already in the high-temperature region. Consequently, for comparison of the rates of b* → a* in polymers and monomer models, *R* value should be compared at a much lower temperature where both polymers and monomer models are in the low-temperature region. From the discussion above, the differences in *R* values between polymers and monomer models should be larger at low temperature. Details of temperature dependence will be published elsewhere.

(14) While the decay of the b* band is multiexponential and the exact kinetic solution is difficult to obtain, the decay of the a*

band is nearly constant at ~5 ns for both 1d and poly(MMA-co-2) in EAc at 25 °C. Preliminary study on the temperature dependence of *R* value reveals that back-reaction from the b* state is negligible in these polymers at room temperature.

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Adsorption of Block Copolymers in Selective Solvents

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ABSTRACT: We study the adsorption of A–B diblock copolymers on a solid plane in a highly selective solvent. The A part is in a poor solvent and forms a molten layer on the solid wall where the solvent does not penetrate. The B part, in a good solvent, forms a brush grafted on this molten layer. The structure of the adsorbed copolymer film is governed by the chemical potential in the solution in contact with the wall. Copolymer chains have a tendency to self-aggregate in this solution forming several different mesophases. We present first a scaling theory of micelle and lamella formation and then study the geometry of the adsorbed film in equilibrium with these two phases. An important issue of this work is the role of the van der Waals interaction between the wall and the adsorbed A layer. If the copolymer asymmetry is large enough, i.e., if the B part has a higher molecular mass than the A part, in a wide range of concentration, and this quite independent of the phase behavior of the solution, the thickness of the molten A layer results from a balance between the van der Waals energy and the stretching energy of the brush. The B chains are almost fully extended in the brush. Various other adsorption regimes are found when the asymmetry of the copolymer is decreased.

I. Introduction

Block copolymers provide a simple and versatile method for steric stabilization of colloidal particles suspended in a solution.[1,2] The most direct scheme for colloid protection amounts to adsorbing a diblock chain from a solution in a selective solvent. Then the insoluble block A (which we sometimes call the "anchor") precipitates near the particles surface and adsorbs on it forming a dense film, whereas the soluble block B (called the "buoy") extends into the solution and forms an external layer ("brush"). For example,[3] for particles suspended in water, A may be an aliphatic chain, while B may be a water-soluble polymer such as POE or polyacrylamide. The relevant parameter for steric stabilization is then the density of chains in a "brush" σ or equivalently the area per copolymer junction Σ. For small Σ (i.e., $\Sigma < N_B^{6/5}a^2$ where N_B is the "buoy" polymerization index and a the monomer length) the chains in the brush are stretched and when two protected surfaces are brought together they repel each other. Such interactions have been studied by using Israelachvili force measurement apparatus for model block copolymers, polystyrene–polyvinylpyridine in cyclohexane, by Hadzioannou et al.[4] The aim of the present work is to estimate Σ, assuming that the protective layer is obtained by equilibrium adsorption from a solution of diblock copolymers in a selective solvent. In particular, we study the role of the molecular parameters of the chains, such as their composition or molecular weight, and of the solution concentration on the structure of the protective layer.

The structure of a protective layer in equilibrium with a reservoir containing copolymer chains is determined not only by the free energy of a chain in the layer but also by the external chemical potentials of the chains and the solvent. Hence adsorption processes are complicated by the tendency of copolymer chains to self-associate and form organized structures (micelles, lamellas, ...).[5,6] For a description of the adsorption we thus need a model for both the protective layer and the solution of copolymer chains.

We shall simplify the description by considering the case of a highly selective solvent, very poor for A and very good for B. Then the solvent does not penetrate the A layer precipitated against the solid surface, which is essentially a molten A film. We shall also neglect the concentration gradients in the copolymer layer. An important issue of this work is the role of long-range forces.[7] We will consider the simple case of van der Waals forces and neutral polymers, but the results could easily be extended to different kinds of long-range forces. In such a highly selective solvent, we have constructed a simple model of self-association of the copolymer solution. We consider two simple limiting cases, that of spherical micelles and that of lamellar structures; we limit our considerations to dilute solutions and situations close to the critical micelle concentration.

The paper is organized as follows: In the next section, we study the spreading of a copolymer droplet of finite volume on the wall; in section III, we derive the general properties of the adsorbed copolymer layer when the chemical potentials in the solution are known. These chemical potentials are calculated in section IV for micellar phases and lamellar phases and adsorption in equilibrium

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with these phases is discussed. Section V discusses the effect of the penetration of the solvent in the molten anchor layer.

II. Structure of A Block Copolymer Wetting Film: "Pancakes"

When the adsorbing wall is in contact with a pure solvent, a small droplet of block copolymer of finite volume V is deposited on the wall. At equilibrium, the drop spreads and forms a very thin wetting film on the wall. We study here the properties of this wetting film assuming that no polymer is dissolved in the bulk of the liquid. Although this is not a geometry where experiments are likely to be made, we consider it here for two reasons:

i. The absence of copolymer in the solvent makes the problem quite simple and one can compare the relative importance of the interaction of the copolymer with the solid surface and of the entropic contribution of the copolymer to the free energy.

ii. The equilibrium thickness of the film in this geometry plays a major role in the general discussion of the statility of block copolymer adsorbed layers which will be made later on.

