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Surface fluctuations of polymer brushes probed by diffuse X-ray scattering

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Abstract

The diffuse scattering from the surfaces of melt and glassy polymer brushes has been studied systematically for the first time using polystyrene (PS) and poly(*n*-butylacrylate) (P*n*BA) brushes synthesized by free radical polymerization. The data show unambiguously that the diffuse scattering behavior varies systematically with brush thickness for both types of brushes. We attribute a cross-over in scattering with q_x, the in-plane scattering vector, to the presence of surface thermal fluctuations and their suppression for longer wavelengths, a phenomenon already reported for films of untethered chains. Long wavelength fluctuations are suppressed more strongly on the surface of a PS brush than on the surface of a film of untethered ('free') PS chains of comparable thickness, so that even in films of thickness, d, such that $d/R_g > 5$ clear evidence of the suppression of fluctuations can still be seen in the experimentally available range of q_x. Fluctuations are suppressed for q_x less than a lower wavevector cut-off, $q_{l,c}$, which changes with film thickness, though much more weakly than for films of free chains. For values of $d/R_g < 4$, where R_g is the unperturbed radius of gyration of a comparable free chain, $q_{l,c}$ drops as d increases. For $d/R_g > 4$ $q_{l,c}$ begins to increase with brush thickness, in qualitative agreement with theory, indicative of a transition to a true 'brush' state in which stretching of the chains makes longer wavelength fluctuations at the surface unfavorable. Measurements with P*n*BA brushes having T_g substantially below room temperature confirm the trends mentioned above. Further, they give evidence that the value of $q_{l,c}$ is temperature insensitive above T_g.

Keywords: Polymer brush; Surface fluctuations; X-ray scattering

1. Introduction

The study of surface deformations in soft condensed matter is important to the use of these materials in structures and devices of increasingly small dimensions. In nanoscale devices interfacial behavior is dominant and when materials have small dimensions, confinement effects are often important in dictating the interfacial behavior. One type of soft matter thin film that has recently received considerable attention is the 'polymer brush'.

A polymer brush film is formed when one end of each polymer chain in a film is tethered to a substrate and the grafting density is sufficiently high that the chains are forced to stretch from their preferred dimensions [1]. Both the tethering of the chains and the stretching thereby induced can potentially cause the film to have properties different from those of a corresponding polymer film in which the chains are not tethered. In particular, theoretical studies [2,3] have suggested that the surface wave dynamics of a polymer brush should differ from those of a film of free chains. However, to date no experimental verification of these characteristic features in the surface waves of polymer brushes has been published. In this study, we consider films of tethered chains that span ranges of grafting density and molecular weight across the dividing line between films that are simply tethered and those that are sufficiently stretched to rigorously warrant the name of 'brush'. For convenience,

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and following widespread convention, we will refer to all of the samples in general as brushes, but in the discussion of the results will make clear which films formally meet the criterion for being a brush.

One incisive means of studying surface fluctuations on soft materials and liquids is X-ray scattering [4–6]. Helpful information can be gathered from both X-ray reflectivity (XR) and off-specular scattering measurements, with XR having been used to reveal surface wave modes of liquid surfaces before off-specular scattering techniques began to be developed [7,8]. In XR the incident angle is equal to exit angle ($\alpha_i = \alpha_f$), the scattering vector, q, lies perpendicular to the surface, and the experiment is sensitive to the structure of thin films in the direction normal to the surface. With the normal direction denoted as z, q has only a q_z component. However, with an appropriate model, the contribution of intrinsic roughness and capillary wave fluctuations to the total observed roughness can be separated [7]. In off-specular diffuse scattering, at least one in-plane component of q (q_x or q_y) is nonzero as shown in Fig. 1(a). This allows one to explicitly study lateral length scales of the surface fluctuations [9–11]. Since this is a static scattering experiment, it is actually the structure of the surface that is probed and the information about the surface dynamics is inferred from characteristics of the surface structure. In the case that the surface of the brush is vitrified before the measurement is made, a ‘snapshot’ of the surface fluctuations is studied. If the surface is in the melt state during the measurement, we collect information pertinent to a time average of the surface structure.

