

Surface Fluctuations on Polymer Brushes

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Introduction

Thermally excited surface fluctuations on simple liquids have been described theoretically and studied experimentally by x-ray reflectivity [1] and off-specular scattering. Capillary wave theory [2] predicts that the diffuse scattering should show a power law behavior with in-plane scattering vector, $I \sim q_x^{\eta-1}$, for sufficiently high values of q_x (small fluctuation wavelengths), with $\eta = Bq_z^2/2$ and $B = k_B T/\gamma$, when the scattering is measured with integration in the q_y direction, as was done here. The variables k_B , T , and γ represent the Boltzmann constant, temperature, and surface tension, respectively.

For thin films of simple liquids, van der Waals interactions with the substrate lead to a suppression of the capillary waves at longer wavelengths, corresponding to $q_x < q_{l,c}$ where $q_{l,c}$ is a lower wave vector cutoff. The cutoff should vary with thickness d as $q_{l,c} = a/d^2$, with length a being equal to the square root of $A_{eff}/2\pi\gamma_{eff}$, where the effective Hamaker constant A_{eff} describes the extent of interaction and γ_{eff} is an effective surface tension.

Recently, attention has turned to surface fluctuations on complex polymeric liquids [3, 4]. The scattering from molten poly(*tert*-butyl acrylate) (PtBA) [4] has been shown to be consistent with capillary wave theory. Two scattering studies [4, 5] of the surfaces of films of polystyrene (PS) chains offer somewhat different views of the behavior for that system. Wang et al. [3] reported on observing values of the cutoff wave vector for annealed PS free-chain films that varied as $q_{l,c} \sim d^{-1}$ and interpreted those results as indicative of a suppression of surface fluctuations of the polymer film that is stronger than suppression in simple liquids. Lurio et al. [5] used a different scattering geometry and measurements at temperatures above the glass transition temperatures T_g and reported that surface tensions derived from the diffuse scattering were consistent those of “bulk” samples.

The focus of this work is to study the manner in which the surface fluctuations on a polymer film are constrained by the tethering to the substrate of one end of each polymer chain in the film. A monomolecular film of such tethered chains is referred to as a “brush” if the grafting density is sufficiently high that the chains are forced to stretch from their preferred dimensions [6]. Both the tethering of the chains and the stretching thereby induced should cause the surface fluctuations of a polymer brush to be different from those of a film of free chains [7]. In

particular, the wave vector cutoff corresponding to suppression of the larger wavelength fluctuations is expected to vary with brush height. Static scattering experiments have been employed here, so it is actually the structure of the surface that is probed, and information about the surface dynamics is to be inferred from the characteristics of the surface structure.

Here the surface fluctuations of PS brushes are investigated. Polystyrene, which has a T_g of $\sim 100^\circ\text{C}$ in the bulk sample, is glassy at room temperature. Measurements are done at room temperature after cooling a sample annealed above T_g , as in the work of Wang et al. for films of untethered chains of PS [3]. The effects of both the variation in grafting density and of the variation in molecular weight on the surface fluctuations have been considered.

Methods and Materials

PS brushes were synthesized by using surface-initiated free-radical polymerization techniques [8]. Two strategies were used to control the thickness of the polymer brush films. In the “GDV” series, brush film thickness was increased by increasing grafting density at a fixed molecular weight. In the “MWV” series, brush film thickness was increased by increasing the molecular weight of the surface-attached polymers at a fixed grafting density.

Some brushes were annealed in a high-vacuum oven (1.04×10^{-4} Pa). Because of limitations in the heating and cooling rates of the heating device in the oven, in addition to spending 20 minutes at 140°C , the samples spent about 25 minutes at temperatures above their T_g when they were first heated to 140°C and then again when they were cooled after a residence time at 140°C . When the sample’s temperature dropped below T_g , the sample was taken out of the oven and put on a large, cold aluminum plate to cool rapidly.

The surface fluctuations of the brush surfaces were characterized by x-ray off-specular scattering measured at beamline station 1-BM-C at the APS. The spectrometer used a double-crystal monochromator to choose a wavelength of 1.127 \AA with a resolution of $\delta q_x \approx 8 \times 10^{-5} \text{ \AA}^{-1}$ at $q_z = 0.20 \text{ \AA}^{-1}$. After measuring the specular reflectivity, off-specular scattering was measured by using both longitudinal and transverse scans. Transverse scans were collected as step scans for four different values of q_z :

0.15, 0.2, 0.3, and 0.35 \AA^{-1} . The values of q_x used for the scans were optimized for each sample to provide an approximately logarithmic spacing of data points. Samples were translated perpendicular to the beam direction after each scan to limit radiation damage. Typically, one position was exposed for 10 to 20 minutes, with the duration depending on beam attenuation. The unattenuated beam had a flux of about 2×10^{13} photons/cm²/s.

