Evolution of Layer Density and Thickness during Poly(ethylene oxide) Adsorption onto Silica

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Introduction

The conformation of polymer layers adsorbed on solid surfaces is an important concern for applications such as steric stabilization[1] and controlled bridging flocculation of colloidal particles.[2,3] Usually, the conformations of adsorbed homopolymer chains are described as trains, loops, and tails and can be characterized by different measurables: the bound (train) fraction of segments, the layer thickness, and the layer density or density profile. Experimental methods for probing conformational aspects of adsorbed layers are subject to some restrictions. Neutron reflectivity[4] and neutron scattering[5] measurements of layer density profiles are static in the sense that data acquisition typically requires hours and cannot usually accommodate evolving layers. NMR,[6] IR,[7] electron spin resonance (ESR),[8] and microcalorimetry[9] techniques have been used to determine the average bound fraction of adsorbed chains as a function of the adsorbed amount. These methods have yet to be incorporated in a time-based mode; rather, the current state of the art involves interruption of dynamic studies at different points corresponding to different adsorbed amounts. Ellipsometry, in principle, can measure both the adsorbed amount and the layer density on a planar surface *in situ*. However, this method usually requires a highly reflective substrate for sufficient optical contrast. Although the sensitivities of some modern ellipsometers allow the determination of the adsorbed amount on a low optical contrast surface such as polystyrene ($n \approx 1.59$),[10] the resolution of the layer thickness and refractive index *at low coverage* is often poor, leading to large uncertainties in these two quantities.[10,11] Reliable *in-situ* measurements of the evolving polymer layer density have rarely been achieved with ellipsometry.[10−14]

We demonstrate here the utility of Brewster angle reflectivity for *in-situ* measurements of the evolving adsorbed layer density on a relatively low refractive index
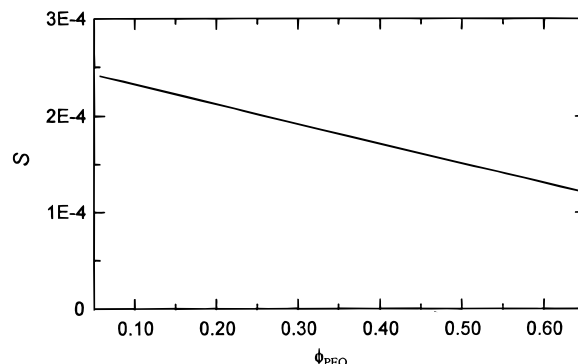

Figure 1. Brewster angle reflectivity sensitivity, S (defined in eq 2, as a function of PEO segment density, ϕ_{PEO}, in adsorbed layers at the silica glass/water interface.

substrate (silica glass). "Silica glass" refers to a soda-lime slide containing an outer layer of silica, due to acid treatment, as described in detail previously.[15] This current work was motivated by previous reflectivity findings[15] for poly(ethylene oxide) (PEO) adsorption kinetics on silica glass.

Background on Reflectivity

The previous work[15] employed Brewster angle reflectivity of p-polarized laser light at a glass/water interface to measure adsorption kinetics under laminar shear conditions in a rectangular flow cell. Monodisperse PEO chains adsorbed onto a silica glass slide which comprised one wall of the flow cell. It was verified that for most wall shear rates and low bulk PEO concentrations, the adsorption was diffusion controlled up to nearly 100% of the equilibrium coverage. In cases such as this, when a pseudo-steady-state concentration gradient occurs near the interface, the adsorption rate, $d\Gamma/dt$, is proportional to a mass transfer coefficient, K_{tr}:

$$d\Gamma/dt = K_{tr}C_b \tag{1}$$

According to eq 1, the adsorbed amount, G, should increase linearly in time, t, with C_b, the bulk solution PEO concentration.

A number of calculations were previously presented for polymer adsorption at the glass/water interface,[15] with refractive indices of the glass and water, $n_g = 1.515$ and $n_s = 1.333$, respectively. It was shown that for an adsorbing PEO layer modeled by a step function of fixed concentration but thickness increasing with coverage, the square root of the reflectivity near the Brewster angle, $R_p^{1/2}$, was proportional to the mass coverage up to 8 mg/m^2:

$$\Gamma(t) = \frac{1}{S}[R_p^{1/2}(t) - R_p^{1/2}(0)]_{np \text{ constant}} \tag{2}$$

Here $R_p^{1/2}(0)$ is the square root of the baseline reflectivity from surface layers (oxides or chemical treatments) on the substrate prior to polymer adsorption, and S is a calibration constant, dependent only on the incident angle and the refractive indices at the interphase, n_g, n_s, and n_p, with the latter for the adsorbed step-function polymer layer.

