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Similar Hydrodynamic Transitions in Adsorbed Layers of Backbone-Adsorbing and End-Adsorbing Polymers

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ABSTRACT: Results concerning the hydrodynamic thickness of adsorbed polymer layers were reanalyzed to reveal a near-universal dependence on surface loading at low and intermediate concentrations. This was found for three poly(ethylene oxide) samples with varying end group−surface attractions (hydrophobicity). The finding detracts from the previous interpretation of a pancake-to-brush transition for polymers containing end groups with strong surface affinity, because the control samples without hydrophobic end groups experienced an equally sharp transition in hydrodynamic thickness as a function of surface coverage.

Introduction

The outer region of a polymer layer adsorbed from solution onto a solid substrate strongly influences its hydrodynamic properties, its capacity for lubrication, and, for dispersed substrates, its colloidal stability. The hydrodynamic thickness of a homopolymer layer (all segments have equal adsorption energy) is predicted and observed[1] to increase sharply with surface coverage as crowding forces the chain ends (“tails”) into solution. Very few tails are necessary for a large hydrodynamic layer thickness.

Homopolymer layers[1] and end-adsorbed polymer brushes[2−4] constitute two morphological extremes for adsorbed polymers. Associative polymers (APs)[5,6] fall between these extremes: the chain ends and main backbone compete for the surface. APs consist of water-soluble poly(ethylene oxide) (PEO) segments, of ∼8000 molecular weight, linked together with isophorone diisocyanate (IPDI) to build chains with an overall molecular weight, in this case, near 100 000, and end-capped with hydrophobic groups. Figure 1 illustrates an abstract version of the chemistry. The PEO−IPDI backbone and the hydrophobic end groups are known to adsorb on polystyrene (PS).[7−10]

Ou-Yang and Gao[11] presented an adsorption study of APs on PS latex, focusing on the impact of molecular architecture and the hydrodynamic properties of the layer. Three APs of nominal molecular weight 100 000 contained different end group hydrophobes (by which each sample is named): hexadecane, attached to the chain ends with IPDI (C16); dodecane, attached to chain ends with IPDI (C12); and chain ends containing no hydrophobic groups (C0), which served as a control adsorbate. The polymers were adsorbed onto a dilute 91 nm diameter PS latex, and after appropriate equilibration, the hydrodynamic layer thicknesses were determined by dynamic light scattering.[11]

Figure 2, a plot of the hydrodynamic layer thickness as a function of the total AP in the dispersion,[11] suggests a striking influence of molecular architecture. The hydrophobe-containing C12 and C16 samples experience a sharp transition in the hydrodynamic thickness near 300 chains/particle. In contrast, for the polymer without hydrophobic end groups, the layer thickness increases gradually. Ou-Yang and Gao interpreted this behavior semiquantitatively according to the predictions of Alexander[4] for a pancake-to-brush transition. For the chains with hydrophobic end groups at low coverages, both the main backbone (in this case the PEO and IPDI linkages) and the hydrophobic end groups adsorb to the surface. As the coverage increases, however, crowding forces the main backbones off the surface such that only the ends remain adsorbed. A brush of loops (both ends adsorbed) and tails (one end of each chain adsorbed) results. Alexander predicted that such a transition should be a first-order phenomenon. The result in Figure 2 is, therefore, significant: If it truly reflects a pancake-to-brush transition, it is the first experimentally observed transition of this type.

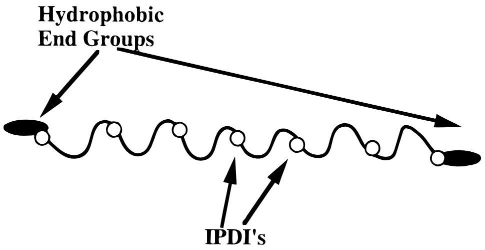

Figure 1. Structure of associative polymers.

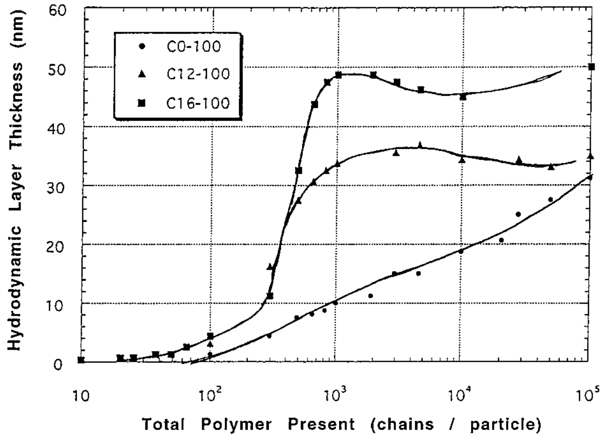

Figure 2. Hydrodynamic layer thickness as a function of total polymer in each dispersion for (■) C16 associative polymer, (▲) C12 associative polymer, and (●) C0 control polymer. Adapted from ref 11.