Here, the surface dynamics of tethered films of two polymers of very different glass transition temperatures (T_gs) have been investigated. Polystyrene, with a T_g in the bulk of ~ 100 °C, is glassy at room temperature [12]. Poly(n-butylacrylate) has a bulk $T_g \approx -54$ °C and is rubbery at room temperature [12]. The effects on the surface fluctuations of different methods of varying the brush thickness, variation of grafting density, and variation of molecular weight have all been considered. Where possible, the results for the tethered films are compared with those of analogous films of free polymer chains.

2. Experimental section

2.1. Preparation of polymer brushes

PS and P*n*BA brushes with polydisperse chain sizes were synthesized using surface initiated free radical polymerization techniques as described in the literature [13–15]. Such brushes can be synthesized to have thicknesses much larger than those attainable with other synthetic techniques. Briefly, in a first step azo initiators were immobilized on the native oxide of a silicon wafer at room temperature from a solution in dry toluene under an inert atmosphere using triethylamine as a catalyst. The concentration of the initiator was ca 0.5–1.0 mmol/l. After completion of the immobilization reaction the substrates were rinsed with toluene and methanol (analytical grade) to remove non-bound initiators and other by-products of the reaction. The polymerizations of PS were then carried out in toluene at 60 °C under dry argon atmosphere after at least three freeze–thaw cycles to remove traces of oxygen. Two strategies were used to control the thickness of the polymer brush films. First, brush film thickness was increased by increasing grafting density at a fixed molecular weight. This series of samples will be denoted for convenience by the label ‘grafting density varied’ (‘GDV’). Grafting density is a function of initiator decomposition rate, initiator efficiency, reaction temperature, and reaction time. The latter parameter was used to adjust the conversion of the initiator and thereby the number of polymer chains generated at the surface. To make molecular weights the same throughout this series of samples, the same concentrations of styrene monomer were used (50 vol%).

In the second series, brush film thickness was increased by increasing the molecular weight of the surface-attached polymers at a fixed grafting density. This series of samples will be denoted with the label ‘molecular weight varied’ (‘MWV’). Molecular weight of the brush chains is a function of monomer concentration and reaction temperature. To make grafting densities the same throughout this series of samples, polymerizations were carried out for 5 h for each sample. Because all other polymerization parameters were the same except for monomer concentration, molecular weight was determined only by monomer concentration.

The thicknesses of P*n*BA brush films were controlled by varying reaction time in the bulk monomer in order to vary grafting density except for the thinnest brush. The thinnest one was prepared with a 50 vol% solution. A summary of the estimated molecular weights, grafting densities and sample thicknesses, d, and roughnesses, σ, measured by X-ray reflectivity (XR) or ellipsometry is given in Table 1.

Some of the PS brushes were annealed in a high vacuum oven (1.04×10^{-4} Pa). Annealing times were constrained by the susceptibility to thermal degradation of the chain linkages to the substrate. Using experience in Rühe’s group with various thermal treatments as a guide, an annealing time of 20 min was chosen to provide substantial opportunity for relaxation of the surface without danger of cleaving chains from the surface. Due to limitations in the heating and cooling rates of the heating device in the oven, in addition to the 20 min at 140 °C, the samples spent about 25 min at temperatures above their glass transition temperature (T_g) as they were first heated to 140 °C and then while 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. This annealing time of 20 min. is not sufficient for center-of-mass diffusion of the chains over distances comparable to R_g, but such large scale