As already mentioned the diblock copolymer is composed of two chemically different chains A and B. The B part has a polymerization index N_B and is in a good athermal solvent; when the copolymer is free in the solvent, the radius of gyration of the B part is given in a Flory approximation by $R_{FB} \simeq N_B^{3/5}a$, a being a monomer length. The B monomers are repelled by the wall. The A part has a polymerization index N_A and is totally incompatible with the solvent. As it is often the case in practice, polymers A and B are highly incompatible, one thus expects the formation of regions of pure molten polymer A where neither the solvent nor monomers B penetrate. This of course is an extreme limit, the molten A layers are always slightly swollen by the solvent, we will discuss this effect in section V, it will be neglected here. The A monomers are strongly attracted to the wall. The characteristic radius of the A part of the polymer is $R_{GA} = N_A^{1/2}a$. The asymmetry between the two parts of the copolymers is measured by

$$\beta = R_{FB}/R_{GA} = N_B^{3/5}/N_A^{1/2}$$

When $\beta = 0$ (homopolymer A) the anchor forms on the solid wall a thin film which has been called a pancake.[8] The important physical parameters are the three interfacial tensions γ_{WA}, γ_{WS}, and γ_{AS} (between wall and polymer A, wall and solvent, and polymer A and solvent) and more precisely the spreading power S defined as $S = \gamma_{WS} - \gamma_{AS} - \gamma_{WA}$ and the long-range interactions between the wall, the polymer A, and the solvent. We study here the simple case where these interactions can be described only in terms of van der Waals forces by a negative Hamaker constant $A_{WAS} = -A$ such that the energy of a film of thickness e per unit surface is written as

$$P(e) = -A_{WAS}/12\pi e^2 = A/12\pi e^2 \tag{1}$$

The van der Waals force has thus a thickening effect on the adsorbed layer. When the spreading power S is positive (the only case which will be considered throughout the paper), the equilibrium thickness of the homopolymer A pancake is

$$e_0 = (A/4\pi S)^{1/2} \tag{2}$$

Notice that although this thickness e_0 is of the order of a few monomer lengths a, i.e., much smaller than a chain radius R_{GA}, no effect related to the confinement of the polymer has been included. de Gennes[9] has shown that
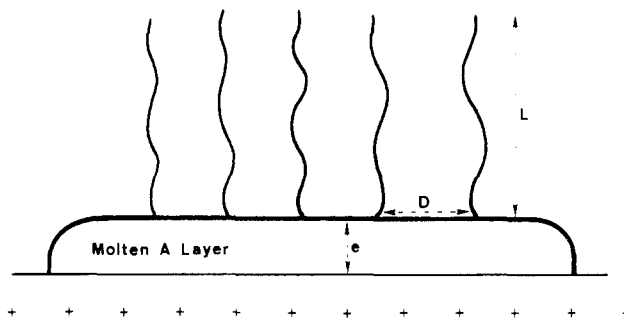

Figure 1. "Pancake formation". The molten A pancake has a thickness e; the grafted B brush has a thickness L. The surface density is $\sigma = (a/D)^2$.

for molten polymers these effects exactly vanish. The end-to-end distance in the direction parallel to the plane is of the order of R_{GA}.

For true copolymers $\beta \neq 0$ (we will restrict ourselves from now on to situations where $\beta > 1$), the A part of the copolymer forms a thin pancake of thickness e where neither the solvent nor the B monomers penetrate. The B parts of the copolymer, the buoy, forms thus a grafted layer of thickness L outside the pancake (see Figure 1). We call $D = \Sigma^{1/2}$ the average distance between "heads" (junction points of the copolymer), the surface density is $\sigma = a^2/D^2$. The pancake is composed only of molten polymer A so that

$$N_A \sigma a / e = 1 \tag{3}$$

The structure and energy of grafted layers with a surface density σ have been studied in detail by Alexander[10] (see Appendix A). When $\sigma < \sigma_1 \sim N_B^{-6/5}$ the B chains are unperturbed. When $\sigma \gg \sigma_1$ the chains are stretched; the layer equilibrium thickness is

$$L \simeq N_B a \sigma^{1/3} \tag{4}$$

The energy per unit surface of the layer is (throughout the paper, the temperature unit is such that the Boltzmann constant k_B is equal to 1)

$$F_B^S = \frac{T}{a^2} N_B \sigma^{11/6} \tag{5}$$

The total energy of the copolymer pancake may then be written as

$$\mathscr{F} = \mathscr{A}\left[-S - \tilde{\gamma}_{AS}\frac{e}{N_A a} + \frac{A}{12\pi e^2} + \frac{T}{a^2}N_B\left(\frac{e}{N_A a}\right)^{11/6} \right] \tag{6}$$

$\mathscr{A}$ is the area covered by the pancake on the plane related to the total volume of monomers A by $V_A = e\mathscr{A}$, the first two terms account for the capillary energies (the second term accounts for the presence of junction points and is proportional to their surface density), the third term is the van der Waals energy (we have neglected the contribution of the grafted layer where the concentration is small), and the last term is the energy of the grafted layer. There is no entropic contribution of polymer A in this surface energy; as already explained, there is no confinement energy; if the layer thickness e is larger than the radius of the A chains, a stretching energy F_A^S should be included this term is always negligible here.

