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End-Functionalized Polymer Adsorption Study by Evanescent Ellipsometry

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In recent years the topic of end-grafted polymer adsorption onto a substrate has drawn both theoretical[1-6] and experimental interest.[7,8] The attached polymer layer on colloidal particles causes the particles to repel each other so as to keep them in suspension. The functionalized moiety of the chain is attached to the surface of a colloid while the remainder of the chain is in solution. The nonadsorbed component then produces the steric repulsion between the colloidal particles. This system is simpler than diblock copolymers[9] or random copolymers[10] insofar as understanding of the adsorption properties is concerned because of the one end attachment, rather than multiple anchor points, of the polymer molecules on a particle. Therefore, the end-functionalized polymer adsorption onto a substrate is an ideal system to study and to be used for testing the theoretical predictions.

Most of the earlier experimental studies[7,8] involved force measurements between mica surfaces bearing adsorbed polymeric molecules. By monitoring the activating force on the mica surface with the adsorbed polymer layer, this technique is very sensitive for the length scale measurements. Unfortunately, it does not provide information on the total adsorbed amount of polymers. Furthermore, the interaction range monitored by the force measurements depends not only on the thickness of the adsorbed layer but also on the long range interactions between the adsorbed polymer layers.

In this paper we describe an experimental study measuring in situ the total amount of adsorbed polymer by evanescent ellipsometry,[10,11] which is applicable to liquid/solid interfaces. The experimental procedure has been described in earlier publications.[10,11] These previous experiments[10,11] show that polystyrene does not adsorb on glass in a good solvent. We now investigate the system of end-functionalized polystyrene in toluene (a good solvent) with glass as a substrate for adsorption and compare the results with theories.

Nonadsorbing chains (polystyrene) with a single functionalized group [the zwitterionic group $PS^-(CH_2)_3N^+(CH_3)_2(CH_2)_3SO_3^-$] at one end of the polymer were prepared as described previously.[8] The molecular weights of the polymers we have studied are 58K, 660K, and 780K g/mol. The M_w/M_n ratios of these polymers are 1.10, 1.02, and 1.04, respectively. We use the same notation, PS-X(M), for these polymers as in ref 8, where M is the molecular weight of the polystyrene (PS). For preparation of a substrate, the glass prism was soaked in no-chromix sulfuric acid and washed with distilled water, methanol, and subsequently toluene. Finally, the surface of the glass prism was dried with pure nitrogen. Spectroscopic grade methanol and toluene were used. The polymer concentration was 10^{-4}–10^{-5} g/cm^3, and the solvent was spectroscopic grade toluene.

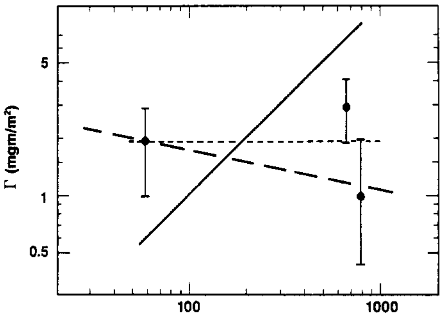

Figure 1. Total amount (Γ) of polymer adsorbed as a function of molecular weight of PS-X(M). The solid, dashed, and dotted lines represent theoretical dependence for the fixed S, the variable S in a good solvent, and variable S in a Θ solvent, respectively.

In the ellipsometry experiment we first measured, with the pure solvent in the background, phase retardation due mainly to the inherent strain in the prism. This background, which is less than 0.5 mrad, was subtracted from the phase retardation measurements with the polymer solution.[10,11] Most of the measurements were done within 60 min of adding the new solution. We did not notice any changes in the phase retardation signal after 30 min. This means that the equilibrium time to achieve the saturation of surface coverage is not long, in agreement with the observation in ref 8. However, we could not monitor the long-time stability of the adsorbed layer due to the long-term temperature variation.

The total polymer excess (Γ) in the interfacial region due to adsorption is[10,11]

$$\Gamma = \int_0^\infty [C(z) - C_b]\, dz = \Delta\Phi(\theta_t)\frac{C_b\epsilon_{solv}}{2k_0\Delta\epsilon_{ss}\epsilon_{ps}{}^{1/2}}$$

where $k_0 = 2\pi/\lambda$, with λ denoting the laser wavelength in vacuum, $C(z)$ the polymer concentration profile, C_b the polymer concentration in the bulk solution, ϵ_{solv} the dielectric constant of the solvent, $\Delta\epsilon_{ss}$ the difference between the dielectric constants of the solution (ϵ_{solut}) and the solvent (ϵ_{solv}), $\Delta\epsilon_{ps}$ the difference between the dielectric constants of the prism (ϵ_{prism}) and the solution (ϵ_{solut}), and $\Delta\Phi(\theta_t)$ the measured phase difference of ordinary and extraordinary beams at the critical angle (θ_t).

Figure 1 shows the total amount (Γ) of polymer adsorbed as a function of the molecular weight of PS-X(M) on a log–log scale. The data show that it is almost independent of the polymer molecular weight. Both the scaling[1] and the mean-field[6] approach predict that a grafted layer thickness (L) varies linearly with molecular weight (M) in the high surface density regime for a given interanchor spacing (S). The total amount of the adsorbed polymer would then be linearly proportional to the molecular weight (M), which is inconsistent with our experimental results. This discrepancy can be resolved if the assumption of a constant interanchor spacing (S) in theory is relaxed. As pointed out by Taunton et al.,[8] experimentally S is determined by the interaction between the adsorption energy of X on the substrate and osmotic interaction between monomers. In this picture,[1,8] the mean interanchor spacing is equal to the size of the blobs[12] that form a stretched adsorbed layer. Then the mean interanchor spacing is proportional to $N^{3/5}$. The total polymer excess (Γ) can be estimated by multipling the surface density of the anchor ($1/S^2$) and the molecular weight of the polymer (N); i.e., $\Gamma \sim (1/S^2)N = N^{-6/5}N = N^{-0.2}$. Therefore, Γ is proportional to $N^{-0.2}$. Using the same argument for the Θ solution, Γ is found to be independent of the molecular weight, i.e., N^0.

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The solid, dashed, and dotted lines represent the theoretical dependence of the adsorbed polymer amount for a fixed S, a variable S in a Θ solvent, and a variable S in a good solvent, respectively. The fixed interanchor spacing model can certainly be ruled out from our data, but the uncertainty of the data is too large to determine the quality of the solvent near the interface in the variable-S model.

We have measured the total amount of the adsorbed end-functionalized polymer on hydrophilic glass as a function of polymer molecular weight by an evanescent ellipsometry technique. We have found that the adsorbed amount is almost independent of molecular weight, in agreement with previous mica force measurements. This can be explained by a variable interanchor spacing of the adsorbed functionalized groups resulting from the balance between the adsorption energy and the excluded volume of monomers.

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