Adsorption Behavior and Potential Interfacial Morphology: Impact of Adsorbing Hydrophobic Groups in Polymers with Weakly Adsorbing Main Backbones

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SYNOPSIS

This study examined the adsorption isotherm behavior within a homologous series of fluorescently end-labeled hydrophobically end-modified ("fluorophobe") poly(ethylene oxide)s (PEOs) on hydrophobic polystyrene (PS) latex. Results were then compared with a model for the adsorption of end-modified chains and previous adsorption studies of associative thickeners, PEOs containing hydrophobes on both ends in addition to regularly spaced weak internal hydrophobes. For both PEO series, an increase in end-group hydrophobicity yielded higher isotherm plateau coverages by up to a factor of 5 over control samples without end hydrophobes. For the fluorophobe–PEOs, an increased end-group hydrophobicity also led to a steeper slope in the low-concentration regime of the isotherm, reflecting the influence of the end group on the net adsorption energy (to the extent that the initial isotherm slope reflected an *equilibrium* partitioning between the interphase and the bulk). In contrast for the associative thickeners, the impact of end-group hydrophobicity on the initial isotherm slope was not apparent, and the initial slopes for the associative thickeners were generally much steeper than for any of the fluorophobe PEOs. These differences in isotherm shapes were thought to reflect differences in the molecular architecture between the fluorophobe–PEO and associative thickener series, and the impact of molecular architecture on the interaction with the substrate. In addition to altering the coverage, the end-group hydrophobes alter the interfacial morphology and the surface selectivity for specific molecular weight populations within a polydisperse PEO sample.
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INTRODUCTION

The field of polymer adsorption has experienced a redirection away from the previous focus on homopolymers toward copolymer systems capable of forming complex interfacial structures. It has been established that diblock copolymers adsorb to form brushes[1,2] and that the chain composition determines the interphase morphology. Less is known about the structural variety in triblock copolymer layers.[3] Most of these fundamental copolymer studies have employed true diblock copolymers with substantial amounts of both constituents in each chain, and a significant difference between the affinity of the two constituents for the substrate. Less work has been done with surfactantlike polymers where the adsorbing end group is small and where both the main backbone and a small head group compete for the substrate. Gast has contributed work in this area with low-molecular-weight hydrophobically modified polyethylene glycols;[4–6] however, the regime of higher molecular weight has, to date, been neglected. Hence, the regime where the classic homopolymer interfacial structure gives way to brushes and interfacial micelles is poorly understood.

Our work focuses on the regime of intermediate molecular weight and chemistry, where a combination of homopolymer and brushlike features potentially coexist. This study employed surfactantlike polymers whose main backbones experienced significant attraction to the surface and whose end

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groups possessed even greater substrate affinity. The work reveals the minimal amount of modification to the backbone that gives noticeable deviation from classical homopolymer behavior and suggests how the adsorbed layer features are altered.

Previous polymer adsorption studies in the regime potentially between homopolymer and brush behavior involved associative thickeners,[7-10] a technology driven by the evolution of the coatings industry toward water-based systems. These water-soluble polymers contain hydrophobic groups, engineered to yield micelles and networks in solution, thereby enhancing rheological properties. The hydrophobes also cause the associative polymers to adsorb onto dispersed hydrophobic moieties (pigment and latex), sometimes inducing flocculation.

Though adsorption, per se, is not the primary intent in associative thickener design, systematic variations in hydrophobe content and molecular weight have made this class of molecules ideal for fundamental adsorption studies linking molecular architecture to secondary interphase morphology.[11-13] Early studies of associative thickeners noted the regimes of adsorption and depletion of these polymers from hydrophobic (acrylic) surfaces, demonstrating correlations with rheological properties and dispersion stability.[7] Santore developed a statistical mechanical treatment of adsorbed layer features,[14,15] based on the concept of a nonadsorbing main polymer backbone with sticky end groups. This model predicted the impact of backbone molecular weight, solvent quality, and end-group affinity for the surface on the partitioning of polymer between an interface and the free solution and, ultimately, the dispersion stability. It was shown that the molecular parameters had a major impact on the macroscopic processing and performance related properties. Of particular importance to the work presented here, Santore's model argued that placement of hydrophobic groups on the chain ends rather than in the middle of the backbone was key to controlling adsorption, for the case where the main backbone did not itself adsorb.[15] The theory also predicted that for end groups with up to 5–6 kT adsorption energy, the adsorption of a single end group per chain was favored over conformations with both hydrophobes on the surface.

Agreement between predicted and observed flocculation and restabilization suggests that Santore's statistical mechanical theory also correctly predicted the layer morphology of end-adsorbing telechelics.[8] It is desirable, however, to experimentally probe the molecular-level features of such adsorbed layers, especially the link between the molecular architecture and adsorbed layer morphology. More detailed studies of adsorbed associative polymers have been conducted by Jenkins[9,11] and later by Ou-Yang,[12,13] using a series of associative thickener molecules whose main backbones possessed significant affinity for the substrate. (This was in contrast to the previous studies where the main backbone was excluded from the substrate.[7]) Jenkins's work included a comprehensive set of adsorption isotherms illustrating the impact of increased end-group hydrophobicity, providing a point of comparison for the current work. Ou-Yang focused on the hydrodynamic properties, revealing a hydrodynamic transition which appeared sharper for the more hydrophobic polymers, but which remains a point of ongoing debate.[16]

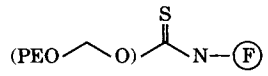
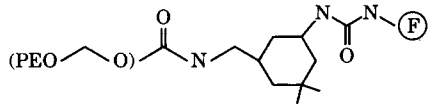
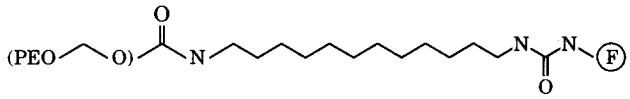
The work presented here employs a series of model polyethylene oxides (PEOs) modified by the addition of fluorescent and hydrophobic sequential units ("fluorophobes") at one end of each chain. The main PEO backbone is shown to adsorb from aqueous solution onto hydrophobic polystyrene (PS) latexes, and the end-group hydrophobicity is increased to illustrate the minimal amount of end-group modification needed to bring about adsorption behavior different from that of the homopolymer PEO. (The fluorescent constituent of the end-group facilitates an easy method by which adsorption can be monitored, both in the isotherm studies here and by other methods such as fluorescence spectroscopy and total internal reflectance fluorescence.[17]) After the adsorption isotherm behavior of the fluorophobe–PEO series is discussed, a comparison is made to calculations and to Jenkins's previous adsorption isotherm studies of associative thickeners on a similar PS latex.[9,11] The associative thickener molecules differ from the fluorophobe–PEO series because the former include regularly spaced internal hydrophobes, plus hydrophobic linking chemistry between the primary end hydrophobe and the PEO chain, potentially increasing end-group hydrophobicity. Comparing the two series of hydrophobically modified PEOs provides insight into the importance of hydrophobe placement and the relative contributions of the main backbone and end groups on the adsorbed layer structure. The two series of molecules also demonstrate the impact of chain end hydrophobicity, as the main backbone–substrate interaction varies.

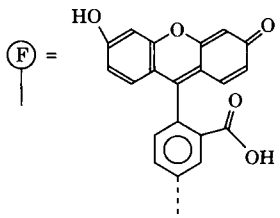
EXPERIMENTAL

Fluorophobe–PEOs

Table I summarizes the three members of the homologous fluorophobe–PEO series synthesized in

Table I. Chemical Structures Modifed PEOs

Sample Name	Hydrophobe	Fluorophore	Structure
FITC–PEO	None	Flourescein isothiocyanate	
FlAm–IPDI–PEO	Isophorone diisocyanate	Fluoresceinamine	
FlAm–C_{12}–PEO	1, 12-Dodecyldiisocyanate	Flouresceinamine	



this work. These molecules consist of the main PEO backbones (~ 100,000 molecular weight, polydisperse) onto which hydrophobic and fluorescent end groups are attached in sequence (to yield a fluorophobe). Only one end of each chain is fluorophobe labeled, since the isothiocyanate chemistry employed for chain end modification attacks hydroxyl groups, and since the standard chemistry employed to synthesize moderate and high-molecular-weight PEOs gives a product with a hydroxyl only on one of end of each chain. Hence, these polymers are surfactantlike in nature, with hydrophobic head groups that are also fluorescent.