The equilbrium thickness e is obtained by minimization of the free energy (6) at constant volume V_A:

$$S = \frac{A}{4\pi e^2} - \frac{5}{6}\frac{T}{a^2}N_B\left(\frac{e}{aN_A}\right)^{11/6} \tag{7}$$

We consider here only complete wetting situations $S > 0$ (monomers A are strongly attracted by the wall) and assume $AN_A/T \gg 1$ which is usually true in real situations; this leads to two different regimes.

a. Homopolymer Regime. When the spreading power S is larger than a critical value

$$S_c = \frac{T}{R_{GA}{}^2}\beta^{20/23}(AN_A/T)^{11/23}$$

the effect of the buoy is small and the pancake thickness is $e = e_0$. The thickness of the grafted layer is

$$L = N_B a\left(\frac{e_0}{N_A a}\right)^{1/3} = R_{FB}\beta^{2/3}\left(\frac{e_0}{a}\right)^{1/3} \quad (8)$$

The chains are extended in the grafted layer, this of course requires $\sigma > \sigma_1$ or $S < (A/a^2)\beta^4$ otherwise the B chains remain unperturbed.

b. van der Waals–Buoy Regime. When the spreading power S is smaller than S_c, it becomes negligible in eq 7, the pancake thickness results from a balance between the grafted layer stretching energy and the van der Waals energy

$$e = a(AN_A/T)^{6/23}\beta^{-10/23} \sim N_A{}^{11/23}N_B{}^{-6/23} \quad (9)$$

The thickness of the grafted layer is

$$L = N_B{}^{21/23}N_A{}^{-4/23}a \simeq R_{FB}\beta^{12/23}(AN_A/T)^{2/23} \quad (9a)$$

In this regime, the thickness of the grafted layer scales with N_B with an exponent slightly smaller than 1. The thickness of the molten A layer decreases with N_B.

In practice if both parts of the copolymer are long polymers and if the copolymer is not too dissymmetric ($\beta < N_A{}^{3/5}$), S should be larger than S_c and the pancake thickness depends only on the anchor A. The other regime is obtained for very dissymmetric copolymer $\beta \gg N_A{}^{3/5}$; we will not consider such polymers in the following.

III. Block Copolymer Adsorption from Solution: General Results

In most experiments, the adsorbing wall is in contact with a bulk copolymer solution which plays the role of a reservoir. The whole wall is covered by a copolymer layer; the precise structure of the adsorbed layer depends on the structure of the solution in the reservoir. At very low bulk concentration, the solution is isotropic and chains are isolated; it then reaches a critical micellar concentration (cmc) located well in the dilute regime. At higher concentrations the copolymer forms organized mesophases with various structures.[5,6] In the present section, we characterize the reservoir by the chemical potential of the polymer chains μ_{ex} and its osmotic pressure π_{ex}; these two quantities should then be related to the bulk concentration in each region of the phase diagram. The phase diagram of diblock copolymers being very rich and quite complicated, we do not consider here all possible mesophases, but limit the study in the next section to very dilute solutions both below and above the cmc and to the simplest possible organized phase, a lamellar phase.

1. Structure of the Adsorbed Layer. In the presence of a reservoir where the chemical potential is μ_{ex} and the osmotic pressure π_{ex}, the equilibrium structure of the block copolymer layer minimizes the grand canonical free energy[11]

$$\Omega = \mathcal{F} - \mu_{ex}n + \pi_{ex}V_B \quad (10)$$

$\mathcal{F}$ is the total free energy of the copolymer layer, n the number of adsorbed chains, and V_B the volume accessible to the solvent. Assuming no penetration of the solvent into
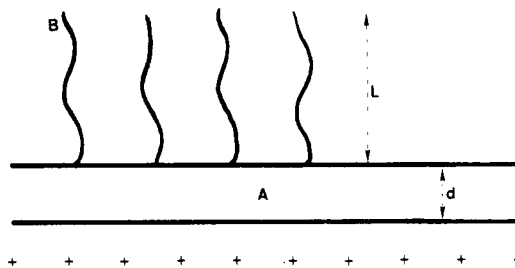
Figure 2. Block copolymer adsorbed film. The anchor forms a molten layer of thickness d on the surface; the B brush has a thickness L.

the molten A layer, the volume V_B is related to the thickness of the grafted buoy layer by $V_B = L\mathcal{A}$ (Figure 2). The area of the plane $\mathcal{A}$ being constant, we consider the grand canonical free energy per unit surface $G = \Omega/\mathcal{A}$. This is written as

$$G = -S - \tilde{\gamma}_{AS}\sigma - \mu_{ex}\sigma a^{-2} + P(d) + G_B{}^S(\sigma,\pi_{ex}) + F_A{}^S(d) \quad (11)$$

As in eq 6, the first two terms represent the contribution of the capillary energies and $P(d)$ is the van der Waals energy of the pure molten A layer of thickness d given by eq 1 (d is related to σ by eq 3).

$F_A{}^S$ is the stretching energy[12] of the A chains which must be included when $d \gg R_A$.

$$F_A{}^S = \frac{3T}{2}\sigma a^{-2}\frac{d^2}{R_{GA}{}^2} \quad (12)$$

$G_B{}^S = F_B{}^S + \pi_{ex}L$ is the Gibbs free energy of a grafted B layer of surface density σ under an external osmotic pressure π_{ex}. It is studied in detail in Appendix A; if the external solution is dilute, the external osmotic pressure might be neglected, the thickness of the buoy layer is given by eq 4, and the free energy $G_B{}^S \sim F_B{}^S$ is given by eq 5.