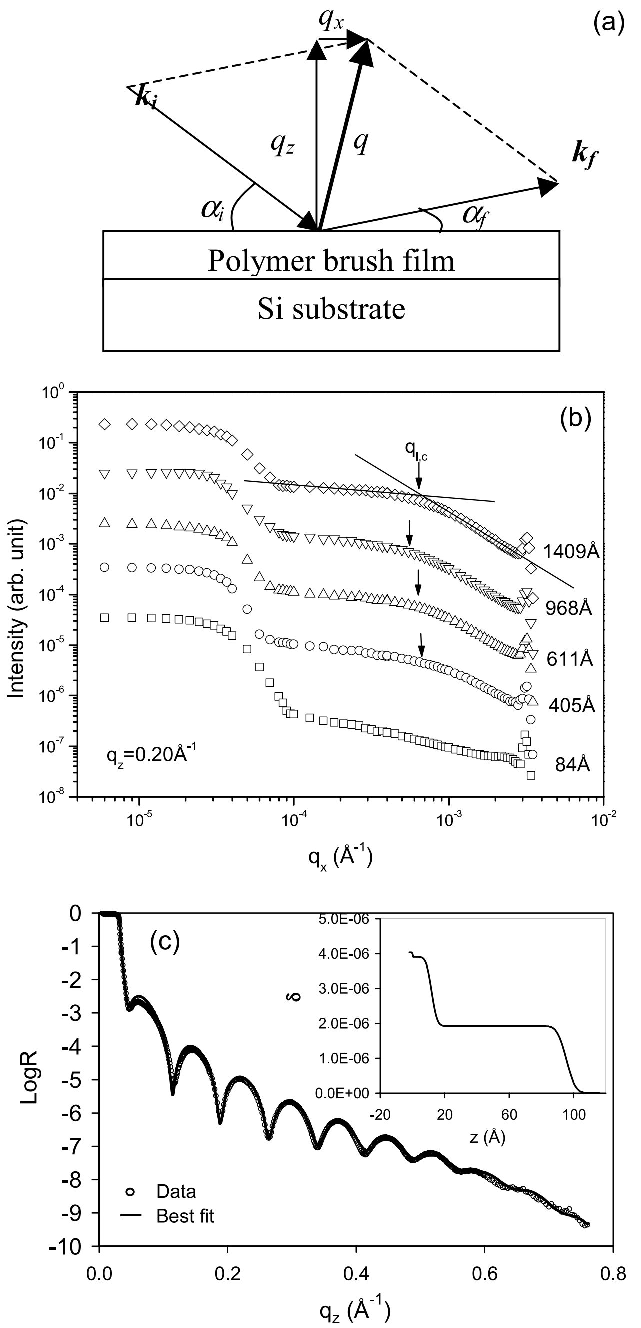

Fig. 1. (a) Schematic of scattering geometry. The wavevectors of the incident and scattered X-rays are $\mathbf{k}_i$ and $\mathbf{k}_f$, with the incidence and exit angles α_i and α_f, respectively. The momentum transfer is defined by $q \equiv \mathbf{k}_f - \mathbf{k}_i$. The so-called 'specular scattering' corresponds to $\alpha_i = \alpha_f$. Otherwise, the scattering is called 'off-specular scattering'. (b) Transverse scans taken at $q_z = 0.20$ Å^{-1} for annealed PS brushes with thicknesses ranging from 84 to 1409 Å. The thicknesses were controlled by varying grafting density at fixed molecular weight. Each curve has been shifted vertically by an order of magnitude for clarity. Arrows indicate the positions of the lower wavevector cut-offs, $q_{l,c}$. Solid lines superposed on the curve of the 1409 Å thick film show how the position of $q_{l,c}$ has been determined. (c) Measured specular X-ray reflectivity (symbols) and fit (solid lines) for 84 Å thick PS brush as a function of q_z. The structure model found to fit the data, plotted as the real part of the refractive index as a function of depth, is shown in the inset.

motion is not needed. The broad agreement seen between the behavior of annealed PS brushes and that of P*n*BA brushes that were far above their T_g for days before measurements confirmed that this approach was valid.

2.2. X-ray scattering

The surface fluctuations of the brush surfaces in the glassy or melt state were characterized by X-ray off-specular scattering measured on the 1-BM beamline at the advanced photon source in Argonne National Laboratory. The spectrometer used a double-crystal monochromator to choose a wavelength of 1.127 Å with a resolution of $\delta q_x \approx 8 \times 10^{-5}$ Å^{-1} at $q_z = 0.20$ Å^{-1}. The heights of the incident beam (h_i) and detector (h_d) slits were set such that $h_d/h_i = 1.89$. The samples were mounted on a goniometer providing translations in x, y, and z and rotation in θ (incident angle). The scattered intensity was collected with a NaI detector. After measuring the specular reflectivity, off-specular scattering was measured using both longitudinal and transverse scans. The longitudinal scan was run with theta offset by 0.07° from the specular condition. This offset was sufficient to insure that the signal measured was representative of the diffuse scattering and not the tail of the specular beam. Transverse scans were collected as step scans for four different values of q_z, 0.15, 0.2, 0.3, and 0.35 Å^{-1}. The values of q_x used for the scans were optimized for each sample to provide approximately a logarithmic spacing of data points. Samples were translated perpendicular to the beam direction after each scan to minimize possible radiation damage to the sample. Typically one position on the sample was exposed for 10–20 min, but not more than 30 min, with the duration depending on whether the beam was attenuated. The unattenuated beam had a flux of about 2×10^{13} photons/cm^2/s.

