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Communications to the Editor

Direct Measurement of Molecular-Weight Driven Competition during Polymer Adsorption

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Competitive adsorption of polymers from solution onto solid surfaces is an important concern in colloidal stabilization, coatings formulation, and some chromatographic separations. While competitive adsorption typically suggests processes driven by chemical differences between two species, in practice homopolymers are polydisperse, raising the issue of molecular-weight driven competition between subpopulations within a single sample of polymer. For instance, based on changes in intrinsic viscosity of a bulk solution, Kolthoff and Gutmacher[1] reported replacement of low molecular weight rubber chains on carbon black by longer ones of the same backbone chemistry. It hasn't been until more recently that theory has quantitatively anticipated the influence of molecular weight on equilibrium surface coverage for single narrow molecular weight homopolymer samples[2−4] and the equilibrium surface composition for bimodal mixtures containing chemically similar chains of two distinct lengths.[5,6]

Confirming theoretically predicted competitive equilibrium behavior and measuring transient interfacial processes involving multiple species remain a challenge. Most classical methods used alone as single probes of adsorbed layers such as ellipsometry, dynamic light scattering, streaming potential measurements in capillary flow, and even FTIR-ATR do not readily allow one to discriminate between adsorbed interfacial populations. Recently Dijt and co-workers[5] employed optical reflectivity to deduce competitive kinetics for poly(ethylene oxide) [PEO] on silica including exchange processes driven by molecular weight differences between to PEO populations. Their study was confined to molecular weight differences sufficiently large such that the short and long chains, when adsorbing noncompetitively, give distinctly different levels of coverage. The approach cannot be applied in general, especially in cases where the competing molecular weight populations are more nearly similar.

We employ a dual approach of combined near-Brewster reflectivity and total internal reflectance fluorescence (TIRF) to separately track the evolution of the interfacial mass and a population of interest. The near-Brewster reflectivity experiment, described in detail elsewhere,[7] is like ellipsometry in its exploitation of refractive index differences to measure the surface excess.[8] Our reflectivity instrument operates in internal reflection and provides a measure of surface mass that is accurate to within 10% when the assumption of a constant layer density is made for the data analysis, but density variations occur in the experiment. The TIRF experiment sees only those adsorbed chains bearing fluorescent labels and operates by the generation of an evanescent wave of excitation light with a 80 nm decay length.[9−12] The TIRF data presented here employ extremely dilute bulk solutions such that free chains containing fluorophores excited by the evanescent wave do not contribute appreciably to the TIRF signal.

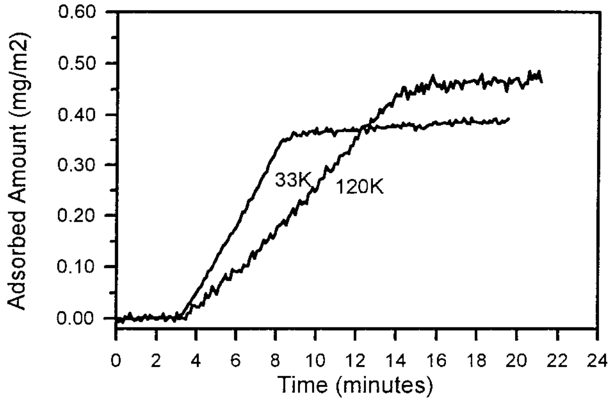

Figure 1. Reflectivity measurements of noncompetitive PEO adsorption kinetics for chains of 33K and 120K molecular weight.