The equilibrium thickness of the anchor d or equivalently the equilibrium surface density σ is obtained by minimization of the free energy G keeping the chemical potential μ_{ex} and the osmotic pressure π_{ex} constant

$$\mu_{ex} + \tilde{\gamma}_{AS}a^2 = -\frac{N_A A a^3}{6\pi d^3} + \frac{11}{6}N_B T\left(\frac{d}{N_A a}\right)^{5/6} + \frac{9}{2}T\frac{d^2}{N_A a^2} \quad (13)$$

According to the value of the effective chemical potential $\tilde{\mu} = (\mu_{ex} + \tilde{\gamma}_{AS}a^2)/T$, we distinguish four adsorption regimes (Figure 3).

i. Rollin Regime. When $\tilde{\mu}$ is negative and large $\tilde{\mu} < -\mu_1 \simeq -(AN_A/T)^{5/23}\beta^{30/23}$ the dominant term on the right-hand side of eq 13 is the van der Waals energy. The thickness of the A film is

$$d = a[AN_A/T\tilde{\mu}]^{1/3} \quad (14)$$

This is the same equation as the equation giving the thickness of undersaturated helium films (first studied by Rollin) on a solid substrate.[13]

ii. van der Waals–Buoy Regime. When the absolute value of chemical potential $\tilde{\mu}$ is small $|\tilde{\mu}| < \mu_1 = (AN_A/T)^{5/23}\beta^{30/23}$, the left-hand side becomes negligible in eq 13 and the equilibrium thickness d results from a balance between van der Waals forces and the stretching energy of the buoy $F_B{}^S$

$$d = (AN_A/T)^{6/23}\beta^{-10/23}a \sim N_B{}^{-6/23}N_A{}^{11/23} \quad (15)$$

iii. Buoy-Dominated Regime. When the chemical potential $\tilde{\mu}$ is positive and such that $\mu_1 < \tilde{\mu} < \mu_2 \simeq$
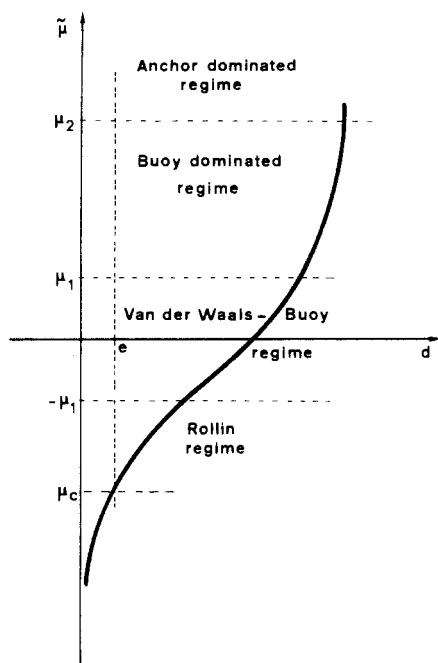
Figure 3. Variation of the effective chemical potential $\tilde{\mu}$ as a function of the anchor molten layer thickness d. Various adsorption regimes are found when $\tilde{\mu}$ is varied; no adsorption is possible if $d < e$ ($\tilde{\mu} < \mu_c$).

$N_A^{5/7}\beta^{20/7}$, the dominant term on the right-hand side of eq 13 is the stretching energy of the buoy

$$d = \tilde{\mu}^{6/5}\beta^{-2}a \tag{16}$$

iv. Anchor-Dominated Regime. At larger values of $\tilde{\mu}$ the stretching energy of the anchor dominates

$$d = N_A^{1/2}a\tilde{\mu}^{1/2}$$

Of course, the maximum size of the A chains is when they are fully stretched $d = N_A a$, the anchor dominated regime exists only if $\beta \ll N_A^{1/10}$ or $N_B < N_A$.

2. Stability of the Adsorbed Film. In any of these adsorption regimes, the adsorbed copolymer film is stable only if the potential G has a lower value at equilibrium than in the absence of any adsorbed film where by construction $G = 0$.

In order to study this stability condition, we rewrite eq 11:

$$G = -S + g(d) - \mu_{ex}\sigma a^{-2} \tag{11a}$$

where $g(d)$ includes both the van der Waals energy and the copolymer elastic energies.

The stability condition reads

$$S > g(d) - d\frac{\mathrm{d}g}{\mathrm{d}d} \tag{17}$$

It can now be directly checked from eq 7 that the pancake thickness e calculated in section II[8] is in this language such that

$$S = g(e) - e\frac{\mathrm{d}g}{\mathrm{d}e} \tag{7a}$$

(One must of course neglect the small difference due to the external pressure between $F_B{}^S$ and $G_B{}^S$ and include in the pancake analysis the stretching energy of chains A which was neglected in section II.)