The first polymer of the series, FITC–PEO (fluorescein isothiocyanate–PEO) is the control sample, with minimal head-group hydrophobicity. Here, FITC is attached directly to the PEO via a thiourethane linkage. In the other two fluorophobe–PEOs, a hydrophobic spacer group tethers the fluorescent end group to the main PEO backbone. The fluorescent group facilitates an easy assay for polymer concentration in these isotherm studies. In most studies employing fluorescent labels, one is concerned that the label may alter the physics which one attempts to study. In this work, however, the combination of sequential fluorescent and hydrophobic units into a single fluorophobe minimizes this concern. Rather, the fluorophobe can be envisioned as a single entity with a net interaction energy with the substrate.

FITC–PEO, containing a direct thio-urethane link between the fluorescein group and the PEO was synthesized as follows: 4 parts (by mass) PEO were dissolved in 3 parts dibutyltin dilaurate catalyst (Aldrich), and twice the stoichiometric amount of FITC (Aldrich) was added. This continuously stirred mixture was held at 70°C for 6 h, and then the reaction was quenched with methanol to deactivate the unreacted FITC.

The PEOs with the hydrophobic linkers followed a two-step synthesis process. First, an excess amount of linking agent, a hydrophobic diisocyanate such as isophorone diisocyanate (IPDI) or 1,12-diisocyanatododecane (C_{12}) was reacted with fluoresceinamine (FlAm) (in a 5 : 1 hydrophobe:FlAm molar ratio) in tetrahydrofuran (THF) at 60°C for 6 h. This yielded the fluorophobe complex, dissolved in a solution of excess reactive hydrophobe. The latter was removed by washing with pentane. In the second step, the fluorophobe was reacted onto the hydroxyl end group of the PEO by dissolving an excess of the fluorophobe in THF and refluxing with PEO and a few drops of tindibutyl dilaurate catalyst for 6 h. The reaction was then quenched by the addition of methanol to cap any unreacted isocyanates.

All reaction mixtures were purified in two steps. First, the catalyst and highly hydrophobic fluorophobes were removed by dissolving the reaction mixture in toluene and precipitating with pentane at least twice. (In the case of the THF-containing

reaction mixtures, the first step was a pentane precipitation.) The product was then dried to remove residual solvent and dissolved in deionized (DI) water. The solutions were filtered through a glass pad to remove insoluble impurities. Then to removed free fluorescein, polymer solutions were dialyzed against DI water for several weeks. Dialysis was considered complete when the dialysate was no longer fluorescent.

A gel permeation chromatography (GPC) analysis revealed no increase in molecular weight of the various samples, therefore it was concluded that the difunctional hydrophobes did not dimerize the PEO chains. As a second test of the reaction chemistry, a dummy reaction exposed FlAm to PEO in the presence of catalyst, and the "reaction" mixture was purified and dialyzed as above. The purification led to a complete loss of color, ensuring that the purification procedure was capable of removing free fluorescein from the reaction mixture. The dummy reaction experiment also demonstrated that the FlAm does not react with PEO. Hence, in the fluorphobe-containing PEO samples, we can be sure that any fluorescent labeling also indicates the presence of a hydrophobic unit on that chain.

The efficiency by which the chains were labeled was determined by comparing the absorbance of the labeled polymer samples with that of free fluorescein solutions. It was found that samples of the control polymer, FITC–PEO, were 100% labeled within experimental error. For the FlAm–IDPI–PEO sample studied here, only 80% of the chains contained fluorophobes on their ends. Finally, the absorbance study revealed that the FlAm–C_{12}–PEO synthesis procedure was the most difficult. Here, the two samples presented represent labeling densities of 30 and 50%.

Adsorption Isotherms on Polystyrene Latex

The PS substrate used in this study was a monodisperse, 300-nm-diameter PS latex, generously donated by Lehigh's Emulsion Polymers Institute. These particles were cleaned by repeated exposure to ion-exchange resin to remove surfactant and ionic materials, yielding a stock solution of 3.23 wt %. A small amount of residual surface acid groups was sufficient to maintain dispersion stability via an electrostatic repulsion; however, the charged surface groups are reported to be sufficiently sparse that the substrate is essentially hydrophobic.[11,18]

For each of the isotherms presented in this study, a series of polymer solutions, ranging from 5 to 600 ppm was prepared, and the fluorescence of each solution measured with a filter fluorometer (blue gel excitation filter with a range from 430 to 490 nm, emission measured above 540 nm via a sharp-cut high-pass filter, Schott optical glass) to generate a calibration curve. Then 10 g of each solution were mixed with 1 g of PS stock latex (3.23 wt % solids), agitated 10 min, and allowed to equilibrate for at least 1 h. After centrifugation to separate the particles from the serum, the serum fluorescence was used to determine the free polymer concentration, and a mass balance employed to calculated the surface loading. For the FlAm–C_{12}IPDI samples, it was desirable to sample the higher concentration region of the plateau. To accomplish this, a second series of data was added to the isotherm by mixing each of the polymer solutions with a smaller amount of latex than employed in the first data series. This increased the overall polymer–particle ratio over that in the first data set, allowing the high concentration regime to be probed.

RESULTS

Fluorphobe–PEO Adsorption

A valid criticism of the centrifugation method for adsorption isotherms is that the centrifugal force may strip polymer from the particle surface or trap additional polymer in flocs. Clearly, gentle centrifugation conditions will minimize the accidental removal of adsorbed chains from the latex, while flocculation effects remain a potential problem in any study employing a dispersed substrate. To address these concerns, Figure 1 illustrates the impact of centrifugation conditions on the isotherm shape for FITC–PEO adsorbing onto PS latex from DI water. Centrifugation conditions ranged from 5000 to 10,000 rpm and 1 to 2 h of exposure to centrifugal force. Figure 1 demonstrates that the main impact of centrifugation comes at the low-coverage region of the isotherm, with minimal impact on the plateau coverages. For centrifugation speeds between 5000 and 10,000 rpm, the initial slope varies approximately by a factor of 2, and the isotherms appear to converge at the most gentle conditions, still sufficient to adequately separate particles from the serum. The most gentle conditions employed in our study, 5000 rpm and 2 h, did not give complete separation of particles and serum and represent the lower limit of centrifugation force which can be employed. Hence, in the remainder of the isotherms presented here, conditions of 7000 rpm and 1 h were utilized.

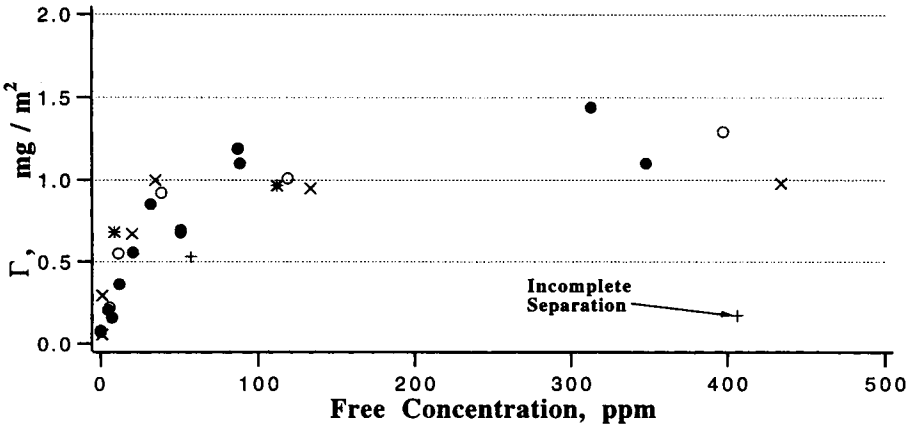


Figure 1 Impact of centrifugation conditions on the adsorption of FITC–PEO on PS particles from DI water. (●) 10,000 rpm for 2 h; (○) 10,000 rpm for 1 h; (×) 7000 rpm for 2 h; (*) 7000 rpm for 1 h, (+) 5000 rpm for 2 h (gave incomplete separation).