3. Results and discussion

3.1. Polystyrene brushes

Experiments were run to probe the variation in brush surface dynamics with brush thickness for the two cases in which grafting density was varied or molecular weight was varied. In Fig. 1(b) are plotted transverse scans for the GDV series measured after the samples had been annealed. Intensities are plotted as a function of in-plane wave vector transfer q_x using a log–log scale. An example of reflectivity data and a fit to that data is shown in Fig. 1(c) for the case of the 84 Å thick brush. The presence of fringes out to $q_z = 0.7$ Å^{-1} attests to the fact that the film is very smooth (5 Å rms) and uniform. Thicker films were somewhat rougher (ca. 12–14 Å rms) and not quite as uniform in thickness. However, the fringes for those films still generally persisted to $q_z = 0.3$ or 0.4 Å^{-1}, indicating reasonably good uniformity.

Table 1
Summary of characteristics of brush samples

	d^{a} (Å)	σ^{b} (Å)	Grafting density (μmol/m^2)	σ (chains/nm^2)	M_n^{c} (10^5 g/mol)	d/R_g	Σ^{d}
PS GDV	92	5.2	0.04	0.025	6.5	0.4	36
	431	14.1	0.09	0.056	6.5	2.0	81
	618	9.9	0.13	0.077	6.5	2.9	112
	960	15.8	0.16	0.097	6.5	4.5	142
	1356	11.9	0.23	0.14	6.5	6.3	203
	2513	–	0.33	0.20	8.1	10.4	370
PS MWV	97	5.4	0.11	0.066	4.2	0.6	63
	229	7.1	0.11	0.066	4.8	1.2	72
	326	8.0	0.11	0.066	5.3	1.7	80
	472	8.7	0.11	0.066	5.9	2.3	89
	545	10.3	0.11	0.066	6.5	2.5	97
	832	12.5	0.11	0.066	8.1	3.4	122
P*n*BA	128	12.0	0.04	0.024	12^{e}	0.3	140
	249	22.0	0.04	0.024	25	0.7	95
	890	–	0.06	0.036	25	2.3	170
	2840	–	0.09	0.054	25	7.4	250
	3300	–	0.13	0.078	25	8.6	360

[a] Measured by either XR or ellipsometry. Uncertainty in d measured by XR is $<\pm 2$ Å.

[b] Values of roughness, σ, are shown only for the samples measured by XR. Uncertainty of σ inferred from the fitting process is about 15–20%.

[c] As determined by gel permeation chromatography (GPC system from Agilent with columns from PSS, Mainz, Germany) calibrated using narrow molecular weight distribution PS standards purchased from PSS (Mainz, Germany).

[d] Dimensionless grafting density, $\Sigma = \sigma \pi R_g^2$.

[e] The molecular weight of the P*n*BA brushes was estimated from the known kinetics of the polymerization process using published values[10] for the graft density of the initiator and all kinetic constants. These values allow for an estimation of the graft density of the polymers which together with the layer thickness and the materials density (taken as 1 g ml^{-1}) allows for the calculation of the number averaged molecular weight. The error of this calculation stems from variables during the polymerization process and may be estimated to be of the order of 30%.

Three general scattering features are observed in the off-specular scattering 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. First, the profile of the specular beam is captured in the region of $q_x < 8 \times 10^{-5}$ Å^{-1} (for the present case of $q_z = 0.20$ Å^{-1}). For our purposes this is uninteresting except as it clarifies the resolution of q_x. Our study of the impact of layer structure on dynamics is limited to those features of the surface fluctuations that manifest themselves for values of q_x such that $8 \times 10^{-5} < q_x < 2 \times 10^{-3}$ Å^{-1}. This corresponds to fluctuations with wavelengths varying from 310 to 7850 nm. The second general feature is a region of very small slope next to the specular peak.

