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A pancake-to-brush transition in polymer adsorption

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Abstract. — We provide the first experimental evidence for a transition from a « pancake » to a « brush » configuration for end-adsorbing polymers at the solution-solid interface. This transition, predicted earlier by Alexander, is a consequence of the competition between adsorptions by the backbone and the end-groups. It occurs when polymer pancakes start to overlap each other. The competition then drives some backbones into solution to form brushes. The transition region varies with molecular weight but does not vary with the end-group's adsorption strength. The thickness of the polymer layer, however, increases with the increasing end-group's adsorption strength.

1. Introduction.

Polymer adsorption at interfaces is a subject of great technological importance [1, 2]. Conventional homopolymers form uniform layers on the surface and therefore have limited applications [2]. The newly developed functional polymers, such as the associative polymers [3-5] and block copolymers [2, 6-9], are more versatile because different parts of the chain can interact differently with the substrate. So far, most of the adsorption studies have been focused on the diblock copolymers [6-9] partly because these polymers are very effective for steric colloid stabilization [2]. In these applications the insoluble blocks, which are the « anchors », adsorb strongly to the surface whereas the soluble blocks, which are the « buoys », are forced to stretch into solution to form brushes [6-8]. The brushes repel each other when the two surfaces approach ; this renders the colloids stable. In most studies the buoys are treated as being repelled by the surface because this is more favorable in most applications and it is also easier to deal with theoretically.

So far, relatively less attention has been paid to the situation in which both backbones and anchors can adsorb but with different strengths. Alexander, in a theoretical paper of 1977, showed that a very interesting phase transition can occur when buoys, although still soluble, have a finite affinity for the surface [10]. In this paper he showed that at a critical surface concentration the polymers transform from a uniform adsorption to a polar head configuration. This transition is first order and is due to competition for surface adsorption between the anchors and the buoys. In more commonly used terms this transition can be described as a « pancake-to-brush » transition [11] and can be visualized as follows.

PANCAKE TO BRUSH TRANSITION: THE SCENARIO. — At low polymer concentrations, when the individual adsorbed polymers are far apart on the surface, the whole chain can adsorb on the surface and assume a low profile. These low profile polymers have been referred to as « pancakes » in different references [1, 6]. When polymers concentrations in solution are increased, the number density of polymers at the surface will also increase. At this point, the pancakes start to touch each other. Since these polymers are in a good solvent, backbones repel each other, and they cannot overlap very much. For homopolymers beyond this overlapping concentration, adsorption will slow down and stop. On the other hand, the polymers with a strong adsorbing end-group (or end-groups) can continue to adsorb because the strongly adsorbing group can displace the weakly adsorbed backbones already on the surface. This competition between the end-groups and the backbones will continue to drive, or « pop », the polymer backbones into solution by anchoring more chains onto the surface until the energy gained by adsorbing another chain is balanced by the pressure in the polymer layer. When this process is ended, the backbones have a relatively stretched configuration, which are usually referred as « brushes » for diblock copolymers near saturated adsorption [1, 9]. The important consequence of the competition described here is a transition from « pancakes » to « brushes », as illustrated in figure 1. Since backbone affinity for the surface is common, as evidenced by the existence of pancakes, this cross-over transition appears to be common for most polymer adsorption processes.

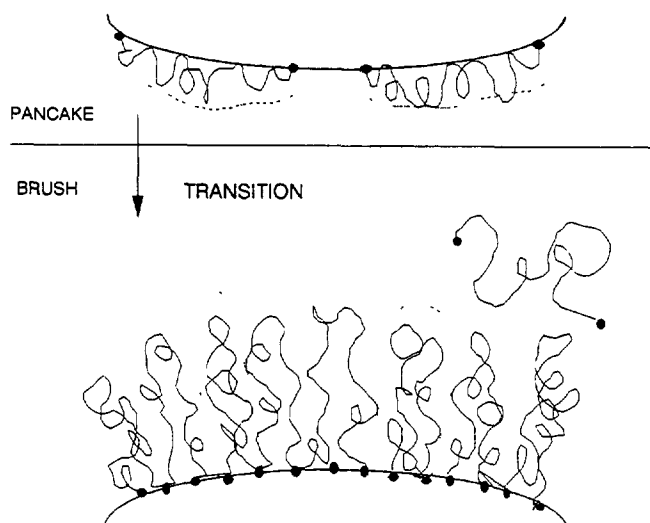


Fig. 1. — Pancake-to-brush transition.

