

# Surface Fluctuations on Poly(*n*-butylacrylate) 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 (CWT) 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  $\gamma$  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 a 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  $\gamma_{eff}$  is an effective surface tension.

Recently, attention has turned to surface fluctuations on complex polymeric liquids [2, 3]. The scattering from molten poly(*tert*-butyl acrylate) (PtBA) [3] has been shown to be consistent with capillary wave theory. Two scattering studies [3, 4] of the surfaces of films of polystyrene (PS) chains offer conflicting interpretations of the behavior for that system. Wang et al. [2] 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. [4] used a different scattering geometry and measurements at temperatures above the glass transition temperature  $T_g$  and reported that surface tensions derived from the diffuse scattering were consistent with 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 [5]. 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 [6]. 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.

In a companion activity report [7], our studies on brushes of PS chains are described. Those measurements allow for the most ready comparison to existing results for films of untethered (“free”) chains. However, work with PS brushes has a disadvantage in that measurements made at room temperature are done with the vitrified brush. Measuring at temperatures above the  $T_g$  of PS makes the samples much more sensitive to radiation damage.

To address these complexities, measurements were done with poly(*n*-butylacrylate) (PnBA) brushes, which have  $T_g$  values below those of PtBA films and markedly below room temperature. The  $T_g$  of bulk, untethered PnBA is  $-54^\circ\text{C}$ . Thus the brushes are molten at room temperature. These measurements allow one to consider the possible suppression of the surface fluctuations by tethering, in cases where the brush is in the melt and the temperature of the state for which the dynamics are being probed is better defined than it is in the case of PS brushes.

## Methods and Materials

PnBA brushes were synthesized by using surface-initiated free-radical polymerization techniques [8]. The brush thicknesses were controlled by varying the reaction time in the bulk monomer in order to vary grafting density, except for the thinnest brush. The thinnest brush was prepared with a 50 vol % solution.

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  $1.127 \text{ \AA}$  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  $0.35 \text{ \AA}^{-1}$ . 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  $2 \times 10^{13}$  photons/cm<sup>2</sup>/s. Sample heating was achieved in a temperature-controlled cell with a He purge to reduce radiation damage.

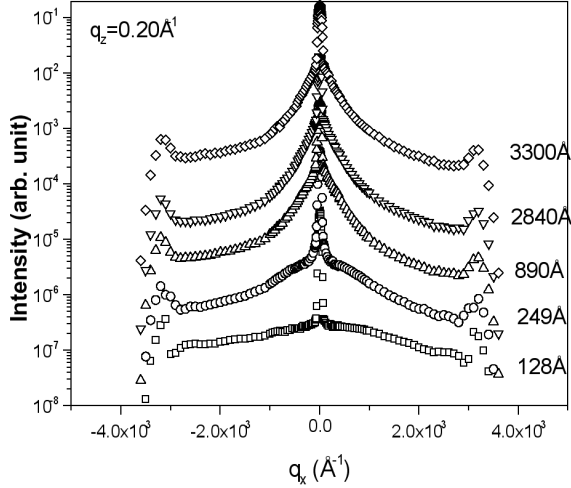


FIG. 1. Transverse scans taken at  $q_z = 0.20 \text{ \AA}^{-1}$  for PnBA brushes, the thicknesses of which range from 128 to 3300  $\text{\AA}$ . The curves have been offset vertically for clarity.

## Results and Discussion

Measured intensities from transverse scans taken at  $q_z = 0.20 \text{ \AA}^{-1}$  are plotted on a log-linear plot as a function of  $q_x$  in Fig. 1. The diffuse scattering is weakest and most nearly flat for the thinnest film, and the scattering from the thicker films is more liquidlike in character. This suggests that the longer wavelength fluctuations increase as the brush becomes thicker. However, no substantial broadening of the specular peaks themselves is observed with increasing thickness. This observation is consistent with the contention that longer waves corresponding to values of  $q_x$  that fall within the specular peak are suppressed on the PnBA brush.