In Figure 1 for FITC–PEO adsorption, it is apparent that this control sample, with minimal hydrophobic content on the single-chain end, exhibits significant adsorption to the PS. At first glance, it is not clear if the adsorption is caused by the interaction of the FITC chain end with the substrate or if the main backbone adsorbs. The potential for main backbone adsorption was tested in the experiment illustrated in Figure 2. Here, an isotherm with a fully labeled FITC–PEO sample was compared to one where the sample had been deliberately doped with unlabeled chains, such that only 50% of the mixture was labeled. In determining the isotherm for the 50–50 mixture, a calibration curve was first generated, per the usual procedure but now employing solutions in which only 50% of the chains were labeled. (The concentration units on this particular calibration reflected the total polymer mass in each solution.) This curve was then employed to analyze the supernatant solutions after the mixtures had been allowed to contact the PS particles, with the assumption that the labeled chains in each mixture behaved identically to the unlabeled ones. The fact that the resulting isotherm for the 50–50 mixture is nearly identical to that of the completely labeled FITC–PEO sample in Figure 2 suggests that this assumption is indeed a good one, and that the surface does not distinguish between FITC-labeled and unlabeled PEO chains. At the other extreme, if the FITC end groups were solely responsible for the adsorption, one would anticipate an apparent plateau surface coverage of 2 mg/m^2 in the 50% labeled sample, an expectation that was not realized experimentally. A test for free FITC adsorption on this PS latex, by a similar isotherm centrifugation method revealed negligible adsorption. Hence these data suggest that

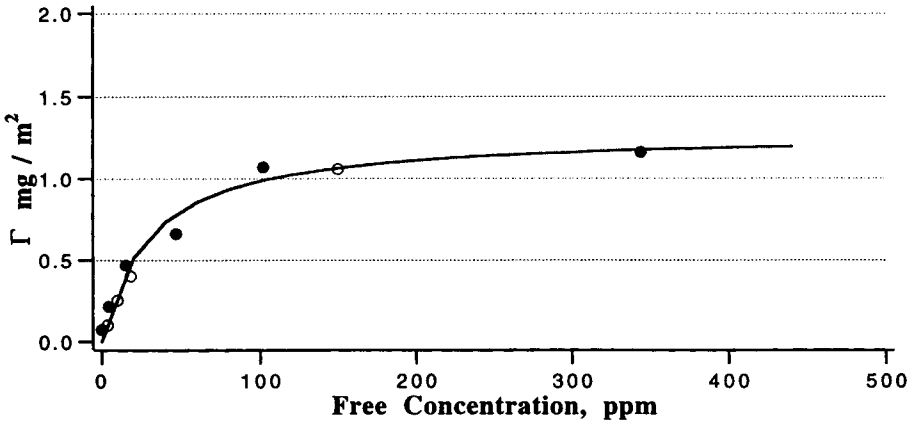


Figure 2 Impact of fluorescein labeling on the adsorption of FITC–PEO on PS particles from DI water. (●) Sample is 100% labeled with fluorescein; (○) sample is doped by 50% unlabeled PEO. (From Ref. 17, Fig. 1).

the main PEO backbone adsorbs significantly onto PS, and that the fluorescent end groups have little additional affinity for the substrate.

Figure 3(a) illustrates the adsorption behavior of two FlAm–C_{12}–PEO samples, with labeling densities of 30 and 50%, respectively. Two features should be noted. First, the overall adsorbed amounts for both FlAm–C_{12}–PEO samples significantly exceed the plateau coverages from the control FITC–PEO sample. Second, the more densely labeled FlAm–C_{12}–PEO sample appears to adsorb less than the more mildly labeled sample. These observations demonstrate that the hydrophobic component of the end group significantly enhances the polymer–substrate interaction (since it was previously established that the fluorescent constituent alone did not significantly affect adsorption). It would therefore follow that C_{12}-containing PEO chains will adsorb preferentially from a mixture of FlAm–C_{12}–PEO and unlabeled PEO, and further that the labeled chains detected by the fluorescence assay are not representative of every chain in the sample. The surface selectivity for the labeled (hydrophobe-containing chains) leads to the apparently different surface coverages of the two samples in the following way: the x and y axes in Figure 3(a) are intended to represent the total free and adsorbed polymer, respectively; however, the polymer assay sees only the labeled chains in solution. If labeled chains adsorb preferentially over the unlabeled chains, then the calculated adsorbed amounts become artificially high. This error increases with larger unlabeled populations in the samples, causing the apparent differences in the two FlAm–C_{12}–PEO samples.

An attempt to isolate the behavior of the C_{12}-containing chains was based on the fact that the fluorescence assay was sensitive only to the fluorescently labeled (and therefore hydrophobe-contain-

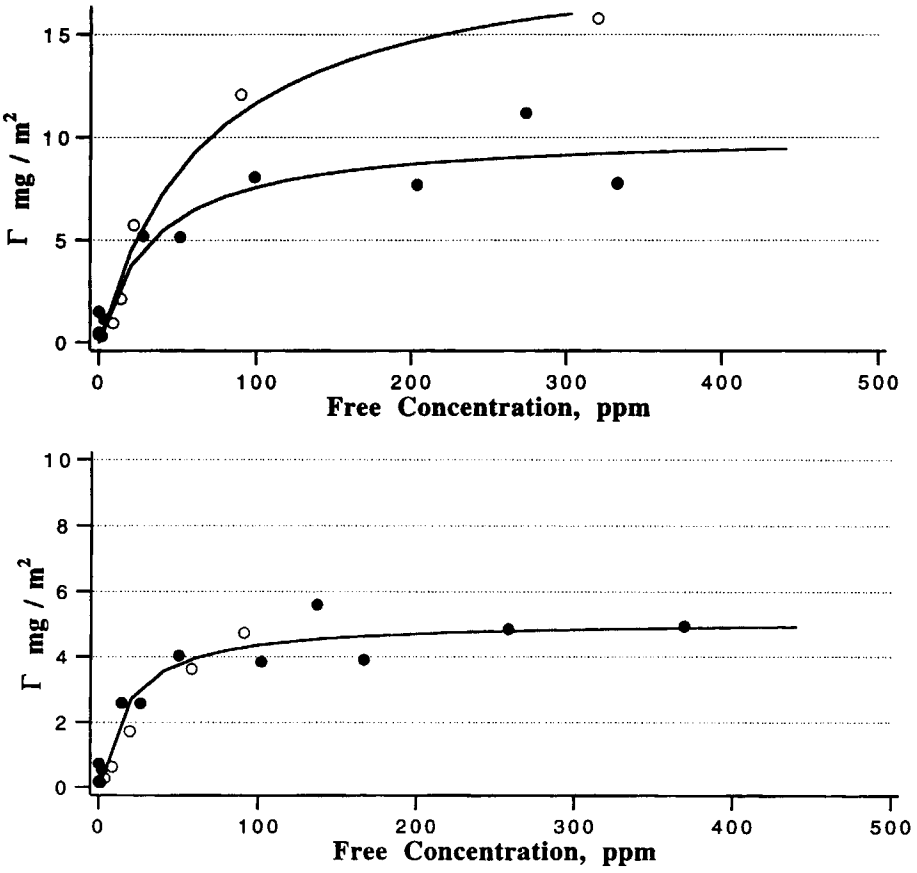


Figure 3 Adsorption isotherms for FlAm–C_{12}–PEO on PS particles. (○) Sample is labeled at 30%; (●) sample is labeled at 50%. (a) The free concentration and adsorbed amounts are calculated directly from the calibration curves without correction and hence supposedly represent the total polymer in the sample. (b) The free concentration and adsorbed amounts on these axes have been corrected to represent only the labeled (hydrophobic) populations of chains.

ing) population within each of the sample. Since it was independently determined that 30 and 50% of the two samples were labeled, respectively, we could calculate the partitioning of the labeled population between the surface and free solution, illustrated in Figure 3(b). Figure 3(b) was obtained by performing independent calculations with the two data sets in Figure 3(a): The free and adsorbed concentrations reported on the axes in Figure 3(a) were multiplied by the labeling efficiency of each of the samples, so that in the corrected graph, only the partitioning of the labeled (hydrophobically modified) chains is reported. In Figure 3(b), the x axis represents the concentration of FlAm–C_{12}–PEO chains, although there are also unlabeled chains present in solution. The y axis in Figure 3(b) represent the surface coverage of the C_{12}-containing chains, although there may also be unlabeled chains on the surface. The extent to which the C_{12}-containing chains displace or coexist with the unlabeled chains is not known; however, the calculations in Figure 3(b) represent the worst-case (lowest) coverage, since any adsorption of the unlabeled chains reduces the area available to the C_{12}-containing chains. It is particularly encouraging to note in Figure 3(b) that the two isotherms for the 30 and 50% labeled samples collapse to a single isotherm, when data are analyzed in this fashion.