Although the competitions between anchors and backbones were known to be common in practice [1], there had been no systematic experimental studies of their effects. In fact, for a system composed of three components (polymer/solvent/substrate), the interactions between these components can be varied by changes in temperature, pressure, surface charge, etc. The competition can have important consequences because the morphology of the polymer on the surface can be quite different from simple predictions [6-9, 12]. Due to this competition colloidal stability can be affected, because the brush will not be very stable. Moreover, dynamics due to the competition can cause a transition from tightly adsorbed pancakes to

brushes. In this paper we show, for the first time, experimental evidences of the predicted phase transition.

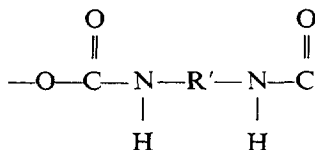
We used the Dynamic Light Scattering (DLS) technique to study polymer adsorption on colloidal latex spheres. In dilute solutions, DLS measures the hydrodynamic radii of spheres, which can increase due to the adsorbed polymer layer on the surface [13, 14]. Systematic measurements were made by varying the strength of the anchor adsorption relative to the backbones. We used R-B-R triblock copolymers instead of a diblock copolymer for this study; in this case R ends can serve as anchors. The backbone, B, is poly-ethylene-oxide (PEO). The end-group, R, is a short hydrophobic hydrocarbon segment. Since the end-group R is not soluble in aqueous solutions, it adsorbs strongly on the hydrophobic polystyrene latex surfaces used in this study. The backbone B dissolves in water, but it can also weakly adsorb on the colloidal surface. Eighteen different polymers composed of six different backbone lengths, each with three different end-groups, were used in this study.

We are interested in both the equilibrium configuration and the kinetics of the polymer adsorption. Equilibrium measurements for associative polymers showed that, when the polymer concentration is increased, the adsorbed layer thickness increases sharply over a very narrow range of concentration, then saturates to a plateau value. We did not see the same transition for homopolymers. This adsorption curve is also very different from what is expected for diblock copolymers with surface-repelling-backbones [9]. The effects of molecular weights and hydrophobic strength upon the transition point were investigated. The dependence of the height of the plateau and of the transition region on the molecular weight and the anchoring strength of the terminal groups were also studied. All of these studies support qualitatively the existence of the suggested transition; however, we are unable to confirm that the transition is first order.

We will also discuss some preliminary results on the kinetics of the adsorption and desorption. The hydrodynamic layer appeared to have been established very quickly after polymers were mixed with the colloidal particles. This unusually fast adsorption kinetics disagrees with a recent theoretical calculation [9]. Possible reasons of this disagreement are discussed. We found, however, that fully developed adsorption layers were indeed unwashable by dilution with pure solvent.

2. Experimental.

2.1 POLYMERS. — The associative polymers used in this study were R-B-R triblock copolymers in aqueous solutions. The molecular structure of R-B-R triblock copolymers is $\text{R-O-(DI-(OCH}_2\text{-CH}_2)_q)_p\text{-DI-O-R}$ as obtained from Union Carbide. The number q is a large fixed number (~ 380) and p is an integer between 2 and 12 with increments of 2; pq is the degree of polymerization. We studied polymers with three different end-groups, each with six different molecular weights. The backbones B are primarily water soluble polyethylene oxide whereas the end-groups R can be either hydrophobic hydrocarbon chains, $\text{C}_{16}\text{H}_{33}$, $\text{C}_{12}\text{H}_{25}$, or simply terminating hydrogens. The DI (diisocyanate) is present for synthetic purposes only; it has the structure:



The R' is composed of hydrocarbons with a ring structure. Both DI groups and the $\text{—CH}_2\text{—CH}_2$ elements along the backbone contribute to the weak backbone adsorption. In the

aqueous solution, we expect the end-groups $C_{16}H_{33}$ and $C_{12}H_{25}$ to adsorb strongly on the hydrophobic surface of polystyrene spheres. For simplicity we label our samples in three groups, C16, C12 and H, which correspond, respectively, to $C_{16}H_{33}$, $C_{12}H_{25}$, and H terminated polymer chains. Each group has six different molecular weights from 17,000 to 100,000 g/mole with increments of approximately 17,000 g/mole, determined from stoichiometry [15]. Thus, C12-51 represents polymers terminated by $C_{12}H_{25}$ with $M = 51,000$ g/mole, and H-100 represents polymers terminated by H with $M = 100,000$ g/mole, etc.