The third general feature is a power-law 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. The value of the exponent for typical liquid films is close to -1 [16]. The reason for the higher values of α seen here is not apparent from the measurement itself. Even though the values of α are close to those observed for dewetted polymer films on which capillary waves exist [11], dewetting has not been observed for our brushes and dewetting is precluded by the chemical attachment of the chains to the substrate.

The shape of the transverse scan from the 84 Å thick PS brush is different from those from the brushes of larger thicknesses. For each of the thicker brushes there is a transition at some intermediate value of q_x, call it $q_{1,c}$, from a region of very slowly changing intensity to the power-law behavior. The value of $q_{1,c}$ at which the power-law behavior is arrested is referred to as the lower wave vector cut-off. In contrast to that from the other brushes, the scattering from the thinnest brush reveals no clear cut-off. The shape of the transverse scan is, however, almost identical to that seen by Wang et al. [9] for an annealed film of PS free chains of thickness 68 Å. Both show a small damped fringe next to the Yoneda [17] peak which we believe is due to dynamical scattering [18]. The presence of this dynamical scattering feature may obscure the location of a cut-off at a value of q_x close to that of the Yoneda peak.

The dependences of $q_{1,c}$ on sample thickness are summarized in Fig. 2 for the four values of q_z investigated and the two different sample series. When the thickness of the brush is increased by increasing molecular weight, the value of $q_{1,c}$ decreases logarithmically with brush thickness, as shown with the log–log plot in Fig. 2(b). Thus, as the film gets thicker, the surface fluctuations are less strongly suppressed by tethering, and the longest fluctuation wavelength present on the surface grows. The values of $q_{1,c}$ do not vary exactly according to a power law for $q_z = 0.15$ Å^{-1}, and the data point for the thinnest film, in particular, seems to violate the general trend. This is probably due to the difficulty of determining the value of $q_{1,c}$ when it is obscured by the dynamical scattering feature near the Yoneda peak. When thickness is varied by changing grafting density, as is the case in Fig. 2(a), there is no consistent relationship between thickness and $q_{l,c}$ over the range of thickness studied. However, for three values of q_z there is a decided change in behavior with thickness. For the smaller thickness, it may be that $q_{l,c}$ decreases with thickness. On the other hand, the value of $q_{l,c}$ for the film of thickness 1356 Å is decidedly above that for the film of thickness 960 Å. This appears counter to the trend seen otherwise and raises the question of what may be special about those brushes. For reference, the thickness, d, corresponding to a value of the ratio d/R_g (with R_g the unperturbed radius of gyration) of four has been indicated in Fig. 2(a). While all the data collected for the MWV series correspond to values of d/R_g below four, the value of the ratio for the thickest brush considered in the GDV series exceeds four. Thus, it appears that the maximum wavelength on a brush surface increases with d/R_g until a critical ratio of d/R_g around four, above which the largest wavelength may decrease. In other words, when the chains are more strongly stretched than d/R_g of four, the long-wavelength modes on the brush surface are more strongly suppressed, as has been proposed by Fredrickson [2]. The ratio d/R_g of four is a boundary that distinguishes between films having truly brush-like surface dynamics from films having surface dynamics influenced by grafting, but not truly brush-like. Genzer and coworkers [19] reported measuring a transition from 'mushroom' to 'brush' behavior in polyacrylamide layers swollen in solvent ('wet brushes') for a grafting density of about 0.065 chains/nm^2. That transition occurred at a ratio of the 'wet' height to R_g of about 2.1, which corresponded to a ratio of the dry height (our d) to R_g of less than two.