An adsorbed copolymer film on the wall is thus stable if the equilibrium thickness d is larger than the pancake
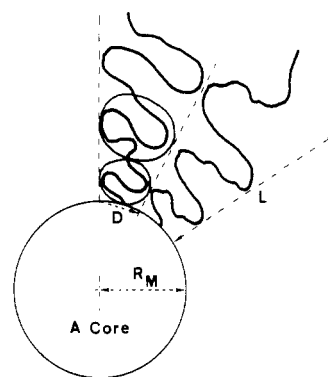
Figure 4. Block copolymer micelle. The core of radius R_M is formed of molten polymer A; the external layer has a thickness L.

thickness e. This determines a threshold for adsorption in the chemical potential $\mu_{ex}{}^c$ such that

$$d(\mu_{ex}{}^c) = e$$

As we have seen, e is generally in the range of a few angstroms, i.e., on the order of a few monomer lengths, and the adsorption threshold will thus be in the Rollin regime. This corresponds to extremely small concentrations as shown below, it is thus probably not a measurable effect for large N_A where as soon as the block copolymer has a finite concentration in the solution, it adsorbs on the wall.

IV. Block Copolymer Adsorption from Micellar and Lamellar Solutions

The important parameter which governs the structure of the adsorbed copolymer layer is the effective chemical potential $\tilde{\mu} = (\mu_{ex} + \tilde{\gamma}_{AS}a^2)/T$; we now calculate this chemical potential for micellar solutions and lamellar phases.

1. Adsorption from a Micellar Solution. a. Critical Micelle Concentration. At extremely low bulk volume fraction Φ_b, the block copolymers do not aggregate and in a first approximation different chains behave independently. The chemical potential of a chain is

$$\mu_{ch} = T \log \Phi_b + \Delta F \tag{18}$$

ΔF is the free energy of one isolated chain. As we have implicitly done earlier, we take as a reference state for B chains isolated chains in a good solvent and for A chains the molten state. The contribution of the B part to ΔF is small, the contribution of the A part has been shown to be dominated by surface properties,[14,15] in a very poor solvent.

$$\Delta F = 4\pi\gamma_{AS}R_A{}^2$$

In the extremely selective solvent which we consider, the A part of the copolymer is collapsed and forms a small molten globule of size $R_A = N_A^{1/3}a$ so that

$$\mu_{ch} = T \log \Phi_b + 4\pi\gamma_{AS}a^2 N_A^{2/3} \tag{18a}$$

As the concentration is increased, it reaches the cmc where micelles begin to form. We study the properties of these micelles following a simplified theory quite similar to the one proposed in ref 6. For the sake of simplicity, we consider only a bimodal distribution of aggregates: single chains and monodisperse micelles. Polydispersity of the micelles could be treated along the lines of ref 24. A given micelle is formed with p copolymer chains and its core has a radius R_M (Figure 4). The junction points of the copolymer are located on the surface of the core; the surface density is $\sigma = pa^2/4\pi R_M{}^2 = p^{1/3}/N_A^{2/3}$.

The buoy B forms a grafted layer in a good solvent around this spherical core. The properties of such grafted layers were studied in detail by Daoud and Cotton;[16] the main results are rederived in Appendix B.

Whenever the concentration of the micelles is small, each micelle might be considered independently as being in equilibrium with a reservoir composed of the free chains in solution. The chemical potential μ_{ex} imposed by the reservoir is related to the concentration of free chains by eq 18. The number of chains in a micelle p minimizes the grand canonical free energy

$$\Omega = F_M - \mu_{ex}p + \tfrac{4}{3}\pi[(R_M + L)^3 - R_M^3]\pi_{ex} \quad (19)$$

where F_M is the free energy of a micelle. The effect of the reservoir osmotic pressure π_{ex} is small (see Appendix B) and will be neglected hereafter.

With only leading order terms the micelle free energy F_M is written as

$$F_M = 4\pi\gamma_{AS}R_M^2 + F_B^S \quad (20)$$

The first term is the interfacial energy between the molten A core and solvent; F_B^S is the energy of the grafted buoy layer. We consider here the case where the grafted layer thickness L is larger than the core radius R_M. The energy F_B^S is then given by eq B.5

$$F_B^S = Tp^{3/2} \log N_B^{3/5}/N_A^{1/3}p^{2/15}$$

Several small corrections were neglected in the micelle free energy F_M: The contribution of the junction points in the surface energy gives a correction $4\pi\bar{\gamma}_{AS}R_M^2$.

A careful consideration of the long-range van der Waals forces leads to curvature corrections to the surface tension [17] $\gamma_{AS} \rightarrow \gamma_{AS}(1 - \delta/R_M)$; the length δ is in general of the order of a monomer length a, i.e., much smaller than the micelle radius R_M. The junction point entropy $Tp \log \sigma$ is negligibly small when the surface density σ is small. The elastic energy of the chains in the micelle core has been studied in ref 25. It can be checked that this contribution is always negligible here.