Polydispersity. — As determined by chromatography [16], the distribution of molecular weights for the polymer groups is not very narrow ($M_w/M_n \sim 2$). Normally, polydispersity of this degree can cause great complications in adsorption studies for homopolymers as well as for surfactant polymers; for the former the longer chains in the distribution always win, for the latter the shorter chains win. For polymers discussed here, competitions between anchor and backbone make the situation less simple, and the effects due to polydispersity become a very interesting issue. What we have found is that when two groups of very different molecular weight R-B-R polymers are present in solution both groups adsorb. Studies of the effects due to polydispersity on equilibrium distribution and kinetics are in progress. As of the demonstration of the phase transition the polydispersity did not pose serious problems, different molecular weight groups are well distinguished as shown in figure 3.

2.2 POLYSTYRENE LATEX SPHERES. — We used 91 nm diameter polystyrene spheres (PS) in aqueous suspension from DOW Chemical as adsorption substrates. In order to determine accurately the thickness of the adsorbed layer, we first carried out a size determination of bare spheres by DLS. We found that the diameter for the spheres determined by DLS is about 1 ~ 5 % higher than the labeled value depending on the concentration. Adding KOH up to 1 mM does not significantly improve the discrepancy. We used the values from DLS without adding salt for the calculation of polymer layer thickness.

2.3 SAMPLE PREPARATION. — We used double distilled and deionized water. Water was successively filtered through 0.8 μm and 0.22 μm Millipore filters and then centrifuged at 1 000 G for 100 min to eliminate remaining dust particles.

In order to keep the viscosity of the solution equal to that of the solvent, in all of our measurements, we kept the absolute polymer concentrations in solution as low as possible by adjusting the PS particle concentration. In lowering the polymer concentration we had to lower the particle concentration which also lowered the scattering signal. The best compromise between low viscosity and high scattering intensity was for particle volume fractions to be around 2×10^{-5} with polymer concentrations lower than 0.1 % in weight. When the polymer concentration is increased, the viscosity of the solution also increases, which makes the determination of the particle radius difficult. In the high polymer concentration regime, interesting phenomena, such as the development of multiple layers or bridging between particles, can occur. However, in that case, the interpretation of the data from DLS can be ambiguous. In this study we avoided the multiple layering or bridging and focused only on the very dilute cases.

A particular value of polymer/latex-sphere/water composition can be achieved by starting with a fixed volume fraction of latex spheres and then adding the desirable amount of polymers. Alternatively, we could start with a higher volume fraction of latex spheres, add the appropriate amount of polymers, and then dilute the mixture with pure water to obtain the desired final composition. The two procedures would give the same adsorption results only if the established adsorbed layer could be washed off by the added water. We shall discuss the results of these different procedures in section 3.3.

2.4 DYNAMIC LIGHT SCATTERING MEASUREMENTS. — We determined the diffusion coefficients of latex particles with adsorbed polymers by the dynamic light scattering (DLS) technique. In DLS the autocorrelation function of the scattered light intensity is measured as a function of delay time τ . Since we were dealing with very dilute suspensions of particles, the measured scattering intensity autocorrelation function $G(\mathbf{q}, \tau)$ is directly related to the diffusion coefficient D_0 by [14]

$$G(\mathbf{q}, \tau) = 1 + f \cdot [\exp(-2 q^2 D_0 \tau)] . \quad (1)$$

Here f is a constant (of order 1) that depends on the optical arrangement, q is the magnitude of the scattering wave vector,

$$q = \frac{4 \pi n}{\lambda_0} \sin \left(\frac{\theta}{2} \right) , \quad (2)$$

where n is the index of refraction of the solution, λ_0 is the wavelength of laser light *in vacuo*, and θ is the scattering angle.

According to the Stokes-Einstein relation, in the dilute limit, we could write D_0 for a spherical particle in terms of the hydrodynamic radius R_h as

$$D_0 = \frac{k_B T}{6 \pi \eta R_h} , \quad (3)$$

where k_B is the Boltzmann constant, T is the Kelvin temperature, and η is the solvent viscosity. From the viscosity and the temperature, we could determine R_h of particles for various conditions. The adsorbed layer thickness h was determined by $h = R_h - R_0$, where R_0 is the bare particle radius.

