Interface Roughness Correlation in Diblock Copolymer Brushes Synthesized by Atom Transfer Radical Polymerization

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The degree to which the surface of a film replicates an underlying surface is very important for a variety of applications such as coatings and biomimetics. The correlation of interface morphology, or roughness, between two interfaces of a film has been studied both for films of small molecules[1] and for films of polymers spun-cast onto a substrate.[2] For small molecule liquid films, the film surface follows that of a smooth substrate for thicknesses less than about 6 nm because van der Waals interactions with the substrate suppress thermally stimulated capillary waves on the surface.[1] The observation[3] of partial suppression of thermally stimulated waves on the surface of thin polystyrene films as thick as 50 nm raised the question of whether this peculiarity of polymer films is due to long-range interactions with the substrate or whether it is intrinsic to the viscoelastic character of polymer films. Shin et al.[4] showed that even in the absence of a supporting substrate, the interfaces of a polystyrene film may have correlated structures if the film is thinner than twice the radius of gyration of the chains (R_g) due to confinement effects. For polystyrene films[2] that vitrify rapidly upon the loss of solvent during spin-casting, correlation of the surface with the substrate may be observed in "as-spun" films 22−116 nm in thickness ($2R_g \cong 18$ nm), but this correlation is an artifact of the hydrodynamic flow that occurs upon spinning and is lost when the films are annealed at a temperature above the glass transition temperature. Spun-cast films of symmetric block copolymers[5] show such metastable interface correlation over a smaller range of thicknesses than do films of homopolymer, and this has been attributed to the presence of ordered lamellar domains. Replication of the substrate roughness over all length scales is not possible because the surface roughness occurs on a much smaller length scale than the length associated with the microphase separation. That is, the free block copolymer thin film cannot be considered as a simple liquid, at least in the lateral direction, and this hinders replication of the roughness.

Polymer brushes are versatile monomolecular coatings that have properties very different from those of films of untethered polymer chains. In a brush, one end of each chain is tethered to the substrate, and the density of this tethering is sufficiently high that the chains must stretch away from the surface.[6] It is of interest to know whether this tethering mediates interactions with the substrate such that the probability that the surface of a brush is correlated with the underlying substrate is enhanced. Certainly in the theoretical extreme of a strongly stretched brush the thickness of the brush is less than $2R_g$, and one could expect correlation based on the findings of Wang et al.[3] Diblock copolymer brushes, shown schematically in Figure 1, are the focus here because their surfaces can rearrange in response to a change in the environment, particularly changes in an adjacent solvent.[7,8] However, the diblock brush also represents a special case of enhanced confinement, since by its nature a strongly segregated diblock brush must contain, next to the substrate, a brush layer that closely approximates an Alexander brush.[9,10] That is, one end of each chain is tethered at a definite location on the substrate and the "free" end of that block is required to be at the interface between the bottom and top domains. This enhanced degree of confinement could make interface correlation possible for thicknesses larger than in the case of films of small molecules. Here we show for the first time that, indeed, the interfaces of diblock copolymer brushes can be correlated over a wide range of thicknesses, that the existence of the correlation is not an artifact of deposition history, and that weakening the segregation at the internal interface by swelling with a nonselective good solvent weakens the interface correlation.

Deuterated polystyrene-*b*-poly(methyl acrylate) (dPS-*b*-PMA) diblock copolymer brushes have been synthesized by atom transfer radical polymerization (ATRP) using synthetic techniques described previously.[11] However, since this deuterated diblock copolymer brush is reported here for the first time, details of the synthesis are given in the Supporting Information. (Deuteration of one block was done to enable future studies with neutron scattering methods but has no bearing on the correlation phenomenon of interest here.) A self-assembled monolayer (SAM) of 11-(2-bromo-2-methyl)-propionyloxy)undecyltrichlorosilane initiator was deposited atop a silicon substrate. Polymerization of the first monomer A was initiated from the SAM to form the first block by ATRP. Then the polymerization was continued with a different monomer, B, to create the second block. High grafting density (0.5 chains/nm^2) brushes were synthesized both with dPS as the A block and with PMA as the A block. Implicit in the vast majority of reports of diblock copolymer brush synthesis has been the presumption that the brush, as deposited, has a lamellar morphology, as depicted in Figure 1, with a layer rich in A lying next to the substrate and a layer rich in B adjacent to the surface.