Figure 4 compares the adsorption behavior of all three samples from Table I. Data for the FlAm–C_{12}–PEO samples have been corrected to represent the partitioning of the fluorophobe-labeled populations, as in Figure 3(b). Data for the FlAm–IPDI–PEO sample have been corrected to account for the 80% labeling density; however, this only slightly altered the shape of the isotherm. It is clear from comparing the shapes of the three isotherms that increased hydrophobicity of the linker portion of the fluorophobe leads to higher surface coverages and steeper initial isotherm slopes. These trends are summarized quantitatively in the upper portion of Table II.

In Table II, the plateau of the isotherms are converted to the surface area per chain, employing the nominal chain molecular weight of 100,000 and converting this to $N = 1136$ chain segments, with segment length of $l = 0.4$ nm. The standard Flory form for the free coil radius in good solution yields a free coil area of $Nl^2 = 182$ nm. Hence, to first order, adsorption of the FITC–PEO chains gives an ultimate surface coverage with an area per chain similar to that in free solution. With the small hydrophobes incorporated into the end groups, the coverage is increased and the area per chain is as much as 5 times less than chains without hydrophobes.

To the extent that these adsorption isotherms represent the equilibrium partitioning of the polymer between free solution and the interface, the initial slope of the isotherm contains information about the adsorption free energy, E_{ads}, of single chains onto a bare PS surface. This adsorption energy can be determined by representing the initial slope in dimensionless form, accomplished by converting the free chain concentration to the mass of free chains per unit area of surface. This accounts for the relative amounts of polymer solution and latex surface in a particular experiment. Then, with the initial slope in dimensionless form, a Boltzmann distribution describes the adsorption energy:

$$\frac{\text{Slope}}{\left(10^{-6}\dfrac{\text{ppm}}{\text{mass fraction}}\right)\left(\dfrac{\text{solution volume}}{\text{total area}}\right)} = e^{(E_{ads}/kT)} \tag{1}$$

In Table II, these adsorption energies have been summarized for the three polymers. It is clear that increasing end-group hydrophobicity leads to increased adsorption energy, but in all cases, the adsorption energy per chain is lower than expected for polymer adsorption.[19]

DISCUSSION

Associative Thickener Adsorption

The adsorption behavior of the fluorophobe–PEO series is put into better perspective when it is compared with Jenkins's studies of associative thickener adsorption.[9,11] These particular associative thickeners (donated by Union Carbide) were comprised of PEO backbone units (8000 molecular weight, polydisperse, hydroxyls on both ends of the units) linked together by IPDI units to generate a higher molecular weight polymer chain.[11] Then, hydrophobic end groups were attached to both chain ends, employing an IPDI linkage between the outermost PEO segments and an alkane hydrophobe of 12 or 16 carbons. For a control case, the same PEO–urethane backbone had its outermost IPDIs capped with hydrogens rather than hydrophobic groups. This chemistry is summarized in Table III.

These associative thickeners are two-ended versions of our fluorophobe–PEOs, with some additional differences. First, the associative thickeners studied by Jenkins contain internal hydrophobes which are thought to have minimal impact on their properties, as evidenced by rheological studies.[11,20]

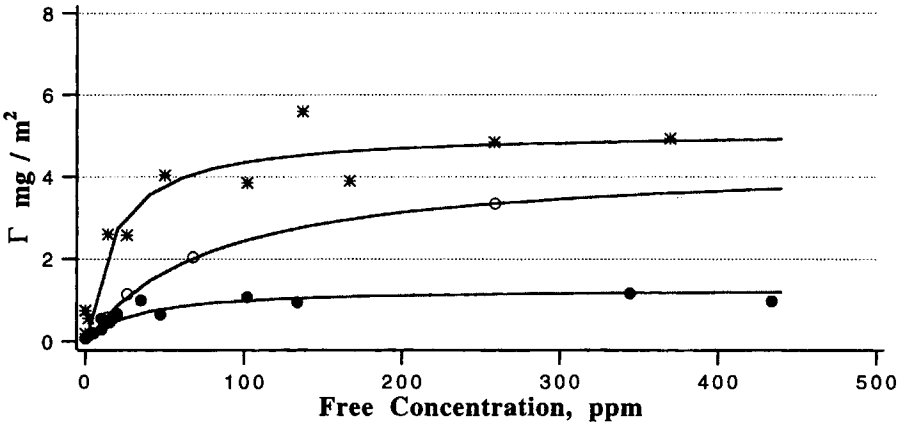


Figure 4 Summary of adsorption behavior of (●) FITC–PEO; (○) FlAm–IPDI–PEO; (*) FlAm–C_{12}–PEO. Axes have been corrected to reflect only the labeled populations of chains within the FlAm–IPDI–PEO and FlAm–C_{12}–PEO samples, the latter per Fig. 3(b). (Some data, FITC–PEO, FlAm–C_{12}–PEO are from Ref. 17, Fig. 3.)

Our fluorophobe–PEOs contain no internal hydrophobes. Second, the main hydrophobes on the associative thickeners such as the C_{12} and C_{16} end groups are attached to the PEO backbone by IPDI, which our studies have shown to have a significant impact when placed near the chain end, and which we were able to use as a hydrophobe, on its own.

The adsorption of the associative thickeners onto 190-nm PS latex (similar in surface chemistry to the 300-nm latex employed in the fluorophobe–PEO work[18]) from Jenkins's study is shown in Figure 5[9] for a nominal backbone molecular weight of 100,000 and C_{16}, C_{12}, and hydrogen-capped chain ends. These adsorption isotherms have been generated by a serum replacement method, detailed elsewhere.[9,11] This technique maintains a stirred latex suspension into which a polymer solution is slowly added and from which serum is slowly removed through a membrane. The free polymer content in the serum was determined by its refractive index. In Figure 5, two sets of data are shown for each polymer sample: The filled points represent the adsorption isotherm and the hollow points represent the retention as the dispersion with its adsorbed layer is washed with DI water, essentially a desorption isotherm. The difference between the adsorption and desorption curves represents the apparent irreversibility of adsorption, for the time scales employed in this study, where the concentrations for a single isotherm are ramped over a period of several days.

The similarity between the adsorption curves for the associative thickener series and the fluorophobe–PEO series, summarized in Table II, is striking. The directly labeled FITC–PEO most closely resembles the adsorption of the control hydrogen-capped associative thickener, with the latter giving a slightly higher plateau coverage of 1.5 mg/m^2 compared to 1.0 mg/m^2 for the FITC–PEO. The plateau coverage for the FlAm–IPDI–PEO samples falls just short of that seen with the C_{12}-capped associative thickener, and the FlAm–C_{12}–PEO shows plateau coverages closest to that of the C_{16}-capped associative thickener.

An important difference, however, between the associative thickener and fluorophobe–PEO series occurs at the low-coverage portion of the isotherm. In Jenkins's studies, the initial isotherm slopes were generally very steep, within experimental error. Further, there is no obvious impact of the end-group modification on this low-coverage region for the associative thickeners. In contrast, the fluorophobe–PEO series gave finite initial slopes and the impact of the end groups on the initial slope, though not drastic, is apparent.