3. Results and discussions.

3.1 HOMOPOLYMERS. — To determine the backbone adsorption properties of the associative polymers, we first measured the hydrodynamic layer thickness of PEO homopolymers (H-17, H-51 and H-100) adsorbed on PS latex spheres. The DLS measurements were made for these

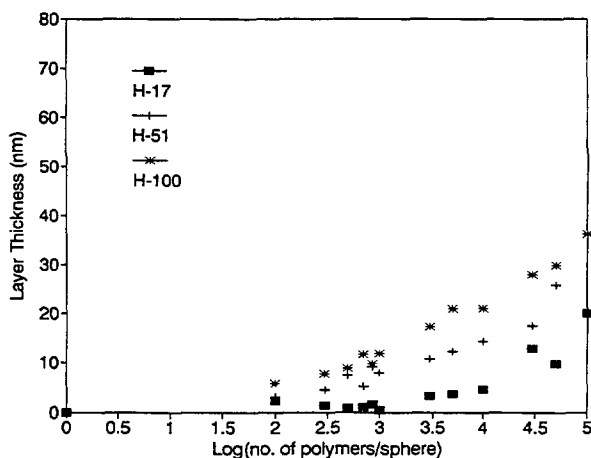


Fig. 2. — Normal-log₁₀ plot of hydrodynamic layer thickness vs. number of chains per sphere for homopolymers H-17, H-51 and H-100.

polymers adsorbed on 91 nm PS spheres in aqueous suspensions with a volume fraction of 2×10^{-5} . The results in figure 2 indicate that the layer thickness of the adsorbed homopolymers increases gradually with the increased polymer concentration. The layer thickness also increases with molecular weight. The adsorption of the polymers is attributed to of the ethylene groups and the diisocyanate groups [17]. Since PEO dissolves in water very well, the adsorption of homopolymers onto the polystyrene surfaces should not be very strong.

It is important to note that, in figure 2, the number of polymers per sphere was obtained by dividing the total number of polymers by the number of PS particles in solution. This is also the case for figures 3 and 4. We could not determine directly how many polymer chains were actually on the sphere.

3.2 ASSOCIATIVE POLYMERS. — Figure 3 shows the measured hydrodynamic layer thickness for six associative polymers, C12-17 to C12-100, as a function of number of polymers per latex sphere (total numbers of polymer chains added divided by particles in solution). The latex spheres have a volume fraction of 5×10^{-5} . The layer thickness builds up gradually at low concentrations, but over a narrow concentration range it increases sharply and then reaches a plateau. These adsorption curves are very different from those of both the homopolymers and the diblock copolymers with surface repelling backbones. Qualitatively, we assume all the polymers are adsorbed on the surface up to the transition region. After the transition the polymer layers are saturated; adding more polymers in solvent will not increase polymers on the surface. From the results of Jenkins *et al.* [17], we can estimate that, at saturation, there are approximately 300 ~ 1 000 chains per sphere depending on the molecular weights and end-groups.

We found, except at low concentrations, that the shape of the adsorption curve in figure 3 was very different from that of the homopolymers shown in figure 2. Except for the plateau area, we found that the curves were also very different from what was expected from diblock copolymers with attractive end-group and surface repelling backbones [9].

The transition. — The sharp transition shown in figure 3 supports the scenario suggested in the introduction, i.e., the pancake to brush transition. At low polymer concentration, because backbones can adsorb, polymers assume low profiles or «pancakes». When polymer concentration is increased, the pancakes start to overlap. In a good solvent, because

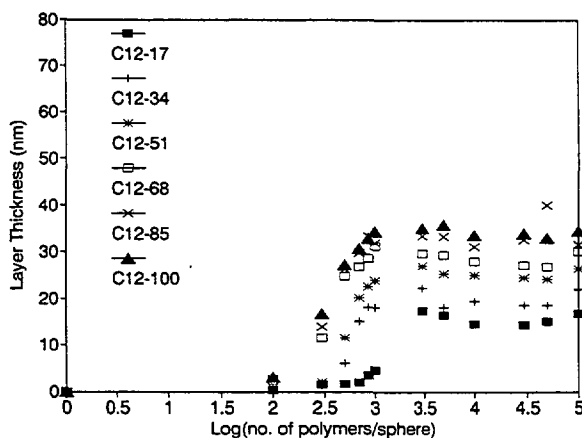


Fig. 3. — Normal- \log_{10} plot of layer thickness vs. number of polymer chains per sphere for associative polymers C12-17, C12-34, C12-51, C12-68, C12-84 and C12-100.