The structure of the film in the direction perpendicular to the surface was probed using X-ray reflectometry (XR). The data are typically plotted, as shown in Figure 2, as some function of the ratio of specularly reflected intensity to incident intensity, R, as a function of the magnitude of the scattering vector component perpendicular to the surface, q_z ($q_z = 4\pi \sin\theta/\lambda$, where θ is the incident angle and λ the wavelength), as illustrated in Figure 1. From regressing the data with a model of the film structure one may estimate values of the film thickness, integrated microroughnesses at the air/film and substrate interfaces, and parameters of the interfaces inside the film, if they exist and if sufficient contrast is available. All X-ray measurements were

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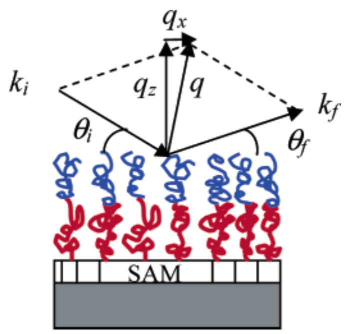

Figure 1. Schematic of a diblock copolymer brush with the incident and exit X-ray beams, corresponding scattering vector, **q**, and components perpendicular to the surface, $\mathbf{q}_z$, and parallel to the surface and in the plane of incidence, $\mathbf{q}_x$. The wavevectors of the incident and scattered X-rays are $\mathbf{k}_i$ and $\mathbf{k}_f$, with the incidence and exit angles θ_i and θ_f, respectively. Specular scattering corresponds to $\theta_i = \theta_f$. Otherwise, the scattering is called "off-specular scattering".

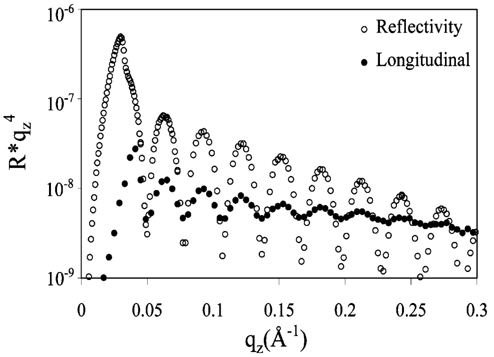

Figure 2. Specular reflectivity (open circles) and longitudinal diffuse scattering (solid circles) from a dPS-*b*-PMA diblock copolymer brush with total thickness of 21 nm, dPS layer thickness of 15 nm, and PMA layer thickness of 6 nm. Multiplying the scattering intensities by q_z^4 emphasizes the fringes and normalizes for a trivial q_z^{-4} dependence. The longitudinal scan intensity has been offset by an arbitrary amount for clarity.

performed at beamline 1-BM at the Advanced Photon Source (APS). The spectrometer used a double-crystal monochromator to choose a wavelength of 1.24 Å. The samples were mounted in a helium-filled sample chamber on a goniometer providing translations in x, y, and z and rotation in θ, and the scattered intensity was collected with a NaI detector. The reciprocal space resolution δq_z was 0.001 Å^{-1}.

Details of the structure in the plane of the interface were obtained by collecting scattering data for scans in which the scattering vector q had a component in the plane of the interface (i.e., $q_x \neq 0$), so-called off-specular longitudinal diffuse scattering scans. These data were measured with a resolution of $\delta q_x \approx 1 \times 10^{-4}$ Å^{-1} at $q_z = 0.30$ Å^{-1}. The longitudinal scans were performed by increasing the incident and detector angles in a coordinated manner, but with the incident angle offset by 0.07° from the specular condition. This is far enough away from the specular peak, which has a half-width of 0.03° at its base, so that the measured scattering is all diffuse scattering. These longitudinal scans contain information on the interface lateral structure. Samples were translated perpendicular to the beam direction between the measurements of the reflectivity and longitudinal scans to minimize radiation damage to the sample. The unattenuated beam had a flux of about 2×10^{13} photons/(cm^2 s).

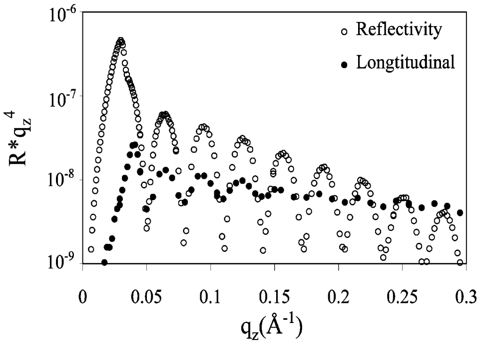

Figure 3. Comparison of the XR and longitudinal scans from the same dPS-*b*-PMA brush as in Figure 2 (thickness of 21 nm) after annealing reveals that the correlation persists.