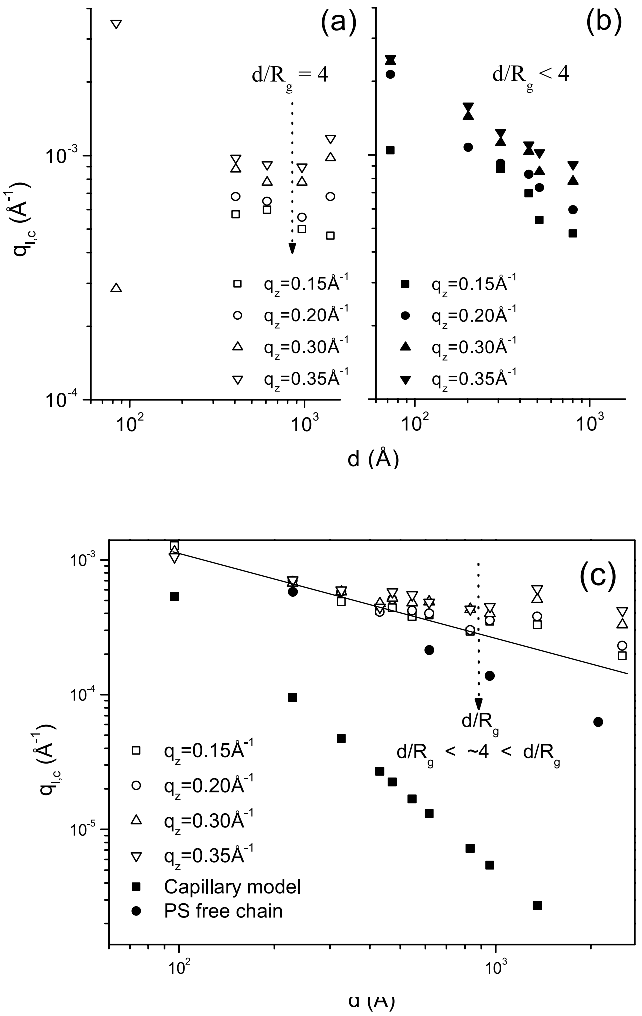

Fig. 2. Thickness dependence of lower cut-offs taken at four different q_z values for annealed PS brushes. (a) GDV series and (b) MWV series and that for (c) unannealed PS brushes of both series. A solid line superposed on the data set for $q_z = 0.20$ Å^{-1} indicates a guide for the eye only for the data for $d/R_g < 4$. For comparison, the thickness dependencies of the lower cut-offs for PS free chain films and capillary wave model are plotted as well.

Fig. 2(c) replots the thickness dependence of $q_{l,c}$ for the PS brushes of both series and for all four values of q_z in order to make comparison with the behavior expected from the liquid capillary model and the experimentally observed behavior for films of free PS chains [9]. Results from both the GDV and MWV series are plotted to give the whole picture of thickness dependence of $q_{l,c}$. Results are shown for the unannealed brushes rather than for the annealed brushes because we were unable to measure all the annealed samples due to limitations on beam time. However, the trends are qualitatively the same. For both liquids with capillary waves and brushes $q_{l,c}$ is expected in theory to decrease with d as $q_{l,c} \sim a/d^m$, where a is a characteristic length related to a ratio of van der Waals interaction to surface tension $\left(a = \sqrt{A_{\mathrm{eff}}/2\pi\gamma_{\mathrm{eff}}}\right)$. $q_{l,c}$ is expected to scale as d^{-2} in the case of pure liquids [16] and as d^{-1} in the case of PS free chain thin films on substrates [9].

Experimentally it is seen that for the thinnest films the values of the cut-off wavevector for the brush and free chain films seem to come together. For larger thickness long wavelength fluctuations are more strongly suppressed on the brushes than on either the liquid or the free chain film. At the point at which $d/R_g = 4$ a strong change in behavior is seen. Upon crossing that boundary the value of $q_{l,c}$ first increases with thickness and then perhaps begins to decrease again. There are two reasons for the stronger suppression for the brushes. First, the chains interact more strongly with the substrate through covalent bonds. Secondly, the lateral displacement of chains necessary to create fluctuations is unfavorable for vertically stretched chains under the assumption of constant density. When only the brushes with d/R_g ratios between 1 and 4 are considered, $q_{l,c}$ scales roughly as $d^{-0.42}$. This is qualitatively consistent with the Fredrickson's theory [2]. However, the result is quantitatively different from the theoretical expectation of d^{-1} or $d^{-0.75}$ dependence for the two cases of large q_F and small q_F, respectively, where $q_F = 2\mu_0/\gamma$ is the ratio of bulk shear modulus, μ_0, and surface tension, γ, of the polymer. Our observations differ from Fredrickson's predictions in another aspect as well. The values of $q_{l,c}$ for the brush films are about one order of magnitude smaller than those expected from the theory. The theory anticipates a cut-off at a value of q_x in the order of $2\pi/d$. In this case, the values of $q_{1,c}$ at $q_z=0.20$ Å^{-1} for PS brush films with thicknesses below 1000 Å should fall in a range of q_x that is experimentally inaccessible for us. However, the cut-offs are still observed, even for the thinnest film. One possible reason for the differences between theoretical predictions and the experimental behavior is that the brushes studied here have polydisperse chain sizes, while the theory considers monodisperse chains.