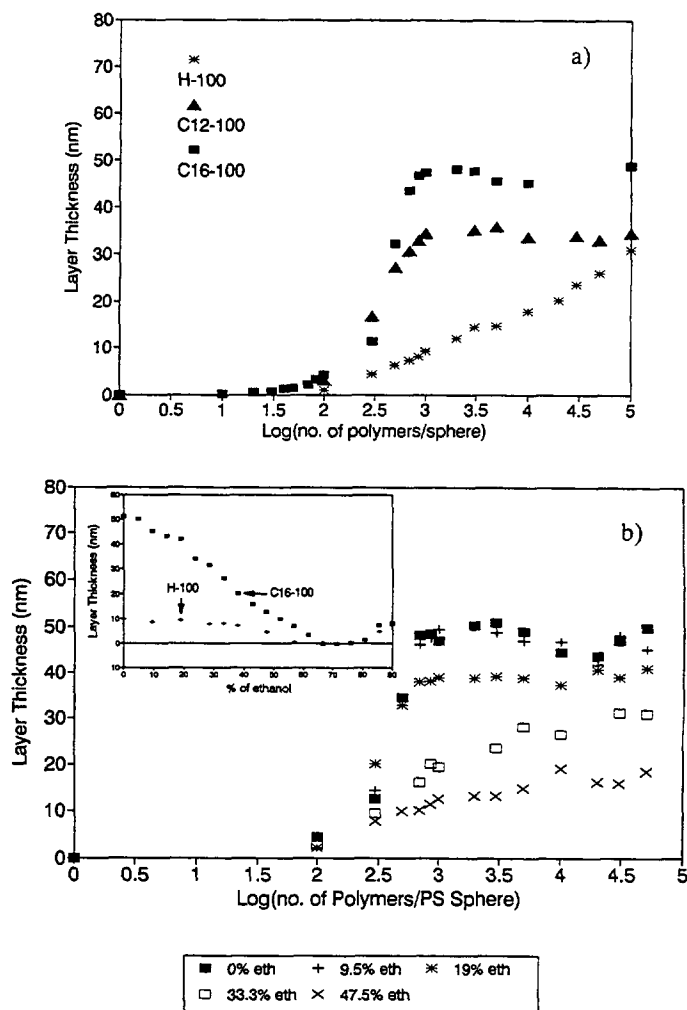


Fig. 4. — a) Hydrophobic strength dependence. Normal- \log_{10} plot of layer thickness vs. number of chains per sphere for C16-100, C12-100 and H-100 polymers. b) Effect due to added ethanol. Inset, layer thickness varies with added ethanol for C16-100 and H-100 with 1 000 chains/sphere.

backbones cannot overlap very much, the stronger adsorbing end-groups will start to displace the weakly adsorbed backbones from the surface. Most of the displacement of backbone by the anchoring ends occurs at the transition. This competition between the end-groups and the backbones will continue to « pop » the polymer backbones into solution by anchoring more chains onto the surface until the energy gained by adsorbing another chain is balanced by the osmotic pressure build-up in the polymer layer. When this transition process is ended, the polymer layer reaches a plateau. In the plateau region the backbones have the « brush » configuration. The polymers in the brush are stretched to about four to five times of R_g in solution, depending upon the hydrophobic strength of the end-groups. We note here that although the polydispersity is significant (comparable to the molecular weight increment within the group), the distinction among the plateau values is clear.

To support this view, we illustrate more details of the transition in terms of molecular weight and hydrophobic strength dependence.

(a) *Competition between anchors and backbones.*

Hydrophobe dependence. — In figure 4a, we show adsorption results for the same molecular weight polymers with different end-groups. Sharp transitions occur for both C12 and C16 groups but not for the H group. We found that the transition regions are almost overlapping for C12 and C16 polymers. This has to be the case in terms of the pancake-to-brush transition picture, because the pancake size depends only on the molecular weight but not on the hydrophobic strength of end-groups. However the plateau height does increase with hydrophobic strength because the brush is stretched by the anchoring force of the hydrophobic groups on the surface.