Potential Artifacts

The adsorption isotherms from the fluorophobe–PEO and associative thickener series reveal a significant impact of end-group modification. Before discussing if the observations reflect the different molecular architectures within the two families of samples, we first address the potential for differences to arise from the centrifugation and serum replacement methods, and the potential for artifacts from nonequilibrated adsorbed layers.

Centrifugal force in the fluorophobe–PEO studies may compact the sediment, squeezing chains from the surface, or rapid particle motion may shear chains from the surface. This would lead to artifi-

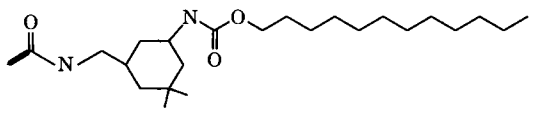
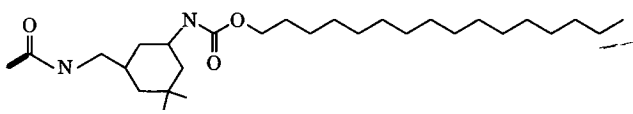
Table II Summary of Isotherms

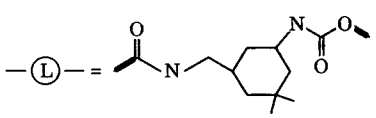
Sample	Plateau Coverage (mg/m^2)	Adsorption Energy (kT)	Area/Chain (nm^2)
Fluorophobe PEOs			
FITC-PEO	1	0.4	167
FlAm-IPDI-PEO	3	1.25	56
FlAm-C_{12}-PEO	5	1.5	33
Associative thickeners			
C0-AP-100	1.6	Large	104
C12-AP-100	3–4	Large	42–56
C16-AP-100	4–5	Large	33–42

cially low isotherm coverages; however, the processing conditions chosen for the fluorophobe–PEO work minimize the centrifugal forced utilized. Further, the retention of fluorophobe–PEO layers in gentle solvent shearing flow (up to 20 s^{-1}), as measured by total internal reflectance fluorescence, demonstrate that fluorophobe–PEO chains are not easily removed by moderate shear.[17] Separate tests on sediments from the FITC–PEO isotherms also revealed that layers were not removed by the dilution of the sediment by fresh DI water, in agreement with Jenkins's observations. Because chains were not readily removed from the PS substrate on the time scale of a few hours, it is likely that the isotherms represented in Figures 1–4 do not suffer from these centrifugation-related artifacts.

The serum replacement method is also potentially subject to artifacts since membrane equilibrium must be established at the exit of the cell. If equilibrium is not achieved, the measured surface coverages would exceed the true equilibrium values. While Jenkins has taken extreme care to avoid artifacts in the associative thickener study,[11] unusual isotherm shapes persist for the most associative (C_{16}-capped) samples. At this point, we cannot determine whether the sigmoidal isotherms truly reflect the state of the surface (as is Jenkins' belief) or reflect deviations from membrane equilibrium for the cell effluent. Notably, Jenkins documented that an isotherm run employing a C_{16}-capped sample with a more dilute stock concentration (163 ppm) did not give the shoulder in the isotherm that was seen for the same associative thickener with a more concentrated stock solutions (342 and 400 ppm).[11] Hence micelle equilibrium or deviations from membrane equilibrium are likely to be complicating factors. Indeed, clustering phenomena with slow dynamic response times have been reported for PEO for concentrations as low as 70 ppm[21-23] and may be more drastic for hydrophobically modified PEO. The sedimentation method avoids these problems, since no membrane is present and since stock solutions of varied concentrations are prepared well in advance of their contact with latex.

Table III Chemical Structures Associate Thickeners (in Jenkins' Study[11])

Sample Name	End Group = (S)	Overall Structure
CO–AP–100	—OH	(S)—(PEO8000—(L)—)—PEO8000—(S)
C12–AP–100		(S)—(PEO8000—(L)—)—PEO8000—(S)
C16–AP–100		(S)—(PEO8000—(L)—)—PEO8000—(S)



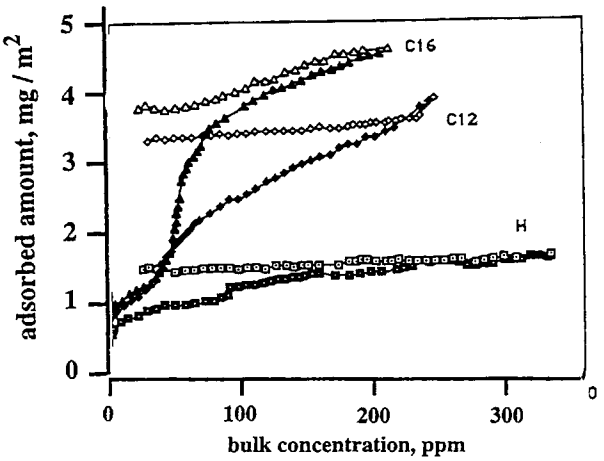


Figure 5 Adsorption isotherms for associative polymers. (■, □) C0-AP-100; (♦, ◇) C12-AP-100; (▲, △) C16-AP-100. Solid symbols designate adsorption runs while hollow symbols designate desorption runs. (Data rescaled from Ref. 11).

Other differences between the two sets of studies may potentially arise from the different batches of latexes (190 and 300 nm) employed. One would not expect curvature effects to be important since the particle size is an order of magnitude greater than the single coil dimension. Also, because both batches of latex were synthesized via similar recipes, it is unlikely that the surface chemistries of the two latex samples were sufficiently different to be reflected in the initial isotherm slopes.[18]

A final potential complication common to both studies are history-dependent artifacts and the possibility that the adsorption has not completely equilibrated. Any history dependencies should be manifest differently in the two studies. In the centrifugation method, each datum represents the exposure of the substrate to an excess of chains from the bulk, which decreases as adsorption proceeds. In the serum replacement technique, the bulk concentration is ramped up by the addition of new polymer at a constant rate. It is not possible to determine the extent of equilibrium or nonequilibrium behavior except to note that in both studies, isotherms were generated at different conditions to test the history dependence and little was seen.[11,24,25] Notably, both studies demonstrate retention of adsorbed layers, even for the control polymers of minimum hydrophobic modification, over periods of hours and days of exposure to solvent washing.[11,17] In the polymer physics community, this phenomenon is a point of ongoing debate, with some arguing that such slow washing processes are consistent with equilibrium behavior[26,27] and others arguing for kinetically trapped adsorbed layers.[28–30] The PEO–PS interaction is thought to be moderate due to hydrogen bonding and the shallow isotherm slopes exhibited by FITC–PEO argue in favor of layers near equilibrium.

Impact of Molecular Detail

If one accepts that experimental methods themselves were not responsible for differences in the associative thickener and fluorophobe–PEO isotherms (with the possible exception of the shoulders in the C_{16}-capped associative thickener isotherms) and that the isotherms do indeed reflect the equilibrium partitioning of the polymers between free solution and a PS surface, then a comparison between the fluorophobe–PEO series and the associative thickeners may be used to elucidate the role of molecular architecture in adsorption. A primary difference between the fluorophobe–PEO series and the associative thickeners was that the latter gave steeper initial isotherm slopes that were insensitive to end-group chemistry. This may result from the internal IPDI hydrophobic units in the associative thickeners, since at low coverage, chains experience many backbone–substrate contacts. The fluorophobe–PEO study (Fig. 4) established that IPDI, placed near a PEO chain end, significantly increased adsorption; however, entropic effects will reduce the impact of the hydrophobe if it is moved away from the end of nonadsorbing backbones.[15,20] Since the associative thickeners contain several internal IPDIs, their collective influence may still be significant and lead to the steep initial isotherm slope.

Further evidence for stronger backbone–substrate interactions in the associative thickener studies (as opposed to the fluorophobe–PEO work) is provided by the insensitivity of the initial slope to end-group identity. In the fluorophobe series the interaction of the PEO backbone with the PS substrate is weaker and hence the end groups have a greater potential impact on the low-coverage region, suggesting they interact with the surface substantially, even at low coverage.