In this communication, we examine the molecular weight driven competition for a bimodal mixture of polyethylene oxide of long (120 000, molecular weight) and short (33 000) chains. The samples were narrow molecular weight standards, used as is from Polymer Labs. To facilitate TIRF experiments, the PEO was also used in a form containing coumarin end tags.[13] Adsorption experiments from 1 mM phosphate buffered saline (0.2 mM KH_2PO_4, 0.8 mM Na_2HPO_4) were conducted from gentle shearing flow (a wall shear rate of 7.2 s^{-1}) onto the silica surface that results when microscope slides are treated with acid.[7,14] Notably, single-component noncompetitive adsorption of individual narrow molecular weight PEO standards onto silica from aqueous solution has been found to be transport-limited.[5,7]

Figure 1 illustrates the adsorption kinetics for the untagged 33K and 120K molecular weight PEO adsorbing noncompetitively in separate reflectivity experiments, each from a bulk solution concentration of 2.5 ppm. (At concentrations exceeding 0.1 ppm, the system is on the plateau of the adsorption isotherm, for either molecular weight.[7]) The adsorption rate of the 33K chains exceeds that of the 120K chains because the former has a more rapid diffusivity.[7,15] The long time coverage, is, however, greater for the long chains.

Figure 2 illustrates different facets of the competitive adsorption for a 50−50 wt % mixture of long and short chains with a total concentration of 5 ppm. Curve 1 illustrates the reflectivity results which have a stepwise appearance. The initial signal rise is observed to be the sum of the two signal rises in Figure 1, which suggests that at low coverages, both species adsorb independently at their mass transport limited rates. This persists until the total coverage reaches a level corresponding to the equilibrium coverage of the short chains in Figure

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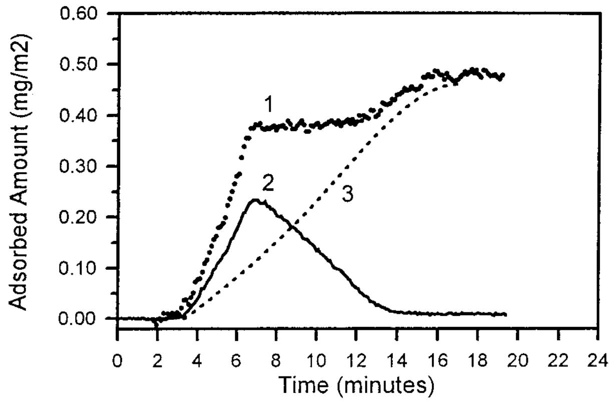

Figure 2. Combined reflectivity measurements of competive PEO adsorption kinetics for a 50−50 wt % mixture of 33K and 120K molecular weight chains.

1: The surface appears full to the short chains. Next, a period of nearly constant interfacial mass ensues, followed by a second rise to an ultimate coverage equal to the adsorbed amount of the long chains in Figure 1.

Figure 2 also shows the TIRF signal for coumarin-tagged short chains (curve 2) adsorbing from the mixture. Initially, the short chains from the mixture are uninfluenced by the long chains, apparent through a comparison of curve 2 in Figure 2 to Figure 1. This persists up to the time when the surface appears saturated to the short chains, ie when the total coverage for the mixture is equal to the equilibrium coverage for the 33K chains in Figure 1. After this point, the short chains are displaced from the surface by incoming long chains, a process which continues at nearly constant interfacial mass until nearly all the short chains are desorbed. The ultimate complete desorption of short chains is consistent with theory.

Figure 2 also shows, in curve 3, the competitive adsorption of the long chains, determined by subtracting curve 2 from curve 1. A comparison of curve 3 with that in Figure 1 shows that the long chain adsorption during competition is not influenced by the adsorbed short chains. The rate-limiting step of the exchange process between long and short chains is the arrival of long chains from solution, not the release of short chains from the surface. We therefore conclude that the competitive adsorption of PEO driven by molecular weight differences (in this range of chain lengths) is a transport-limited process. Our results for the displacement of 33 000 molecular weight PEO agree with Dijt's conclusion for transport-controlled displacement of PEO's of lower molecular weights. The significance of our work is that the range of molecular weight amenable to quantitative analysis has been greatly extended.

In an upcoming article we will show that the fluorescent tag is noninvasive for measuring molecular weight-driven exchange, examine the molecular weight dependence of the equilibrium competitive adsorption process, and discuss the results in the context of competitive equilibrium. The upcoming publication will also address the influence of molecular weight on the extent to which local equilibrium can be maintained.

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