The presence of a cutoff behavior and any power law regime in the data are most readily studied by using a log-log plot, as shown in Fig. 2(a) for the specific case of  $q_z = 0.20 \text{ \AA}^{-1}$ . For all thicknesses, a transition between two regions can be identified, as would be expected in the presence of capillary wave suppression. For convenience, the positions of these transitions are denoted as values of  $q_{l,c}$ , although the exact origin of the transition is left open for the moment. The dependence of  $q_{l,c}$  upon thickness is summarized for all four values of  $q_z$  in a single plot in Fig. 2(b). One sees roughly two regimes of behavior. For the lower thicknesses,  $q_{l,c}$  decreases with increasing  $d$ , apparently according to a power law behavior. Deviation from this behavior is seen for a thickness for which the value of  $d/R_g$  is approximately 4. Whether  $q_{l,c}$  actually increases with  $d$  when  $d/R_g$  is  $>4$  is not clear because the

sampling of thicknesses is sparse. However, it is clear that the surface fluctuations of brushes when  $d/R_g$  is  $>4$  are qualitatively different from those of brushes when  $d/R_g$  is  $<4$ .

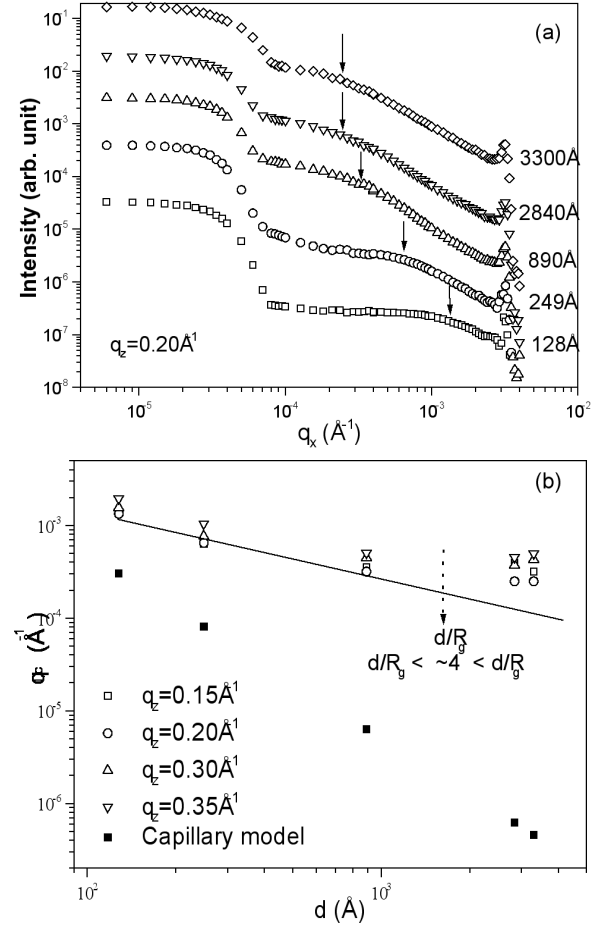


FIG. 2. Plots demonstrating the variation of  $q_{l,c}$  with brush thickness for the PnBA brushes. (a) Transverse scans taken at  $q_z = 0.20 \text{ \AA}^{-1}$  for brushes, the thicknesses of which range from 128 to 3300  $\text{\AA}$ . Each curve has been shifted vertically for clarity. Arrows indicate the positions of the lower cutoffs  $q_{l,c}$ . (b) Plot summarizing the thickness dependence of  $q_{l,c}$  for all the PnBA brushes and all four values of  $q_z$ . The experimental data are shown with open symbols. The solid line superposed on the data for  $q_z = 0.20 \text{ \AA}^{-1}$  is intended as a guide to the eye only for the data below values of  $d$  corresponding to  $d/R_g = 4$ . For comparison, the thickness dependence of  $q_{l,c}$  expected for the capillary wave model is shown with solid squares.