It remains a challenge to explain why the ultimate plateau coverages of the associative thickeners so closely parallel those of the fluorophobe–PEO series, since the associative polymers contain two hydrophobic end groups on each chain while the fluorophobe–PEO series contains one hydrophobe on each chain. To approach this problem, we start with a comparison between the adsorption behavior of FITC–PEO and H-capped associative thickener, which yielded plateau coverages of 1.0 and 1.5 mg/

m^2, respectively, and markedly different initial slopes. While FITC–PEO backbone is comprised exclusively of PEO, the associative thickener contains regularly spaced internal IPDI hydrophobes in addition to hydrophobic IPDI end groups. If one thinks of the IPDI hydrophobicity to be smeared along the backbone in a mean field sense, then the associative thickener shows an average backbone–substrate interaction that exceeds that of the FITC–PEO, leading to the moderately higher coverage of the former.

Since the fluorophobe–PEO molecules are modified at one end only and still exhibit coverages up to 5 mg/m^2, the end groups appear to have a greater impact in the fluorophobe–PEO series than in the associative thickeners. Two possible explanations arise: First, when the main backbone is attracted to the surface, the impact of end group–substrate attractions may be diminished, with strong backbone–substrate attractions potentially requiring greater end-group–substrate attractions for the chain ends to have a visible effect on adsorption, and second, polydispersity within each sample and the competition between high- and low-molecular-weight populations may affect the isotherm.

The idea that end groups will have a visible impact on adsorption only when their interaction with the substrate significantly exceeds that of the main backbone is one that has not been previously tested. To do so would require systematic experiments with extremely well-characterized and monodisperse polymers to obtain convincing results. Further, it is likely that the apparent end-group influence (or minimum end-group strength to influence the layer) will depend on the property being probed.

The potential for polydispersity to alter the apparent isotherm behavior has been established and derives from the selectivity of the surface for chains of a particular molecular weight from a polydisperse sample. For the case where adsorption is driven by backbone–substrate attractions, higher molecular weight chains are favored on the surface.[19] Conversely, when adsorption is driven exclusively by the adsorbing chain ends, lower molecular weight backbones are favored on the surface.[25] Hence, increasing the end-group hydrophobicity inverts the molecular weight selectivity of the adsorption process.

In comparing the fluorophobe–PEO and associative thickener isotherms and attempting to account for polydispersity, one must consider the different assays for the free polymer concentration. In the associative thickener studies, a refractive index assay led directly to the free chain mass concentration and the mass concentration on the substrate; and the measurement itself was not affected by polydispersity or selectivity. In the fluorophobe–PEO study, a fluorescence assay counted the number of chains in free solution, where each chain contained only one label. This chain number was then converted to a mass surface coverage employing the nominal backbone molecular weight of 100,000. Hence, surface selectivity in the fluorophobe–PEO study would potentially reduce the accuracy of the scale of the y axis (although the isotherm shapes are represented more accurately.) Further, in the fluorophobe–PEO study, when the end-group hydrophobicity becomes significant, the surface selectivity and any error in the calculation of the surface coverage become inverted together.

Consider, as an example, the case of FITC–PEO adsorption, where it has been established that fluorescein labeling minimally affects partitioning between the interface and bulk solution. These chains adsorb as homopolymers, with higher molecular weight chains favored on the surface. The serum after PS contact contains many small chains that bear a denser labeling (than the stock polymer solution), on a per-polymer mass basis, such that the serum fluorescence, when mapped onto the calibration curve for the stock solution yields an apparent mass concentration that exceeds the actual value. Hence, the surface coverage of the polydisperse FITC–PEO samples will tend to be underestimated in Figures 1 and 2. (This effect was identified in parallel studies of FITC–PEO supernatant from contact with silica.[31])

The FlAm–IPDI–PEO and FlAm–C_{12}–PEO samples exhibit the impact of end-group hydrophobicity through their elevated surface coverages compared with FITC–PEO, and through the impact of an unlabeled population on the apparent isotherm behavior [Fig. 3(a)]. One would therefore expect that in these samples the lower molecular weight populations should be favored on the surface. With the higher molecular weight species remaining in solution, the fluorescence assay will underestimate the concentration of free polymer and overestimate the adsorbed amount. As the end groups become more hydrophobic (going in series from FITC–PEO toward FlAm–C_{12}–PEO), the fluorescence assay switches from underpredicting to overpredicting the surface coverage, as the molecular weight selectivity of the substrate becomes inverted. Hence, as the end-group hydrophobicity becomes important to the adsorption process, its effect on the adsorbed amount is magnified by the fluorescence assay.

As the molecular weight selectivity argument holds the most promising explanation of the relative

magnitude of the fluorophobe and associative thickener coverages, it is fair to ask how great this effect should be. For homopolymer adsorption, the plateau coverage increases with molecular weight, but the trend is most apparent when the molecular weight varies several orders of magnitude.[19] For brushes with a fixed end-group adsorption energy and bulk concentration near the isotherm plateau, the surface coverage decreases approximately exponentially with increasing backbone length.[2] Jenkins, however, observed nearly similar surface coverages for the 100,000, 87,000, and 74,000 molecular weight versions of the associative thickeners, comparing molecules of analogous hydrophobic modification. The lower molecular weight member of the series (50,000) actually gave lower mass coverage, typical of homopolymer behavior and not brushes. We feel these results are probably more an artifact of polydispersity within individual associative thickener samples and the fact that the overall molecular weight varied only by a factor of 2. While there is rarely a drastic difference in mass coverage with sample molecular weight, the molecular weight selectivity that occurs when chains adsorb in competitive situations is a more marked phenomenon.

In summary, the relative interactions of the backbone and end groups with the substrate may contribute to the similarities and differences in the adsorption behavior of the fluorophobe–PEO and associative thickener molecules. It is more certain, however, that the molecular weight selectivity of the substrate will be inverted by increased end-group hydrophobicity. The latter will exaggerate the impact of the end-group hydrophobicity on the adsorbed amount, illustrated in Figure 4. This selectivity inversion, though it tends to exaggerate the spread in Figure 4 is, itself, a significant effect of the end-group modification. It therefore follows that the IPDI and C_{12} linkers in the fluorophobe–PEO series are indeed less hydrophobic than the IPDI–C_{12} and IDPI–C_{16} end groups in the associative thickeners.

Statistical Mechanical Treatment of End-Adsorbing Polymers: Adsorption Energy and the Difference between Singly and Doubly Capped Chains

The experimental evidence up to this point demonstrates that even weak hydrophobic modification at a single chain end can influence adsorption, manifest either in the surface excess, initial slope, or the molecular weight selectivity of the surface. Qualitative ideas have been put forth to rationalize the relative behaviors of the 1-ended fluorophobe–PEO series and the doubly capped associative thickeners also containing internal hydrophobes. To gain perspective as to whether observations are consistent with expectations for the hydrophobe size, number per chain, and placement, we attempt here a quantitative discussion of the interaction strengths anticipated to affect adsorption. Polymer brushes comprise one possible morphology for the adsorbed layers. Brushes are well understood from a theoretical standpoint but require strong hydrophobic interaction with a substrate at the chain ends only.[32] The established brush theory for singly capped chains is easily extended to doubly capped chains, using scaling arguments.[32] It follows that doubly capped chains should act as singly capped chains but of half the molecular weight. The doubly capped chains should therefore give higher coverages and dominate in competitive situations. Whether the samples discussed here can be modeled as brushes is open to debate: One might argue that only the most strongly end-modified chains could form brushes because of the significant backbone–substrate attractions that favor classic homopolymer layers. No simple theories exist for chains with significant backbone–substrate interactions and mild end group–substrate attractions just exceeding those of the main backbone. Therefore, in addition to the brush theory, a simple treatment of end-adsorbing chains with weak attractions for the surface is presented as a point of departure for interpreting the experiments presented here.