At the time of this work, only hydrodynamic evidence favors a pancake-to-brush transition; however, sharp hydrodynamic transitions have been predicted and observed for homopolymer layers.[1] One may, therefore, ask (1) how does molecular architecture affect the

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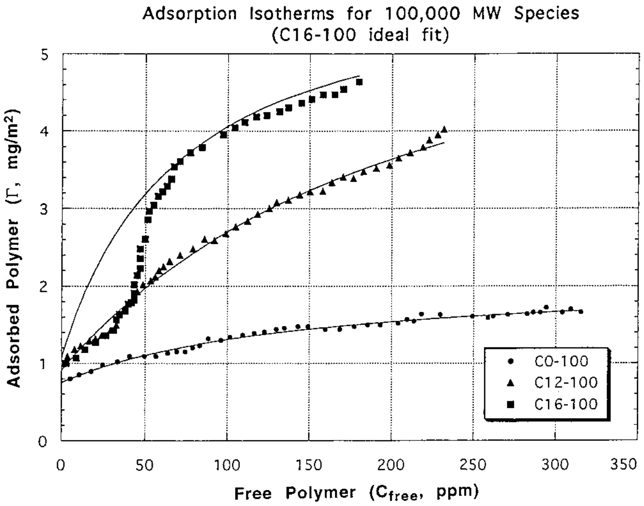

Figure 3. Adsorption isotherms for associative polymers: (■) C16 associative polymer, (▲) C12 associative polymer, and (●) C0 control polymer. Adapted from ref 13, thesis Figure 5.10, with axes rescaled for this publication. Lines indicate parametrization done for this publication.

hydrodynamic properties of an adsorbed polymer layer and (2) do Ou-Yang and Gao's results truly demonstrate unusual behavior for samples with hydrophobic end groups?

Notably, the *x*-axis in Figure 2 represents the total polymer in each dispersion, on a per-particle basis. To arrive at the conclusion that *only* the C12 and C16 APs underwent a transition, it was assumed that all the polymer in each test dispersion was adsorbed to the particles. A complete analysis, however, requires a quantitative determination of the polymer's partitioning between the solution and the latex surface, shown by Jenkins[12] and later by us[9] to be highly sensitive to the polymer's end groups. In this work, we determine, for each datum in Figure 2, how much polymer was actually adsorbed and reconsider the hydrodynamic thickness's dependence on the adsorbed amount, as opposed to the total polymer.

Results

Our reanalysis of the data in Figure 2 employs the adsorption isotherms in Figure 3, taken from Jenkin's work with the same APs.[12,13] In our representation of these isotherms, the axes have been converted from the dimensionless form presented by Jenkins to units of mg/m^2 for the adsorbed amount, Γ, and ppm for the free polymer, C_{free}. Three sets of data, for the C16, C12, and C0 polymers, are shown, with the highest coverages obtained for the most hydrophobic polymers. All three isotherms exhibit a very steep, almost vertical initial rise up to a coverage near 1 mg/m^2 and then rise more gradually with increasing free polymer concentration. Because the C16 isotherm contains an unusual kink which *may* (in our view) be an artifact of intermolecular associations confounding the membrane separation employed by Jenkins, also included in Figure 3 are our parametrized versions (the lines) of Jenkins's experimental data which preserve the essential features of the isotherm. The very steep initial slope is approximated mathematically by a positive *y*-intercept according to

$$\Gamma = \frac{RC_{\text{free}} + S}{1 + TC_{\text{free}}} \qquad (1)$$

where C_{free} is the free polymer concentration at equilibrium, and the values of the fitting parameters *R*, *S*, and *T* are summarized in Table 1 for the three adsorbate samples.