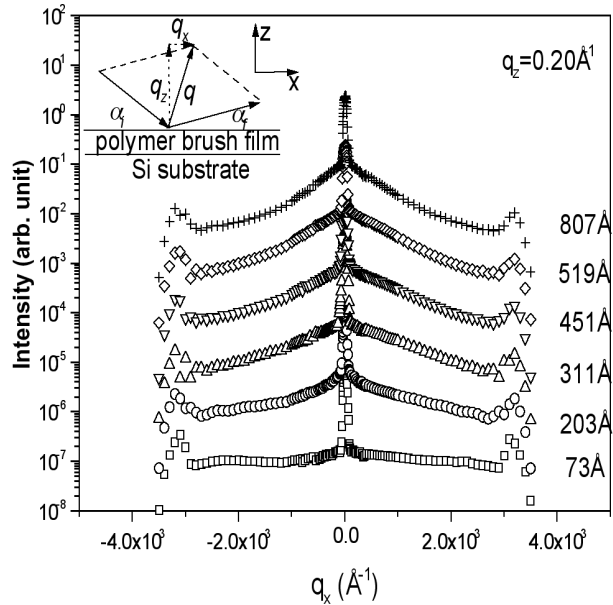


FIG. 1. Transverse scans at $q_z = 0.20 \text{ \AA}^{-1}$ for annealed PS brushes with thicknesses ranging from 73 to 807 Å. The thicknesses were controlled by varying molecular weight (MW) at a fixed grafting density. Each curve has been shifted vertically for clarity. Inset is a schematic of the scattering geometry showing the incident and exit angles, α_i and α_f . When $\alpha_i \neq \alpha_f$, the scattering vector q has a finite component q_x in the plane of the surface.

Results

Figure 1 has plots of transverse scans for the MWV series measured after annealing. Intensities are plotted as a function of in-plane wave vector transfer q_x . In every scan, there are two prominent features. The Yoneda peaks at $q_x = -0.0032 \text{ \AA}^{-1}$ and 0.0032 \AA^{-1} result from the enhancement in the electric field at the surface when either the incident angle or the exit angle is equal to the critical angle for the sample. The intense peak in the center of the scan ($q_x = 0$) captures the specular reflectivity when the incident and exit angles are equal. Between the specular and Yoneda peaks are two regions in which details of the surface structure manifest themselves.

Two variations in the character of these regions with increasing brush thickness can be discerned. First, the scattering intensity is nearly constant in these regions for

the thinnest film. This shape is typical for surfaces like semiconductors that have a surface roughness characterized only by small in-plane length scales. As the brush thickness increases, the intensity of the surface scattering increases and the shape of the scattering curve grows to look more like that characteristic of liquid surfaces. This suggests that the longer wavelength fluctuations on the brush surface increase with brush thickness. However, no substantial broadening of the specular peaks themselves is observed with increasing thickness (see also Fig. 2). This suggests that fluctuations with wavelengths long enough to yield diffuse scattering superposed on the specular peak at the smallest values of q_x are suppressed on the PS brush.

Two key features of the surface scattering can be analyzed by focusing on log-log plots of the part of the transverse scan corresponding to $q_x > 0$. Data are plotted in this way for annealed GDV series samples in Fig. 2. Three general scattering features are observed regardless of the brush thickness and method of preparation, and these features are also commonly observed for films of free chains placed on a substrate [1]. First, the profile of the specular beam is captured in the region of $q_x < 7 \times 10^{-5} \text{ \AA}^{-1}$ (for $q_z = 0.20 \text{ \AA}^{-1}$). Our study of surface fluctuations is limited to wavelengths with values of q_x such that $7 \times 10^{-5} < q_x < 2 \times 10^{-3} \text{ \AA}^{-1}$. The second general feature is a region of small slope next to the specular peak.