A previous model[14,15] loosely extended to the experiments here, in the limit of low coverage, involves nonadsorbing gaussian backbones with "sticky" end groups weakly attracted to the surface. In the experiments the main backbone does indeed adsorb. Hence, this theoretical treatment will be employed only as a point of departure to explain the influence of weak hydrophobes (as opposed to the stronger hydrophobes of polymer brushes) and to suggest a lower bound on the end group–substrate interaction where macroscopic effects become apparent. The model's utility also stems from its ability to quantify the relative molecular weight and adsorption energy effects, and the impact of adding hydrophobes on 1 vs. 2 chain ends. The model of singly and doubly capped chains, detailed in the appendix, predicts the fraction of chains adsorbed to a surface, by either 1 or 2 ends. This correlates with the initial isotherm slopes. The plateau coverages are not predicted explicitly since the lack of repulsions in the model prevents the adsorbed layer from saturating. It is a general rule, however, that the plateau coverage in-

creases with the net energy gain from the adsorption process.[32]

Figure 6 illustrates the predicted impact of end group–substrate attractions for chain molecular weights, corresponding to N = 5000, 1150, and 550, and singly and doubly capped chains. N = 1100 corresponds to the nominal 100,000 molecular weight PEO. The curves are generally sigmoidal, and the inflection point may be chosen as the end-group energy where adsorption becomes favored over free solution, potentially observable in isotherm studies. The sigmoidal shape is also consistent with the idea of a threshold end-group–surface attraction that must be achieved before the impact of the end group on the surface excess is observable in a real experiment.

Because the model applies to the low-coverage region of the isotherm and since the end-group adsorption energy is shown in Figure 6 to be significant for the doubly capped chains, the end groups should influence the initial isotherm slopes of the associative thickeners, in contrast to Figure 5. The model lacks a strong backbone–substrate interaction, making the previously mentioned rationale based on the internal IPDI linkages the best explanation for the hydrophobe insensitivity of the initial isotherm slopes for the associative polymers.

Since the backbone–substrate interaction should be weaker with the fluorophobe–PEO series and since the end group's influence on the initial isotherm slopes generally agrees with predictions, other aspects of the model may well apply to the fluorophobe–PEO series. In Figure 6, for singly capped chains with N = 550 or 1100, the end group's influence becomes visible at end group–substrate attractions of 2 or 3 kT, consistent with hydrophobes of 10–12 carbons.

Figure 6 demonstrates the relative impact of tagging 1 or 2 chain ends. A second hydrophobe reduces the energy per end group needed to achieve an arbitrary adsorbed fraction by 0.5 kT. Doubling the number of hydrophobes does not double the adsorption energy. However, for a particular U_{end} value, e.g., 3 kT, the fraction of singly and doubly capped chains is 0.28 and 0.46, respectively, such that the coverage is almost doubled, or the initial isotherm slope should be twice as steep. This result stems from the fact that the gaussian probability for configurations with both ends adsorbed is several orders of magnitude smaller than that for chains with one end adsorbed, i.e., there is a significant entropic loss to bring the second chain end to the surface. Therefore, for doubly capped chains with $U_{end} < 6$ kT, the majority of chains are adsorbed only by one end. (Compared with our gaussian model, improved solvent quality, imparting repulsions between backbone segments, will more strongly favor configurations with only one end adsorbed.) The effect, therefore, of labeling both chain ends is to double the probability of the singly adsorbed configuration, and also the adsorbed amount at low bulk concentrations. Backbone–substrate attractions will tend to increase the probability of configurations with both ends adsorbed, suggesting even greater differences in coverages between the fluorophobe–PEO and associative thickeners.

In reality, the most significant differences between the fluorophobe–PEO and associative thickener series were observed at low coverage. This suggests the reversal of the molecular weight selectivity

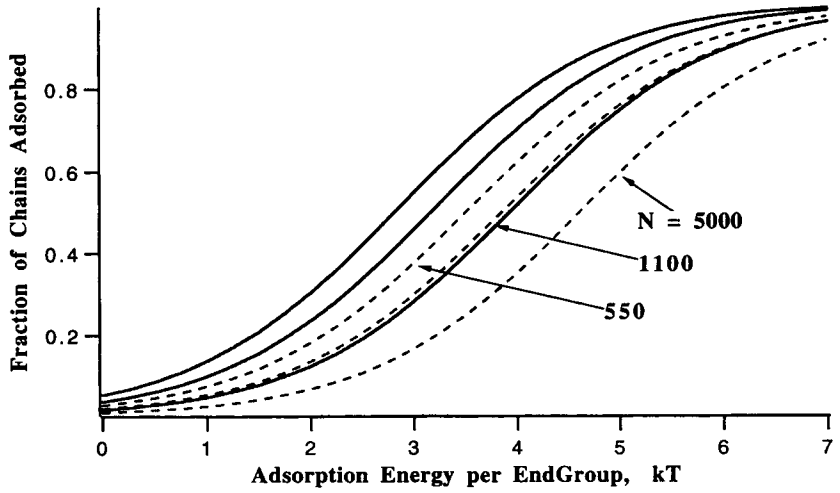


Figure 6 The calculated effect of end-group hydrophobicity on the fraction of adsorbed chains, for polymers with 1 (----) and 2 (——) ends labeled.

and the resulting magnification of the impact of the fluorophobes on the coverages the primary factor leading to the similarity in the fluorophobe–PEO and associative thickener isotherms. The potential for molecular weight selectivity can be gauged quantitatively by examining Figure 6. For chains with $N = 1100$ and $U_{end} = 3$ kT, a fraction (0.27) should be adsorbed. With chain degradation yielding a lower molecular weight population with $N = 550$, the adsorbed fraction becomes 0.35, such that the lower molecular weight chains are favored on the surface.

As a final point, the model can yield further insight into the adsorption behavior for chains with adsorbing main backbones containing hydrophobic ends. Consider a singly capped chain with $N = 1100$ and $U_{end} = 2.5$ kT. According to Figure 6, approximately 18% of these chains will be adsorbed. If one makes a mean field approximation, smearing the effect of the first hydrophobe across the backbone, this state would be similar to that of homopolymer adsorption. Then by considering the incremental effect of adding a second sticker (going from singly to doubly capped chains in the model) one implies a parallel between going from homopolymer adsorption without end-group modification to homopolymer adsorption with one end modified. This increases the surface coverage by a factor of 2, as discussed above. Hence, the observations of the fluorophobe–PEO experiments are in accord with the predictions of this model, taking into account the obvious restrictions.

Morphological Factors

Clearly the hydrophobic end-group modification alters the surface excess, and evidence for its impact on the molecular weight selectivity of the surface stems from a comparison of fluorophobe and associative thickener behavior. The end groups can also potentially impact the interfacial morphology. We discuss the possibilities only briefly here, in the absence of direct evidence favoring a particular morphology.

Without end-group hydrophobicity, classical homopolymer layers comprised of tails, loops, and trains should persist. The other extreme, with strong end group–substrate attractions, and without attractions between the substrate and the main backbone is the polymer brush where chains extend normal to the interface at high coverages. A third possibility is layers with backbone–substrate interactions and polymer–polymer interactions (in micellelike structures or clusters) leading to enhanced coverages compared with the homopolymer coverage. This third morphology is loosely termed "multilayer coverage" because there could conceivably be a population of adsorbed chains which have relatively few direct contacts with the surface but which stay near the interface because of interpolymer interactions. No formal layering is implied.

The influence of backbone–substrate attractions on brush formation has been assessed by Alexander,[33] but experimental confirmation of brushes in systems with adsorbed backbones is a topic of dispute.[13,16] It is conceivable, however, that with sufficient surface crowding, the main backbones could be forced from the surface to yield an end-adsorbed brush. Hence, it is fair to compare experimentally determined isotherm features to the parameters of a brush model. Clearly both series of molecules exhibit elevated coverages and decreased area/chain (in Table II) with increased end-group hydrophobicity, an observation in accord with brush and multilayer models. The adsorption strength, calculated from the initial slope of the fluorophobe–PEO series is far too low for the formation of polymer brushes, although the increase in slope with increased end-group hydrophobicity is consistent with the brush scenario. The steep initial slope of the associative thickener isotherm is consistent with the brush picture; however, the same slope is seen for the H-capped and C_{16}-capped associative thickeners arguing against any correlation between the initial slope and parameters in the brush model. Therefore, the brush model is not entirely satisfactory for the highly modified members of either the fluorophobe–PEO or associative thickener series.