Solvent effect. — The relative adsorption strength of the anchors (alkyl groups) and the backbones can also be varied by changing solvents ; in this case, we use solvents composed of mixtures of ethanol in water. We found that adding ethanol in the suspension does not affect the homopolymer(H-100) adsorption for up to 47.5 % of ethanol in water ; whereas, the same amount of added ethanol decreases the adsorption of C16-100 dramatically (see inset of Fig. 4b). Comparing these results, we can conclude that the added ethanol reduces the adsorption strength of the anchoring hydrophobic groups but not of the backbones. Based on the assumption that the transition is due to competitions between the anchor and the backbones, we expect to see the transition diminish as the anchor strength is reduced. Figure 4b shows that it is indeed the case.

(b) *Molecular weight dependence.* — In figure 3 we also noticed that for polymers with the same end-group, the transition curves shift to the left upon increasing the molecular weight. In terms of the « pancake-to-brush » transition picture, the transition occurs when the pancakes start to overlap. Assuming the area A occupied by each pancake scales with molecular weight by a power law, $A \sim W_n^{2\nu}$, for a fixed surface area of the polystyrene sphere, the maximum number of pancakes per sphere goes like A^{-1} . Therefore the inflection point of the transition decreases with molecular weight and should go like $W_n^{-2\nu}$. Experimentally, we found that the inflection points behave like W_n^{-1} , corresponding to $\nu = 0.5$. Since the area A scales with the radius of gyration R_g as $A \sim R_g^2$, we find the relation between R_g and W_n as $R_g \sim W_n^{0.5}$. Qualitatively, it is not inconsistent with the expectation that the pancakes are formed by random walks of chains on the surface.

(c) *Scaling law of the plateau thickness.* — Figure 3 also shows that the height of the plateau increases with molecular weight. Similar trends were also found for the C16 group polymers. Figure 5 shows log-log plots of the plateau thickness vs. the molecular weight for both C12 and C16 polymers. The fitted slopes are about 0.46 for C12 and C16 slightly less than the value $\nu = 0.5$ predicted by Ligoure *et al.* for high surface coverage [9]. However, due to limited range of data the results are only qualitative.

It is probably worth noting that although these associative polymers have two adsorption end-groups, because of the length of these polymers, the scaling behavior should be similar to that of end-adsorbed diblock copolymers. In our experiments the layer thickness is comparable to the radius of the sphere, it will be interesting to see in more detailed investigations on how surface curvature may affect the scaling behavior of the layer thickness [18-21].

(d) *Thermodynamic nature of the transition.* — At this point, it seems clear that all the evidence qualitatively supports the scenario of pancake-to-brush transition. In Alexander's prediction this has to be a first order transition. Either the layer thickness or the average chain orientation in the layer could be identified as the order parameters. In this case, the order parameter appears to be discontinuous near the transition point. The latent heat involved in

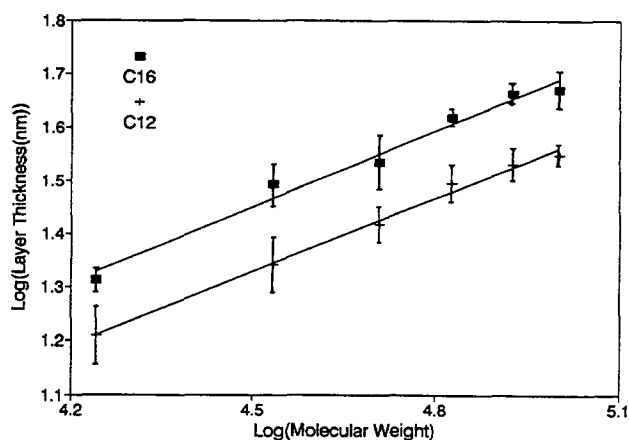


Fig. 5. — Log-log plot of layer thickness vs. molecular weight. The slopes were found to be about 0.46.

this transition is estimated to be less than 10^{-7} cal/cm³; it is very difficult to determine experimentally in these systems because of the extremely low concentrations. More detailed studies are needed to clarify this point.