The third general feature is a region where the diffuse scattering intensity varies as q_x^α . The value of the exponent α varies for the PS brushes from -1 to -2.2 , depending on sample thickness q_z and thermal history. If the surface structure were dictated solely by capillary waves, the slope would be expected to increase with increasing q_z , with the slope remaining close to but larger than -1 . Experimentally, the slopes do generally increase with increasing q_z except at $q_z = 0.15 \text{ \AA}^{-1}$ for annealed PS brushes. However, the slopes in the power law regions are more negative than both those of pure liquids and those for films of PS free chains, for which exponent values of approximately -1 ($\eta \sim 0$) have been reported [3]. Two further trends can be noted. First, the slope becomes less negative upon the annealing of a sample. Second, the slope becomes more negative with brush thickness.

In Fig. 2, note that the shape of the transverse scan from the 84-Å-thick PS brush is different than the shapes of the scans from thicker brushes. For each of the thicker brushes, there is a transition at some intermediate value of q_x from a region of very slowly changing intensity to the power law behavior. It is tempting to associate this crossover in behavior with $q_{l,c}$ of the capillary wave theory. For the present, we denote the position of this crossover with q_c and leave the question of its precise significance unanswered. However, the values of q_c generally increase with decreasing thickness. In contrast to the scattering from the other brushes, the scattering

from the thinnest brush reveals no clear cutoff. The shape of the transverse scan is, however, almost identical to that seen by Wang et al. [3] for an annealed film of PS free chains that are 68 Å thick. Both show a small damped fringe next to the Yoneda peak that we believe is due to dynamical scattering. The presence of this dynamical scattering feature may obscure the location of a cutoff at a value of q_x close to that of the Yoneda peak.

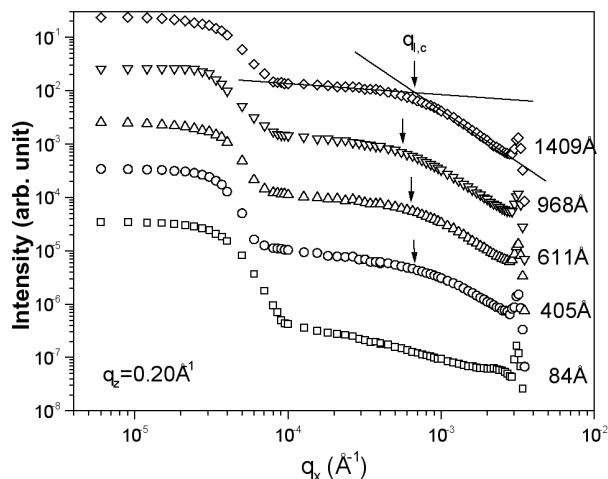


FIG. 2. Transverse scans at $q_z = 0.20 \text{ \AA}^{-1}$ for annealed PS brushes with thicknesses ranging from 84 to 1409 Å. The thicknesses were controlled by varying grafting density (GDV) at a fixed molecular weight. Each curve has been shifted vertically for clarity. Arrows indicate apparent lower wave vector cutoffs, q_c . Solid lines superposed on the curve of the 1409-Å-thick film show how the position of q_c has been determined.

Discussion

Some aspects of the scattering from these brushes fit expectations from capillary wave theory. For example, the value of the apparent cutoff wave vector increases as the thickness decreases, as would be expected if surface fluctuations were more suppressed for thinner films. To assert such a change in suppression with thickness is reasonable, but this assertion cannot be supported by quantitative fitting of the data if only capillary waves are considered. There are important deviations in the scattering behavior from the behavior consistent with pure capillary wave behavior. Most important, the power law exponents cannot be reconciled with the expressions relating the exponent to surface tension. Thus, while capillary waves most certainly play a role in determining the surface structure, there must be some additional facet to the surface structure that remains to be elucidated. It has been shown by Tolan et al. [9] that dewetting of a thin

film can lead to power law exponents more negative than anticipated by the capillary wave theory, but polymer brushes cannot dewet. Nonuniformities in grafting density could also be expected to result in surface correlations that would impact the diffuse scattering [10]. The possibility that such nonuniformities combined with capillary waves can explain the data quantitatively is being investigated. In particular, imaging of the surfaces with scanning probe microscopy is being undertaken to provide complementary information on the surface structure.

Acknowledgments

This research was funded in part by a U.S. Department of Defense Multidisciplinary University Research Initiative (MURI) grant (DAAH04-96-1-0018) from the Army Research Office, the Collaborative Center for Polymer Photonics (F49620-02-1-0428), and the Ohio Board of Regents. Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. We thank the SRI-CAT for use of beamline station 1-BM-C.

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