The multilayer model presents some features consistent with the observations presented here; however, the model hinges on whether or not significant numbers of hydrophobic chain ends face the solvent. For doubly capped chains, the extent to which entropy favors configurations with only one end adsorbed will depend on the strength of the backbone adsorption; but calculations suggest there should be a significant number of dangling hydrophobes, as long as the hydrophobicity is not too great. For the singly capped chains, the extent to which the hydrophobic end remains free also depends on their hydrophobicity. For the fluorophobe–PEO series, the reversal of molecular weight selectivity (the best hypothesis which can explain the relative coverages seen for the fluorophobe–PEO and associative thickener series) implies that there is significant endgroup–substrate interaction, and reduces the likelihood of multilayer structures for the singly capped chains.

At this point, most of the evidence points to the idea that the end-group hydrophobicity brings some of the hydrophobic ends to the surface (where they would otherwise be found in the tails of the classic homopolymer layer). The extent to which the backbone–substrate contacts are diminished by the adsorbed chain ends is not clear; however, there is evidence that the internal IPDI linkages may more tenaciously adhere to the surface than pure PEO. Therefore, in the systems where the end groups are not sufficiently hydrophobic to yield brushes, one can expect a reversal of the surface molecular weight selectivity, and for doubly capped chains some multilayer coverage. With greater hydrophobicity per end group, it would follow that more chain ends would come to the surface to ultimately overcome the entropic barrier, and with the highest hydrophobicity, brushes would be favored over multilayer morphologies and those where both the backbone and the chain ends reside on the surface.

CONCLUSIONS

This work compared the adsorption behavior of two series of hydrophobically end-modified PEOs, a fluorphobe–PEO series containing one hydrophobe per chain and an associative thickener series with two primary hydrophobic end groups in addition to weaker internal hydrophobes. Both sets of polymers exhibited increased coverage as the end-group hydrophobicity was increased; however, it was not expected that the plateau coverages from the singly and doubly capped chains would be so nearly similar. For the fluorophobe–PEO series, the initial slope also increased up to a factor of 3 with increasing end-group hydrophobicity, up to C_{12} groups in one end per chain. The associative thickener isotherms had very steep initial slopes which did not vary with end-group hydrophobicity.

The steep, hydrophobe-insensitive initial slopes seen with the associative thickeners were attributed to the internal IDPI hydrophobes. IPDI, when added to a single PEO chain end, had been shown by the fluorophobe–PEO experiments to almost double the coverage. While hydrophobic groups are generally less influential when placed far from the chain ends, the regular placement of IPDI every 8000 molecular weight units in the associative thickeners appears to increase the overall hydrophobicity of the chain, increasing the initial slope drastically and the plateau coverage moderately, compared with the coverage seen for weakly modified FITC–PEO.

The best explanation of the similar mass coverages of the fluorophobe–PEO and associative thickener series, despite the significantly greater hydrophobicity of the latter, was a reversal of molecular weight selectivity of the surface, a factor important in polydisperse samples. For homopolymer adsorption, high-molecular-weight species are favored on the surface; however, when adsorption is driven by the affinity of the chain ends for the surface, lower molecular weight chains adsorb preferentially from a polydisperse mixture. The preference of the surface for low-molecular-weight species has been previously established for brush-forming systems, and calculations confirmed a similar molecular weight preference for systems with weaker end-group hydrophobicities. The experiments indirectly confirmed the preference for adsorption of low-molecular-weight chains bearing weak hydrophobes, an effect which tends to magnify the effect of the end groups on the apparent mass coverages measured by the fluorescence assay.

Finally, though this investigation did not include any direct probe of interfacial morphology, the potential for the existence of various interfacial features was checked for consistency against the measured isotherms. Plateau coverages of the C_{16}-associative thickeners were consistent with brush formation while the other hydrophobically modified sample coverages suggested the onset of brush formation. The low-coverage region of the isotherm, however, demonstrated that the interaction between the backbone and the substrate was strong, and its insensitivity to end-group hydrophobicity for the associative thickeners did not favor a brush model. A second morphology with enhanced coverage through interpolymer associations was shown to be possible, especially for the associative thickeners. It was concluded, therefore, that as the end-group hydrophobicity is increased over a series of samples, the first effects are a reversal of the molecular weight selectivity of the surface and enhanced coverage through a net increase in the adsorption energy and through interpolymer associations (the latter is an especially important possibility for doubly capped chains and those exhibiting strong backbone–substrate attractions).

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APPENDIX

The statistical mechanical formulation presented here extends a previous model[14,15] to predict the relative adsorbed amounts for different molecular architectures, where the end group–surface attraction (U_{end}) is varied and singly and doubly capped chains compared. This treatment approximates the polymer backbone as a nonadsorbing gaussian chain containing sticky end groups which are attracted to a planar wall of infinite extent. The infinite wall treatment is reasonable in situations such as ours where the polymer coil is considerably smaller than the spherical particles of the latex substrate. The behavior of the chains with sticky ends is modeled by considering the random walk probability for free and adsorbed configurations, with the appropriate weighting to account for the sticky end groups.

A random walk backbone of N steps or statistical segments of length l near an impenetrable wall (placed at the origin) is described by

$$P_N^w(x|x') = 2\sqrt{\pi}\sqrt{\frac{3}{2Nl^2}}\left\{\exp\left[-\frac{3}{2Nl^2}\times(x-x')^2\right]-\exp\left[-\frac{3}{2Nl^2}(x+x')^2\right]\right\} \quad \text{(A1)}$$

where x and x' represent the starting and finishing points of the random walk, or the positions of the two chain ends. Integration of x and x' from 0 to ∞ yields a normalization factor for the probability associated with the various adsorbed configurations. The fraction of configurations available to chains with one end adsorbed is obtained by placing one end at the surface (at $x = l/2$) and integrating the x' (the other chain end) from 0 to ∞. The fraction of configurations available to chains with both ends adsorbed is obtained by placing both chain ends on the surface ($x = x' = l/2$). Hence the fractions of configurations available to chains with $2(P_2^0)$, $1(P_1^0)$, and no ends (P_0^0) adsorbed becomes

$$P_2^0 = \frac{1}{\sqrt{\pi}}\sqrt{\frac{3}{2Nl^2}}\left[1-\exp\left(\frac{-3}{2N}\right)\right] \quad \text{(A2)}$$

$$P_1^0 = \text{erf}\left(\tfrac{1}{2}\sqrt{\frac{3}{2Nl^2}}\right) \quad \text{(A3)}$$

$$P_0^0 = 1 - 2P_1^0 - P_2^0. \quad \text{(A4)}$$

The superscript zero in these terms reminds the reader that these probabilities contain only gaussian statistics and do not yet account for the impact of the end group–substrate attractions. Note that as the molecular weight increases, the fraction of configurations available to the adsorbed chains decreases, primarily because the fraction of configurations available to the free chains increases. Hence, adsorption becomes more entropically unfavorable as the molecular weight increases, so that higher molecular weight chains will require stickier end groups to induce adsorption. Also note that the fraction of configurations available to chains with both ends adsorbed is several orders of magnitude less than that available to chains with one end adsorbed. Hence, unless the end-group attraction to the surface is very strong, the configuration with one end adsorbed will be favored in layers of adsorbed doubly capped chains.

End group–substrate attractions are combined with the raw gaussian probabilities in Eqs. (A2)–(A4) via a Boltzmann distribution to yield the fraction of chains adsorbed for the singly and doubly capped chains:

Fraction adsorbed (singly capped)

$$= \frac{P_1^0 e^{-U_{end}}}{P_1^0 e^{-U_{end}} + P_0^0} \quad \text{(A5)}$$

Fraction adsorbed (doubly capped)

$$= \frac{P_2^0 e^{-2U_{end}} + 2P_1^0 e^{-U_{end}}}{P_2^0 e^{-2U_{end}} + 2P_1^0 e^{-U_{end}} + P_0^0}. \quad \text{(A6)}$$

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