3.2. Poly(n-butylacrylate) brushes

Measurements were also done for P*n*BA brushes which have T_g values markedly below room temperature. The T_g of bulk, untethered P*n*BA is about −54 °C [12]. These measurements allow one to consider the suppression of the surface fluctuations by tethering in the case where the brush is in the melt and the temperature of the state for which the dynamics are being probed is better defined than in the case of PS brushes. Measured intensities from transverse scans taken at $q_z=0.20$ Å^{-1} are shown in Fig. 3(a). As in the case of the PS brushes the diffuse scattering from the thicker films is more liquid-like in character [18]. This suggests an increase in fluctuations of longer wavelength as the brush becomes thicker. However, no substantial broadening of the specular peaks themselves is observed with increasing thickness (Fig. 3(a)). This is because longer waves corresponding to values of q_x that fall within the specular peak are strongly suppressed on the P*n*BA brush due to the chemical tethering of the chains to the substrate.

When the dependence of $q_{1,c}$ upon thickness is summarized for all four values of q_z in a single plot in Fig. 3(b), one sees again, as for the PS brushes, roughly two regimes of behavior. For the lower thicknesses $q_{1,c}$ 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 four. Whether $q_{1,c}$ actually increases with d for $d/R_g>4$ is not clear. The sampling of thicknesses is not quite so extensive as it was for the PS brushes. However, it is clear that the surface dynamics of brushes with $d/R_g>4$ are qualitatively different from those of brushes with $d/R_g<4$, confirming the observation from the PS brushes.

For the P*n*BA brushes also, $q_{1,c}$ varies less strongly with film thickness than in the case of PS free chain films or liquid films. The long wavelength fluctuations on the P*n*BA brush surfaces are suppressed more strongly than on the surfaces of liquids. $q_{1,c}$ scales roughly as $d^{-0.65}$ for normalized thicknesses (d/R_g) below four. This behavior is closer to that predicted by Fredrickson's theory ($q_{1,c}\sim d^{-0.75}$ for small q_F) than is the behavior seen for the PS brush films.

With the P*n*BA brushes the variation in the power law regime exponent with temperature could be probed somewhat more readily than for the PS brushes. Using a temperature-controlled stage, the samples could be heated in the spectrometer and measured after a short time of equilibration, though measurements at elevated temperature had to be done even more rapidly to avoid artifacts due to beam damage. Transverse scans measured at room temperature (about 32 °C) and 80 ± 1 °C for four different q_z values were compared (data not shown here). The positions of $q_{1,c}$ were the same at the two different temperatures.