When the reflectivity and longitudinal scans measured in He for an "as-deposited" dPS-*b*-PMA diblock brush are plotted as in Figure 2, oscillations are observed in both scans, and these oscillations are in phase with one another. Both types of oscillation result from interference of beams reflected from the air/film and film/substrate interfaces. That they are in phase indicates that the interfaces are correlated,[1] despite the fact that the thickness of the film is 4.2R_g of the corresponding diblock chain in its unperturbed melt state. This correlation is observed even though bulk PMA (T_g = 10 °C[12]) is molten at the temperature of the measurement (25 °C). The overall thickness of the film is 21 nm, with the dPS block layer having a (nominal) thickness of 15 nm (as measured by ellipsometry before polymerization of the second block). Thus, interface correlation is observed here for a film thickness more than 3 times that for which correlation is observed for small molecule liquid films.[1] van der Waals interactions alone are insufficient to give correlation over such a long distance. The amplitude of the oscillations in the longitudinal diffuse scattering does get weaker with increasing brush thickness but persists even to an overall thickness of 54 nm. The interactions between the surface and the substrate responsible for the correlation do then decrease in strength with increasing distance from the substrate.

To test whether the correlation is due to a kinetically trapped structure, the specular reflectivity and longitudinal diffuse scattering of the diblock brushes were measured again after the brushes were annealed at 140 °C for 4 h in a high-vacuum oven and then rapidly quenched to room temperature. The oscillations in the reflectivity and longitudinal scans were still in phase, as shown in Figure 3, meaning that the interfaces were still correlated.

Swelling of the brush by a good solvent is found to strongly perturb the correlation between the top and bottom interfaces. Samples were swollen for 8 h in the vapor of dichloromethane, which is a good solvent for both the dPS and PMA blocks, and then the specular reflectivity and longitudinal diffuse scans were measured again. A weakening of the fringes in the reflectivity curve in Figure 4 and a lowering of reflectivity both indicate that the brush gets rougher after swelling. When oscillations remain in the longitudinal scan, they are too weak for one to discern if they are in phase with the fringes in reflectivity. The conformality in interface roughness has been lost. When the polymers are swollen with the solvent vapor, the brush thicknesses increase. In the specific case shown, the film swelled 86%. The

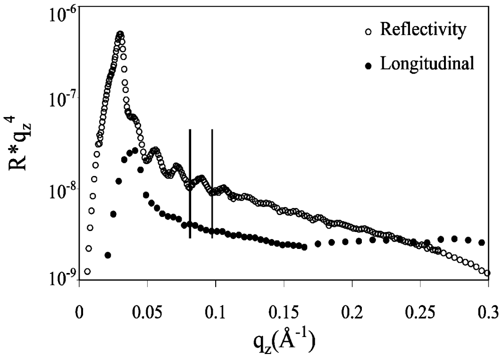

Figure 4. Specular X-ray reflectivity and longitudinal diffuse scattering from a dPS-*b*-PMA brush (thickness of 21 nm before swelling) after swelling in CH_2Cl_2 vapor. The thickness change during the swelling is 86% to 39 nm.

absorption of the solvent brings several changes to the brush. First, the concomitant increase in thickness necessitates that each individual chain stretch more. One anticipates that changing the chain stretching will also change the degree to which the brush surface will replicate an underlying surface. Second, incorporation of the solvent reduces the value of an effective interaction parameter between the blocks, making the internal interface less sharp and thus weakening the "layered" character of the brush. Third, the interfacial tension of the brush surface will be altered, which will influence the propensity for thermal stimulated surface waves. Finally, adding the solvent plasticizes the film, increasing mobility. We conjecture that the most important effects of the solvent swelling are the disruption of the definition of the layered structure and the decrease in interfacial tension. These should favor the roughening of the surface.

In summary, X-ray scattering measurements have revealed for the first time that the air/brush and brush/substrate interfaces of diblock copolymer brushes can be correlated over length scales to which the scattering measurements are sensitive. The correlation is found for film thicknesses much higher than those for which correlation is seen in small molecule liquids. This correlation is intrinsic to the structure of the dry brush, since it persists after annealing at a temperature above the glass transition temperatures of both polymers, proving that the correlation is not due to kinetic trapping of a morphology formed during the brush deposition. However, the correlation is disrupted when the brush is swollen with the vapor of a good, nonselective solvent for the two blocks.

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Supporting Information Available: Details of the synthesis of the d-PS-*b*-PMA diblock copolymer brush. This material is available free of charge via the Internet at http://pubs.acs.org.

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