3.3 KINETICS OF ADSORPTION AND DESORPTION. — As discussed by Ligoure *et al.*, there are two time scales for the kinetics of polymer adsorption [9]. The first time scale τ_1 , is the time for polymers to build « pancakes » that are just overlapping. Since there is no barrier during this process, assuming that the polymer hits the surface and sticks, τ_1 is essentially the time for polymer diffusion in solvent. In dilute solution, this time is short, typically a fraction of a second. The second time scale τ_c , is the time required for the brush to develop and reach equilibrium. This process is much slower because once the first layer is formed the additional polymers have to diffuse through the polymer layer to reach the surface. Ligoure *et al.*'s estimates show $\tau_c \sim 10^6$ s. We could not see τ_1 because it was too short for us to determine by DLS. However, we made an attempt to examine τ_c . By DLS, we found that the hydrodynamic layer thickness reached the equilibrium value within a couple of minutes after the polymers were mixed with the latex spheres. Without a good model we cannot relate the hydrodynamic layer to the true density profile of polymers on the surface. Still the fast build-up of the hydrodynamic layer thickness was a surprise to us. The investigation of this issue is currently underway using static light scattering to measure the density build-up during the adsorption process.

We have also studied the desorption process for C16-100 samples. Figure 6 shows three successive measurements, each separated by 24 hours. The first set of measurements was made 24 hours after the adsorption was started. The second and third sets were made on samples diluted from the original by factors of 2 and 5, respectively. By diluting the solution we found that the layer thickness at the plateau was not changed. The results show that once the layer is formed, the polymers cannot be washed off the surface. The irreversibility of the adsorption was also shown in a desorption study of PS-PEO diblock copolymers on a sapphire surface [22]. In the same study, Ligoure *et al.* also show that the « washing-off time » of the adsorbed layer is longer than the layer construction time. For adsorption energy of a few kT , they estimated that the washing-off time could be as long as 5.5×10^7 s.

We also notice in figure 6 that the layer thickness of the plateau seems to take off again at higher polymer concentration. One possible explanation for this is that the polymer concentration is so high that solution viscosity was substantially higher than that of the

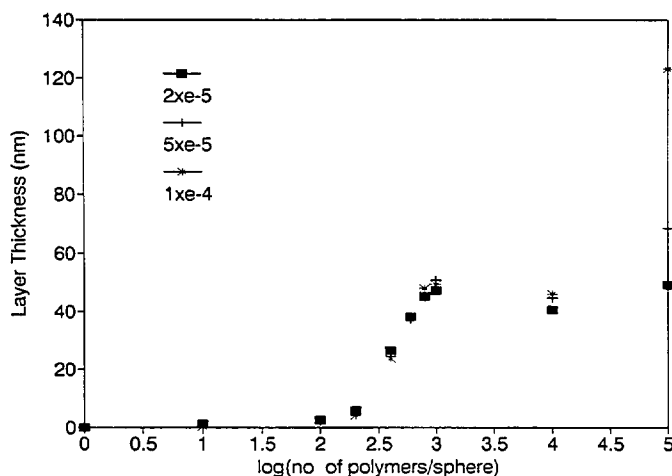


Fig. 6. — Desorption kinetics for C16-100. Normal- \log_{10} plot of layer thickness vs. number of polymer chains per sphere. Solutions with sphere volume fractions of 1×10^{-4} , 5×10^{-5} and 2×10^{-5} were made by successive dilutions. Measurements were made 24 h after the first set of samples was made and after each Dilution. There was no change in the plateau thickness. At high polymer concentration the layer thickness appeared to increase again, probably due to multiple layering or changes in viscosity.

solvent. This was indeed found to be the case by direct viscosity measurements at these concentrations. However, at these concentrations an interesting scenario could occur for associative polymers: polymers in solution could form multiple layers by associating with dangling ends of polymers in solution that have only one end anchoring on the surface. At this point, we could not distinguish the latter effect from that due to a viscosity increase.

4. Conclusion.

In studying the adsorption of associative polymers we observed sharp transitions in the adsorption curve. We believe this transition is the one predicted by Alexander and is due to the competition between the adsorption of backbones and the anchoring end-groups. Because of this competition, polymer « pancakes » are able to cross over to polymer « brushes ». Although our measurements were made on R-B-R type triblock copolymers, we made no distinction in our analysis between these polymers and the conventional diblock copolymers because in this study the two cases should be very similar. We expect that the adsorption of diblock copolymers with weak adsorbing backbones also has this transition.

Although polydispersity did not affect the qualitative evidence of the phase transition, effects due to polydispersity for these types of polymers are found to be extremely interesting because they do not follow the usual behavior of homopolymers and surfactant polymers. Neither the long nor the short chains necessarily win during the adsorption process. Kinetics of adsorption is also affected dramatically. Details of the effects due to polydispersity will be addressed in a separate paper.

Acknowledgments.

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