

# 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) (PnBA) 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,  $q_{1,c}$ , 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,  $q_{1,c}$  drops as  $d$  increases. For  $d/R_g > 4$   $q_{1,c}$  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 PnBA brushes having  $T_g$  substantially below room temperature confirm the trends mentioned above. Further, they give evidence that the value of  $q_{1,c}$  is temperature insensitive above  $T_g$ .

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## 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 ( $T_g$ s) have been investigated. Polystyrene, with a  $T_g$  in the bulk of  $\sim 100^\circ\text{C}$ , is glassy at room temperature [12]. Poly(*n*-butylacrylate) has a bulk  $T_g \approx -54^\circ\text{C}$  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  $60^\circ\text{C}$  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,  $\sigma$ , 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 ( $1.04 \times 10^{-4}$  Pa). Annealing times were constrained by the susceptibility to thermal degradation of the chain linkages to the substrate. Using experience in Ruhe’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  $140^\circ\text{C}$ , the samples spent about 25 min at temperatures above their glass transition temperature ( $T_g$ ) as they were first heated to  $140^\circ\text{C}$  and then while they were cooled after a residence time at  $140^\circ\text{C}$ . 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

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