Table 1. Fitting Parameters Applied to Jenkins's Isotherm Data

polymer sample	*R*	*S*	*T*
C0-AP100	0.0149	0.7484	0.0071
C12-AP100	0.0304	0.9058	0.0046
C16-AP100	0.0892	1.063	0.0146

The isotherms in Figure 3 employ a 190 nm PS latex, as opposed to the 91 nm particles in Ou-Yang and Gao's study. While Jenkins[12,13] argued that particle size affects coverage, the difference between 91 and 190 nm particles should not be significant. The free polymer coil and-to-end distance (for PEO of 100 000 molecular weight, segment number $N = 1140$, and segment length $a = 0.4$ nm) is approximately $N^{0.5}a = 13.5$ nm, several times smaller than the 91 nm particles. Therefore, the curvature effects on coverage should be secondary as the particle size is changed from 91 to 190 nm. To the extent that both latex samples are of similar chemistry,[14] as we expect, the data in Figure 3 on 190 nm latex adequately approximate the coverages expected for the 91 nm PS latex in Figure 2.

In our reanalysis of OuYang and Gao's data, a mass balance was employed for each datum to determine the adsorbed amount, Γ, in mg/m^2 as a function of the total polymer added to the dispersion (the *x*-axis in Figure 2) and the total available area in the sample, *A*, which can be calculated directly from the volume fraction of PS spheres (2×10^{-5}).[11] The mass balance contains two unknowns, the free polymer concentration, C_{free}, and the adsorbed amount, Γ, both at equilibrium. Hence, a second relationship, provided by the isotherm data in Figure 3 or the parametrization in eq 1, was employed in the determination of the adsorbed amount for each datum in Figure 2. The layer thickness was then replotted as a function of the adsorbed amount, Γ, in Figure 4. In Figure 4A, the actual isotherm data from Jenkins's work were employed, while in Figure 4B, the parametrized versions of the isotherms summarized in Table 1 were employed.

In Figure 4, for *all three samples* there appears a sharp change in the hydrodynamic layer thickness as a function of the *adsorbed polymer*. While a sharp transition was evident in Figure 2 only for the C12 and C16 polymers, one is now evident in Figure 4 for the C0 sample as well. Further, the transitions occur near the coverages at which the isotherms bend away from the ordinate (~1 mg/m^2). The main rise of the transition (about 5−15 nm for the C0 polymer, 10−30 nm for the C12 polymer, and 10−45 nm for the C16) polymer is equally sharp for all three sample; however, it is unclear whether the three transitions occur at the same coverage within experimental error.

Discussion

Of primary importance is the observation that, when the hydrodynamic measurements are represented as a function of the adsorbed as opposed to the total polymer, a sharp hydrodynamic change occurs for all three samples. In the previous interpretation,[11] the transition was seen only for the hydrophobically modified samples, with the interpretation being that molecular architectures with surface-attractive end groups were responsible for a pancake-to-brush first-order phase transition. Now that an equally sharp transition is apparent for a

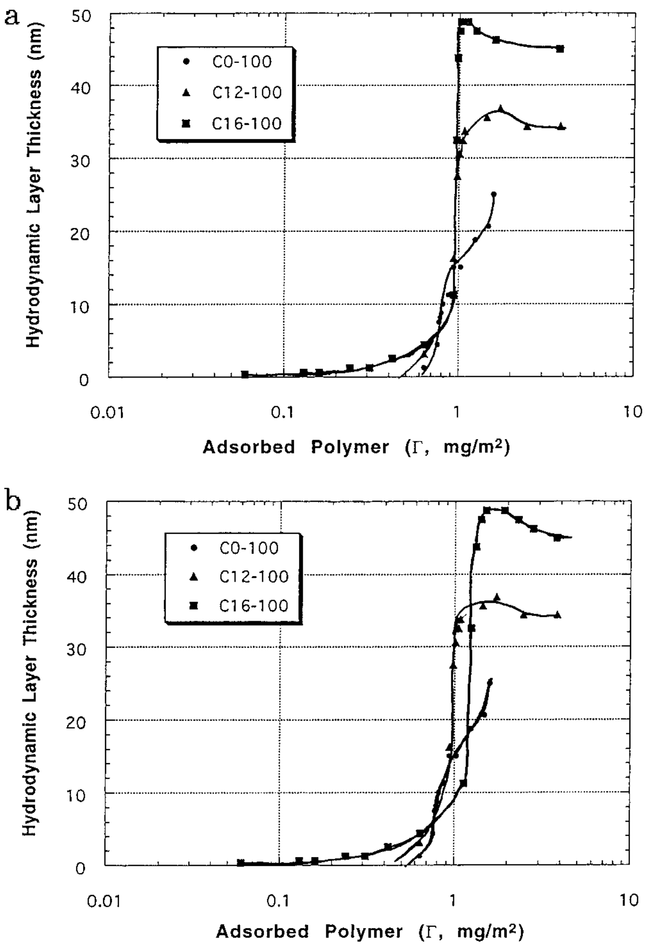

Figure 4. Hydrodynamic layer thickness as a function of *adsorbed* polymer (A) based on actual isotherm data and (B) based on parametrized isotherm data. Symbols as in Figure 2.