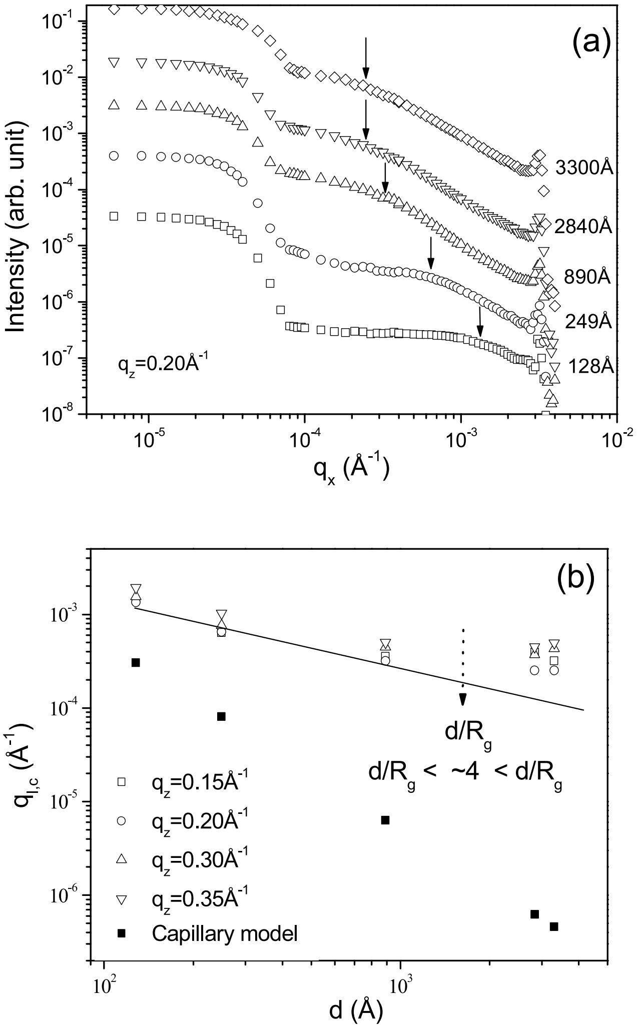

Fig. 3. Plots demonstrating the variation of $q_{1,c}$ with brush thickness for the P*n*BA brushes. (a) Transverse scans taken at $q_z=0.20$ Å^{-1} for brushes, the thicknesses of which range from 128 to 3300 Å. Each curve has been shifted vertically by an order of magnitude for clarity. Arrows indicate the positions of the lower cut-offs $q_{1,c}$. (b) Plot summarizing the thickness dependence of $q_{1,c}$ for all the P*n*BA brushes and all four values of q_z. The experimental data are shown with open symbols. The solid line superposed on the data for $q_z=0.20$ Å^{-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 $q_{1,c}$ expected for the capillary wave model is plotted using solid squares.

4. Conclusions

The diffuse scattering from a polymer brush surface has been studied systematically for the first time. The data show unambiguously that the diffuse scattering behavior varies systematically with brush thickness for both PS and P*n*BA brushes and that the scattering varies with temperature and is thermally reversible. Transverse scans show a power law regime and the presence of a lower cut-off in wavevector, $q_{l,c}$. We attribute this cut-off to the suppression of longer wavelength surface thermal fluctuations, a phenomenon already reported for films of untethered chains. Surface fluctuations are strongly suppressed for in-plane wavevector values lower than this cut-off. The lower wavevector cut-off for the brushes is typically larger than that for the analogous film of untethered PS chains, and $q_{l,c}$ varies more weakly with film thickness for the brushes than for films of free chains suggesting that surface fluctuations are more strongly suppressed on the brushes than on corresponding films of untethered chains. For values of d such that $d/R_g < 4$ the value of $q_{l,c}$ drops with increasing thickness as the interaction between brush surface and substrate becomes less important in dictating the surface fluctuations. The fact that a measurable value of $q_{l,c}$ is still observed for brushes with thicknesses corresponding to such large ratios of d/R_g attests, however, to the importance of tethering in mediating the interaction between surface and substrate even for large molecular weight chains. The effect of the tethering is even more remarkably apparent, however, for thicknesses such that $d/R_g > 4$ for which a true ‘brush-like’ behavior manifests itself for the PS brushes. In that regime the value of $q_{l,c}$ increases with increasing d for d/R_g just greater than four. That is, the increased stretching of the chains with growing brush thickness make long wavelength fluctuations of a given wavelength increasingly unfavorable, even though the surface is moving farther from the substrate. This transition appears to be in qualitative agreement with expectations from the theories of Fredrickson [2] and Xi and Milner [3].

Measurements of the P*n*BA brushes with T_g far below room temperature reveal very similar trends. They confirm the existence of a transition in the variation of $q_{l,c}$ with d at about $d/R_g = 4$. The congruence between the results for the two brush chemistries also gives evidence that the behavior seen for the annealed PS brushes is generally representative of dynamics on the surface in the melt state. The lower T_g of the P*n*BA brushes allows explicit tests of the temperature dependence of the diffuse scattering. The value of $q_{l,c}$ is essentially temperature independent. The surface structure induced by the surface dynamics is thermally reversible, demonstrating that the surface structure seen by the scattering experiment is indeed thermally excited and not an artifact of sample preparation.

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