The value of  $q_{l,c}$  varies less strongly with film thickness than in the case of PS free-chain films ( $q_{l,c} \sim d^{-1}$ ) or simple liquid films ( $q_{l,c} \sim d^{-2}$ ). This suggests the long wavelength fluctuations are suppressed more strongly on the PnBA brush surfaces than on the surfaces of liquids.  $q_{l,c}$  scales

roughly as  $d^{-0.65}$  for normalized thicknesses ( $d/R_g$ ) below 4. This behavior is closer to that predicted by Fredrickson's theory [7] ( $q_{l,c} \sim d^{-0.75}$  for small  $q_F$ ) than is the behavior seen for the PS brush films ( $q_{l,c} \sim d^{-0.42}$ ).

As they did for PS brushes, the values of the exponent for the power law behavior of PnBA brushes do not follow the expectations of CWT. While CWT anticipates values of the exponent being greater than  $-1$ , all the data for the PnBA brushes show values of less than  $-1$  and as small as  $-2$ . Thus it is not possible to associate the observed cutoff unequivocally with that of the CWT.

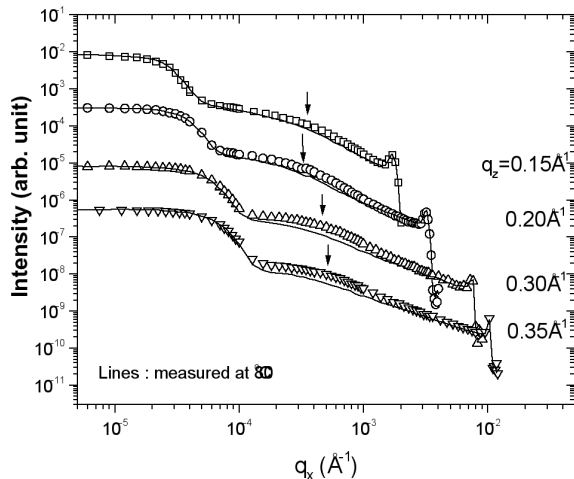


FIG. 3. Comparison of transverse scans, at four values of  $q_z$ , for a PnBA brush of thickness  $890 \text{ \AA}$  measured at room temperature (about  $32^\circ\text{C}$ ) (symbols) and  $80 \pm 1^\circ\text{C}$  (solid curves). The data for different  $q_z$  values have been shifted relative to one another for clarity. Arrows indicate the positions of the lower cutoffs  $q_{l,c}$ .

The variation in the power law regime exponent with temperature was probed as well. The samples were heated in the spectrometer and measured after a short time of equilibration. Measurements at elevated temperature had to be done more rapidly to avoid artifacts due to beam damage. Transverse scans measured at room temperature (about  $32^\circ\text{C}$ ) and  $80 \pm 1^\circ\text{C}$  are compared in Fig. 3. The positions of  $q_{l,c}$  are essentially the same at the two different temperatures. This is consistent with the contention that  $q_{l,c}$  is determined by film thickness, as expected for capillary waves. The fact that the surface fluctuations are due, at least in part, to thermal excitation and are thus temperature sensitive is reflected in the changes seen in the power law exponent at higher  $q_x$ . The slopes are consistently less negative in the scans measured at  $80^\circ\text{C}$ . For simple liquids, the slope becomes less negative as  $T$  increases and as  $\gamma$  drops due to the temperature increase ( $I \sim q_x \eta^{-1}$ ,  $\eta \sim T/\gamma$ ). The scattering

curves are fully thermally reversible, proving that the changes that occur upon heating are due to the thermally excited character of the surface structure and not to artifacts associated with irreversible changes upon heating.

In conclusion, the diffuse scattering from the PnBA brush appears to manifest a cutoff behavior that depends on brush thickness and is independent of temperature. This transition is seen even for very thick brushes for which van der Waals interactions with the substrate cannot be the source of the cutoff. The temperature dependence of the overall diffuse scattering intensity and the reversibility of this intensity suggest that the surface structure is at least partially dictated by thermally excited waves. However, the power law behavior that was observed is not consistent with a surface structure dictated by capillary waves alone. The possibility that other sources of surface correlations, such as grafting nonuniformities [9], are responsible for the curious exponent values is being investigated.

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