The equilibrium value of p is obtained by minimizing the free energy Ω at fixed chemical potential μ_{ex}. Micelles start to form when the value of Ω at the minimum is negative. These two conditions determine the critical micelle concentration.

$$\Phi_{cmc} = \exp\left(\frac{\mu_{cmc}}{T} - \frac{\Delta F}{T}\right) = \exp\left(\frac{\mu_{cmc}}{T} - \frac{4\pi}{T}\gamma_{AS}a^2N_A^{2/3}\right) \quad (21)$$

where μ_{cmc} is the chemical potential at the cmc

$$\mu_{cmc} = TN_A^{2/5}\left[\frac{\gamma_{AS}a^2}{T \log \dfrac{N_B^{3/5}}{p^{2/15}N_A^{1/3}}}\right]^{3/5} \quad (22)$$

The number of copolymer molecules per micelle at the cmc[18] is

$$p = N_A^{4/5}\left[\frac{\gamma_{AS}a^2}{T \log \dfrac{N_B^{3/5}}{p^{2/15}N_A^{1/3}}}\right]^{6/5} \quad (23)$$

If we neglect the logarithmic corrections, the value of the cmc and the number of chains per micelle p depend only on the molecular mass of the anchor N_A. The volume fraction at the cmc is exponentially small, as the cmc is located well in the dilute regime.

The micelle core radius is

$$R_M = N_A^{3/5}a\left(\frac{\gamma_{AS}a^2}{T}\right)^{2/5} \quad (24)$$

This leads to a surface density

$$\sigma \simeq N_A^{-2/5}\left(\frac{\gamma_{AS}a^2}{T}\right)^{2/5} \quad (24a)$$

Finally, the grafted layer thickness L is, by use of eq B-4,

$$L = R_{FB}N_A^{4/25}\left(\frac{\gamma_{AS}a^2}{T}\right)^{6/25} \quad (24b)$$

It is larger than the core radius R_M if $R_{FB} > N_A^{11/25} \times a(\gamma_{AS}a^2/T)^{4/25}$ which is always the case when $\beta \gg 1$.

In an extremely dilute solution, chains are isolated and the chemical potential in the solution μ_{ex} is given by eq 18 which can be rewritten

$$\mu_{ex} = \mu_{cmc} + T \log \frac{\Phi_b}{\Phi_{cmc}} \quad (18b)$$

Above the cmc, in a first approximation, the concentration of free chains remains constant and the chemical potential is $\mu_{ex} = \mu_{cmc}$.

In order to be more quantitative, one should not consider only one isolated micelle but should include in the theory the translational free energy of the micelles and the interactions between micelles; this leads to a slow increase of the chemical potential above the cmc. We neglect this effect here and suppose that above the cmc the micelles have the structure that we have calculated exactly at the cmc.

b. Adsorption of Block Copolymers from Micellar Solutions. We now combine these results with the general results of section II to study the structure of the film adsorbed on the wall from a micellar solution.

The chemical potential μ_{cmc} given by eq 22 is positive and much larger than the thermal energy kT. As we have focused on polymers such that $N_B > N_A$ only two adsorption regimes are obtained, the buoy-dominated regime if $\beta < N_A^{3/50}(A/T)^{-1/6}(\gamma_{AS}a^2/T)^{23/50} = \beta_1$ and the van der Waals–buoy regime if $\beta > \beta_1$.

In general we expect $A/T \sim 1$ and $\gamma_{AS}a^2/T \sim 1$. If β is of order 1 the adsorbed layer is in the buoy dominated regime, but as soon as β becomes much larger than 1 van der Waals forces become important.

i. Buoy-Dominated Regime. The thickness of the anchor layer is from eq 16,

$$d = aN_A^{12/25}\beta^{-2}(\gamma_{AS}a^2/T)^{18/25} \quad (25)$$

β being close to 1, this thickness is approximately equal to the Gaussian radius of the A chains $R_{GA} = N_A^{1/2}a$. The surface density σ scales as

$$\sigma = N_A^{-13/25}\beta^{-2}(\gamma_{AS}a^2/T)^{18/25} \quad (26)$$

This is slightly smaller than the surface density in the micelles given by eq 24. The area per chain $\Sigma = \sigma^{-1}a^2$ is thus larger on the adsorbing wall than in the micelles.

The thickness L of the grafted layer is, from eq 3,

$$L = R_{FB}N_A^{4/25}(\gamma_{AS}a^2/T)^{6/25} \quad (27)$$

which is the same thickness as that of the micelle grafted layer (eq 24b). This has the same scaling behavior with N_B as the unperturbed Flory radius R_{FB} (the chains are not fully extended); however, this is much larger than the Flory radius due to the N_A dependence.

ii. van der Waals–Buoy Regime. As soon as $\beta \gg 1$, van der Waals forces play a dominant role. The thickness of the molten A layer is given by eq 9

$$d = a(AN_A/T)^{6/23}\beta^{-10/23}$$

Although this scales with $N_A^{1/2}$ approximately as $N_A^{1/2}$, it is much smaller than the Gaussian radius due to the N_B dependence.

The surface density is

$$\sigma = \left(\frac{AN_A}{T}\right)^{6/23}\frac{1}{N_A}\beta^{-10/23} \quad (28)$$

This again is smaller than the surface density in the micelle given by eq 24. The thickness of the B layer is given by eq 9a and is almost linear in N_B ($\sim N_B^{21/23}$).