In the previous work which focused on measurements of the adsorbed amount,[15] data were analyzed according to a step-function treatment of the layer, and the assumption that the average segment density or refractive

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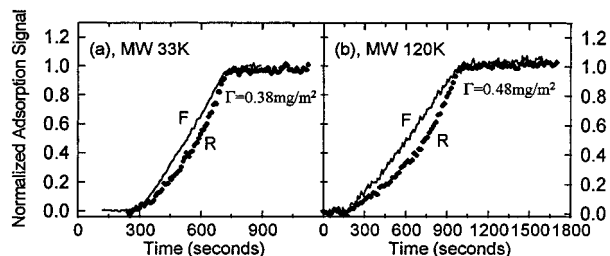(15) Fu, Z.; Santore, M. M. *Colloids Surf.,* in press.

Figure 2. Normalized adsorption signals from reflectivity (R-curves) and TIRF (F-curves) for coumarin dye-labeled PEO of molecular weights 33K (a) and 120K (b). The kinetics were conducted under shear flow at 7.2 s⁻¹ wall shear rate and with bulk PEO concentration of 2.5 ppm.

index of the layer did not evolve significantly during adsorption. Instead, the layer was presumed to grow thicker with increasing surface mass. It was shown that for a reasonable range of average local concentrations in the adsorbed layer close to full surface coverage, this assumption would lead to no more than 10% error in the determination of the adsorbed amount. The key to the argument is the weak dependence of the calibration constant, S, on the average local segment concentration ϕ_{PEO}, shown in Figure 1. In Figure 1, the dependence of S on n_p has been represented as a dependence on ϕ_{PEO}, using the relationship, $\phi_{PEO} = (n_p - n_s)/(dn/dc)$, with $dn/dc = 0.134$ (g^{-1} cm³) for PEO in water. The proportionality in Figure 1 was found to be linear over the parameter range of interest:

$$\frac{S(t) - S(\infty)}{\phi(t) - \phi(\infty)} = -1.833 \times 10^{-4} \quad (3)$$

where $S(\infty)$ and $\phi(\infty)$ correspond to the values at long times. The current work maintains a step function treatment of the adsorbed layer but relaxes the assumption of a fixed average layer density during the adsorption process. On the basis of a comparison of total internal reflectance fluorescence (TIRF) and reflectivity data, we report the evolution of the layer density for PEO on silica, modeled as a step function. Both the TIRF and reflectivity experiments have been described in detail elsewhere.[15-18] The former measures the evolving numbers of fluorescent tags near an interface, giving a signal for monodisperse fluorescently tagged polymer chains that is proportional to the adsorbed mass. The PEO chains were narrow molecular weight distribution standards, fluorescently labeled by coumarin dye covalently attached to one chain end. The silica surface was an acid-washed microscope slide, a substrate previously studied in detail.[15,18]

Results and Discussion

Figure 2 compares TIRF (F-curve) and reflectivity ($R_p^{1/2}$, R-curve) signals during PEO adsorption onto silica glass for two different molecular weights, 33 000 and 120 000. Pairs of TIRF and reflectivity data were normalized by

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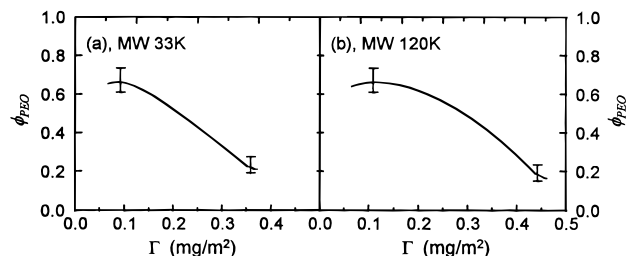(22) Killmann, E.; Maier, H.; Kaniut, P.; Ghtling, N. *Colloids Surf.* **1985**, *15*, 261.

Figure 3. PEO layer density, ϕ_{PEO}, as a function of the surface coverage during adsorption for (a) MW 33K and (b) MW 120K PEO as shown in Figure 2.

their respective long time levels, corresponding to surface saturation (plateau)

$$R(t) = \frac{R_p^{1/2}(t) - R_p^{1/2}(0)}{R_p^{1/2}(\infty) - R_p^{1/2}(0)} \quad (4)$$

$$F(t) = \frac{Fl(t) - Fl(\infty)}{Fl(0) - Fl(\infty)} \quad (5)$$

where Fl represents the measured TIRF fluorescence intensity.