control sample without hydrophobic end groups, the transition can no longer be attributed to specific end group—surface interactions, and its origin must be reconsidered. It appears, based on the isotherms in Figure 3, that a hydrodynamic transition occurs regardless of the end group—surface interaction at the point where the surface approaches saturation. Since the driving force is surface saturation, the transition might loosely be considered universal. Further, the predictions of Alexander's pancake-to-brush transition theory[4] are experimentally indistinguishable (hydrodynamically) from Cohen-Stuart's predictions for homopolymers.[1] In both cases, at low coverages chains lie flat against the surface (pancakes), but when the surface becomes crowded in homopolymer layers, the chain ends reach toward the solvent. For chains with end group—surface attractions, brushes are anticipated at high coverages. We expect classical homopolymer structures to persist in saturated layers of the CO polymer, but due to the morphology of the C12 and C16 samples, an interesting question remains: Do the chain ends desorb or does the main backbone desorb once the surface fills?

If one attributes significance to the different coverages at which the transitions are observed, then the trend is that the transition occurs at lower coverages for the control C0 sample and at higher coverages as the end group hydrophobicity is increased. This may suggest that it is more entropically favorable for the chain ends of a homopolymer to desorb as opposed to the backbone of a chain with surface-attractive ends.

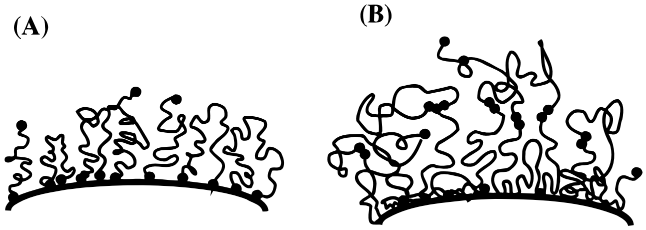

Figure 5. Potential interfacial morphologies at high surface loadings for (A) the polymer brush and (B) the complex associated structure. In B, no sequential multilayering is implied.

The results in Figure 4, that the hydrodynamic thickness increases sharply at nearly the same surface coverage for all three molecular architectures, suggests that the mechanism for the transition is similar for all three adsorbates. Hence, the existence of a transition, without other experimental evidence, does not provide convincing evidence for a pancake-to-brush morphological transition exclusive to samples with hydrophobic end groups. The observation of a more extensive transition for the more hydrophobic samples is, however, an interesting point. Brushes may, indeed, persist at high coverages, as in Figure 5A, for the hydrophobe-containing polymers, since the ultimate thickness of 50 nm is several times the unperturbed R_g, in accord with brush theory.[3] Alternatively, the larger ultimate layer thicknesses for the C12 and C16 samples may be explained by intermolecular associations, as represented in Figure 5B, which are known to persist down to very low concentrations.[15]

The shapes of the data in Figure 4 above coverages of 1 mg/m^2 also hold information. For the C12 and C16 samples, the adsorbed amount increases significantly without further increases in thickness (indeed, the thickness decreases slightly), indicating layer densification by factors of 3 and 5, respectively. The brush model, however, predicts that layer thickness should follow coverage to the 1/3 power. The slight decrease is best explained by sample polydsipersity.[16] Lower molecular weight populations are more hydrophobic and preferred on the surface,[10] giving thinner layers when sufficient low molecular weight material forces the high molecular weight populations from the surface.

The opposite molecular weight selectivity for the C0 sample[1,10] explains why, after about 1 mg/m^2 of coverage, the C0 curve in Figure 4 continues upward. Here high molecular weight populations are preferred on the surface and dominate the hydrodynamics when a sufficient number of them are present in the sample. Again, the results do not argue for a particular interfacial morphology; however, the impact of molecular weight selectivity and the hydrophobe—hydrophil content of individual chains is apparent.

Conclusions

We demonstrate that a sharp change in hydrodynamic layer thickness as a function of surface loading is not dependent on a particular molecular architecture and is not necessitated by end group—surface attractions. The observation of the hydrodynamic layer development at nearly the same surface coverage for polymers with and without hydrophobic end groups suggests that the hydrodynamic growth of the layer occurs universally when the surface becomes saturated. The primary impact of molecular architecture is through its affect on the partitioning of the polymer between free solution and the surface and the ultimate layer thickness.

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