2. Block Copolymer Adsorption from a Lamellar Phase. a. Structure of the Lamellas. Each lamella is composed of a molten A layer of thickness $2d_L$ and two grafted B layers of thickness L_L. It is in equilibrium with the free chains in the solvent between different lamellae where the chemical potential is μ_{ex} and the osmotic pressure π_{ex}. If we neglect any undulations of the lamellae,[16] the thickness d_L minimizes a grand canonical free energy which has the same structure as eq 11

$$G_L = 2[\gamma_{AS} - \tilde{\gamma}_{AS}\sigma_L - \mu_{ex}\sigma_L a^{-2} + \tfrac{1}{2}P_L(2d_L) + G_B^S(\sigma_L,\pi_{ex}) + F_A^S(d_L)] \quad (29)$$

where $\sigma_L = d_L/aN_A$ is the surface fraction on each surface of the lamella.

The main differences between the free energies of the lamella and the copolymer on the adsorbed plane come from the capillary energy and the van der Waals energy. There is just one interfacial tension from the lamella problem γ_{AS}, and the Hamaker constant A_{SAS} is always positive; the van der Waals energy has a thinning effect. The equilibrium thickness of the lamellae is such that

$$\mu_{ex} + \gamma_{AS}a^2 =$$
$$\frac{A_{SAS}N_A a^3}{48\pi d_L^3} + \frac{11}{6}N_B T\left(\frac{d_L}{N_A a}\right)^{5/6} + \frac{9}{2}T\frac{d_L^2}{N_A a^2} \quad (30)$$

The onset of lamellar phase formation would then require a comparison of the free energy of the lamellas with that of any other possible phase. This is far beyond the scope of this work. We will assume here that the lamellar phase exists and has a given surface density σ_L. This might not be the case for large asymmetries $\beta \gg 1$. Equation 30 then gives the chemical potential in lamellar phase μ_{ex} as a function of σ_L. Notice, however, that μ_{ex} is in any case larger than μ_{cmc} (the lamellar phase occurs always at a higher concentration than the micellar phase) and that eq 30 imposes a minimum value for μ_{ex}

$$\mu_{min} = \frac{253}{108}T\left(\frac{9A_{SAS}N_A}{220\pi T}\right)^{5/23}\beta^{30/23}$$

b. Block Copolymer Adsorption. The structure of the copolymer adsorbed layer is obtained from eq 30 and 13. Two different regimes are found.

If μ_{ex} is larger than $\mu_1 = T(AN_A/T)^{5/23}\beta^{30/23}$ (this will be always the case if the two Hamaker constants are such that $A = -A_{WAS} \ll A_{SAS}$), the van der Waals terms are negligible and $d_L = d$; the structure of the adsorbed polymer layer is the same as the structure of the lamellar phase. This result was already suggested by de Gennes.[20]

If $\mu_{ex} < \mu_1$, μ_{ex} is small and the adsorbed layer is in the van der Waals–buoy regime described in the previous section. The area per chain $\Sigma = a^2\sigma^{-1}$ is smaller in the

adsorbed layer than in the lamella.

V. Solvent Penetration in the Molten A Layers

Up to this point, we have considered that polymer A is extremely incompatible both with polymer B and the solvent and forms pure molten regions. Although this is generally true for polymer B if N_A and N_B are large, there is always a small penetration of the solvent in the molten A region. The monomer concentration c in the anchor layer on the adsorbing wall is then smaller than $1/a^3$. Equation 3 should be replaced by

$$N_A\sigma = dca^2 \quad (31)$$

If the chemical potential in the reservoir is μ_{ex} and the osmotic pressure is π_{ex}, the grand canonical free energy which gives the structure of the adsorbed layer is

$$G = -S - \tilde{\gamma}_{AS}\sigma - \mu_{ex}\sigma a^{-2} + P(d) + G_B^S(\sigma,\pi_{ex}) + F_A^S + dF_{MIX}^A(d,c) + \pi_{ex}d \quad (32)$$

The interfacial tensions S and $\tilde{\gamma}_{AS}$ are slightly modified by the dilution of the anchor layer. The Hamaker constant A is also changed, it increases from 0 at zero concentration to a positive value when $ca^3 = 1$. F_{MIX}^A is the mixing free energy of the A monomers in the layer of thickness d. The last term accounts for the penetration of the solvent in the layer; the volume accessible to the solvent is now the total volume $V = \mathcal{A}(L + d)$. This free energy G depends on two independent variables c and σ.

Minimization with respect to c gives the balance of pressures:

$$\pi_A(c) - \pi_{ex} - \frac{\sigma}{a^2}\frac{dF_A^{ch}}{dd} + \pi_d(d) + \left.\frac{\partial P}{\partial c}\right|_d \frac{c}{d} = 0 \quad (33)$$

$\pi_A(c)$ is the osmotic pressure in the adsorbed layer $\pi_A = c^2[\partial(F_{MIX}^A/c)\partial c]$, $F_A^{ch} = F_A^S\sigma$ is the elastic energy per chain which depends only on d, and π_d is the van der Waals disjoining pressure $\pi_d = -dP/dd$.