In Figure 2, the F-curves increase linearly in time up to the final coverages, in accord with eq 1, and confirming the transport-limited behavior.[15,19] The R-curves, however, are slightly concave up. At long times after surface saturation, both the R-curve and F-curve in Figure 2 remained flat for several hours, indicating no detectable PEO layer relaxation during that period of time. We have measured the R-curves with both coumarin-tagged and untagged PEO, and they gave identical results, indicating that the effect of coumarin end-group was negligible.

The linearity of the fluorescence data and the upward curvature of the reflectivity traces were highly reproducible, with the details being somewhat dependent on molecular weight. The differences between these two experiments provide information on the evolving layer density, through variations in S with ϕ_{PEO} in Figure 1 and eq 3.

The linear rise of the F-curve in time indicates that fluorescence is more nearly proportional to the adsorbed amount than the evolving square root of the reflectivity. Therefore

$$F(t) = \Gamma(t)/\Gamma(\infty) \quad (6)$$

Combination of eqs 2, 3, 4, and 6 yields

$$\phi(t) = \phi(\infty) + \frac{S(\infty)}{1.833 \times 10^{-4}}\left(1 - \frac{R(t)}{F(t)}\right) \quad (7)$$

which provides the evolving average layer density, relative to that at long times. The evolving layer thickness, $d_p(t)$, follows from $d_p(t) = \Gamma(t)/\phi(t)$.

Figure 3 show the PEO layer density as a function of $\Gamma(t)$, which is also proportional to time. The average $\phi(\infty)$ values for the two PEO samples (33K and 120K) are unknown for the current experiment but have been estimated based on the volume fraction profile for PEO layers at the quartz/water interface, measured by neutron reflectivity.[4] The molecular weight effect on $\phi(\infty)$ was approximated based on the dependence of the root mean square (rms) layer thickness, d, on MW ($d \sim MW^{0.4}$),[20,21] and the $\Gamma(\infty)$ of the two different molecular weights. As a result, values of $\phi(\infty) = 0.20$ and 0.16 were employed for samples of MW 33K and 120K, respectively.
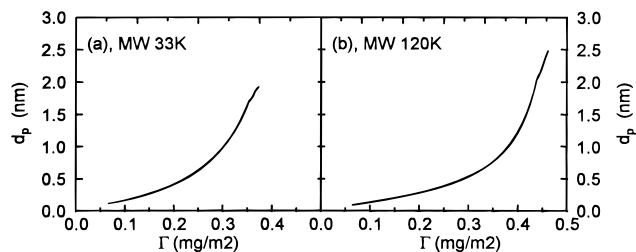
Figure 4. Evolution of step function layer thickness during PEO adsorption for (a) MW 33K and (b) MW 120K as shown in Figure 2.

Figure 4 illustrates, for the two molecular weights, the evolving layer thickness which increases from less than 1 nm to about 2 or 3 nm. The greatest change in thickness occurs as the surface saturates. The values of thickness are small and showed a weak molecular weight dependence, as expected, because these thicknesses represent a first moment mass distribution about the surface, rather than hydrodynamic thicknesses. (The latter, at full coverages, are on the order of 3 nm for MW 20K PEO and 8 nm for MW 100K PEO homopolymer adsorption on silica,[22] while the rms thicknesses of fully covered PEO layers on polystyrene determined by small angle neutron scattering (SANS) are in the order of 2 nm for MW 30K and 4 nm for MW 120K.[23]) At coverages below 0.2 mg/m², there may exist bare patches on the surface giving a very thin average thickness, while those regions containing polymers are mostly trains with a high (near 100%) effective local concentration.

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The results shown in Figures 3 and 4 agree with the studies of adsorbed PEO layers on silica by microcalorimetry,[9] IR,[7,22] and ESR[8] and the prediction by the Scheutjens−Fleer theory.[21] These studies found a high bound fraction at low surface coverages and a decrease of the bound fraction with increased adsorbed amount. Our results and those in the literature suggest a change of PEO chain conformation during the evolution of an adsorbed layer: from chains laying flat on the surface (with more trains) to a more fluffy layer (more loops and tails) at higher coverages. Figure 3 also demonstrates a slight difference of layer density evolution with molecular weight. For the higher MW (120K) PEO, the decrease in the layer density was initially slower than that of the low MW (33K) PEO, indicating that higher coverages must be achieved before tails and loops contribute to layers of high molecular weight.

Summary

This study demonstrates that near Brewster angle reflectivity can provide *in-situ* measurement of the evolving layer density during adsorption. Results confirm that as adsorption proceeds, the layer becomes less dense as loops and tails are formed. The change in layer density appears slightly sharper for higher molecular weight chains.

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