1998**, *81*, 3463−3466.

(20) Koberstein, J. T.; Duch, D. E.; Hu, W.; Lenk, T. J.; Bhatia, R.; Brown, H. R.; Lingelser, J.-P.; Gallot, Y. *J. Adhes.* **1998**, *66*, 229−249.

(21) Mounir, E. S. A.; Takahara, A.; Kajiyama, T. *Polym. J.* **1999**, *31*, 89−95.

(22) Mounir, E. S. A.; Takahara, A.; Kajiyama, T. *Polym. J.* **1999**, *31*, 550−556.

(23) Kobayashi, K.; Dochi, A.; Yajima, H.; Endo, R. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1938−1943.

(24) Falsey, J. R.; Renil, M.; Park, S.; Li, S. J.; Lam, K. S. *Bioconjugate Chem.* **2001**, *3*, 346−353.

(25) Qian, W. P.; Bu, X.; Wu, L.; Wang, C. X.; Yao, D. F.; Yu, F.; Yuan, C. W.; Wei, Y. *J. Colloid Interface Sci.* **1999**, *1*, 16−19.

(26) Qian, W. P.; Xu, B.; Yao, D. F.; Lin, Y. H.; Wu, L.; Wang, C. X.; Lu, Z. H.; Wei, Y. *Mater. Sci. Eng., C* **1999**, *8*, 475−480.

(27) Dee, K. C.; Rueger, D. C.; Andersen, T. T.; Bizios, R. *J. Biomater.* **1996**, *17*, 209−215.

(28) Vlcek, P. Department of Anionic Polymerization, Institute of Macromolecular Chemistry, Czech Academy of Sciences, Prague, Czech Republic.

(29) Tsukruv, V. V.; Bliznyuk, V. N. *Langmuir* **1998**, *14*, 446−455.

(30) Ulman, A. *An Introduction to Ultrathin Organic Films*; Academic Press: Boston, 1991.

(31) For simplicity, we just show D vs t in Figure 2; however, plotting log D vs log t, a slope of 0.7 is obtained over intermediate times.

(32) Brochard-Wyart, F.; Debrégeas, G.; Fondecave, R.; Martin, P. *Macromolecules* **1997**, *30*, 1211−1213.

(33) Debrégeas, G.; Martin, P.; Brochard-Wyart, F. *Phys. Rev. Lett.* **1995**, *75*, 3886−3889.

(34) Ge, S. R.; Guo, L. T.; Rafailovich, M. H.; Sokolov, J.; Overney, R. M.; Buenviaje, C.; Peiffer, D. G.; Schwarz, S. A. *Langmuir* **2001**, *17*, 1687−1692.

(35) Shanahan, M. E. R. *J. Phys. D: Appl. Phys.* **1988**, *21*, 981−985.

(36) Shanahan, M. E. R.; Carré, A. *Langmuir* **1995**, *11*, 1396−1402.

(37) Kobayashi, K.; Yamagiwa, S.; Takahashi, A.; Kato, T. *J. Chem. Soc., Faraday Trans.* **1990**, *9*, 1383−1387.

(38) Jabbari, E.; Peppas, N. A. *J. Appl. Polym. Sci.* **1995**, *57*, 775−779.

(39) Varlot, K.; Martin, J. M.; Gonbeau, D.; Quet, C. *Polymer* **1999**, *40*, 5691−5697.

MA021508K