As shown above the external pressure π_{ex} and the elastic energy of the A chains are small; we will also assume that the solvent is so selective that the disjoining pressure gives a small contribution in the pressure balance. If this is not the case, one must take into account the local variation of the concentration c with the distance z to the wall and in particular include gradient terms in the free energy. Equation 33 might then be approximated by

$$\pi_A(c) = 0 \quad (34)$$

In the same poor solvent, a free A polymer would phase separate into a dense polymer phase and almost a pure solvent; eq 33 thus means that the concentration in the adsorbed layer is that of this equilibrium dense phase. More quantitatively,[12] the osmotic pressure within a Flory approach is given by a virial expansion

$$\pi_A(c) = \tfrac{1}{2}vc^2 + \tfrac{1}{3}w^2c^3 \quad (35)$$

The second virial coefficient v is negative in a poor solvent; it is often proportional to the shift from the Θ compensation temperature $v \sim (T - \Theta)/\Theta$. The third virial coefficient $w \sim a^3$ is positive. This leads to a concentration

$$c = -3v/2w^2 \quad (36)$$

Minimization of eq 32 with respect to σ yields then the equilibrium thickness d

$$\mu_{ex} + \tilde{\gamma}_{AS}a^2 = N_A\mu_A(c) + a^2\frac{d}{d\sigma}F_B^S + a^2\frac{d}{d\sigma}F_A^S + \frac{N_A}{c}\frac{\partial P}{\partial d} \quad (37)$$

This reduces to eq 13 when $ca^3 = 1$. The only extra term

being the chemical potential term $\mu_A(c) = \partial F_{MIX}{}^A/\partial c$ calculated in the dense equilibrium phase, which simply reflects the change in reference state for the A part of the polymer which should not be chosen as the molten state but as the equilibrium phase in the poor solvent.

The penetration of the solvent may be described as usual in a poor solvent in terms of thermal blobs[21] of size $\xi \sim a^4/|v|$ each containing $g = (|v|/a^3)^{-2}$ monomers so that the concentration $c = g/\xi^3$ is given by eq 36.

All the results of section III can then be used if we renormalize N_A by the number of blobs N_A/g and the monomer length a by the blob size ξ, both the Hamaker constant A and the radius ratio β being unchanged. (This transforms eq 13 into eq 37.) The same renormalization should be made for the determination of the external potential μ_{ex} in the study of micelle or lamella formation in the reservoir. (The scaling theory predicts then $\gamma_{AS} = T/\xi^2$.)

VI. Discussion

We have studied the equilibrium adsorption of diblock copolymers in a highly selective solvent on a solid wall taking into account possible mesophase formation in the solution in equilibrium with the adsorbed polymer. Four adsorption regimes have been found depending on the value of the external chemical potential μ_{ex}.

In extremely dilute solutions the theory predicts a threshold for adsorption which essentially depends on the spreading power of the anchor A and on the strength of the van der Waals energy of a film of polymer A in contact with the wall. Just above this threshold, the adsorption is controlled by the van der Waals energy (Rollin regime) and the thickness of the anchor layer d varies as $|\log \Phi_b|^{-1/3}$, Φ_b being the bulk volume fraction (cf. eq 14 and 18b). This, however, occurs at such a low concentration that it is probably not observable in practice except for very short anchor blocks.

At higher concentrations, chains self-aggregate to form micelles in solution. We have built a simplified scaling model of the critical micelle concentration predicting the cmc the number of chains per micelle and the chemical potential at the cmc as a function of the mass of the anchor forming the core of the micelle. Two adsorption regimes are found in equilibrium with a micellar solution depending on the asymmetry ratio β of the copolymer (van der Waals–Buoy regime and buoy-dominated regime). When β is of order 1 the adsorption is governed by the elastic energy of the buoy layer, the thickness of the molten A layer is approximately equal to the radius of gyration R_{GA} (eq 25), and the thickness of the buoy layer scales as the Flory radius of the B chains (eq 27). When $\beta \gg 1$ the geometry of the adsorbed copolymer results from a balance between van der Waals forces and the buoy layer elastic energy; the thickness of the grafted layer increases approximately linearly with its molecular mass (eq 9 and 9a).

If the solution at a even higher concentration is in a lamellar phase, the important result is that when van der Waals forces are small the structure of the adsorbed layer is the same as that of a lamella.

If the copolymer asymmetry is large enough, i.e., if the anchor has a much lower degree of polymerization than the buoy, in a wide range of concentration in solution, the adsorption occurs in the van der Waals–buoy regime; the structure of the adsorbed layer is fairly universal in the sense that it is independent of the concentration and copolymer organization in solution.

Quantitative comparisons could be made between the theory presented here and experimental results, obtained either by using a force measurement apparatus or colloidal

particles coated with copolymers. One of the main results of our work is the dependence of the structure of the adsorbed film on the phase behavior of the copolymer solution, which is not very often considered. Another important point is the role of the long-range van der Waals interactions. We considered here the case of thermodynamic equilibrium, which may be difficult to realize experimentally. These points certainly deserve further theoretical study; experimentally a careful control of the formation of the adsorbed layer is clearly needed.

Finally, we have considered only highly selective solvents although we have discussed qualitatively a small swelling of the molten layer by the solvent. In most experiments, the solvent is not too selective; we wish to study the adsorption of block copolymers on nonselective solvents in a future work.

Appendix A: Grafted Layers on a Flat Surface

We discuss here the structure and energy of a grafted B layer (a brush) of known surface density $\sigma > \sigma_1 \sim N_B{}^{-6/5}$, under an external pressure π_{ex}. The external pressure might be monitored either by osmotic effects or by an external mechanical pressure as in a force measurement apparatus.

The grand canonical free energy which should be minimized at equilibrium is

$$G^S = F_B{}^S(L,\sigma) + \pi_{ex}L \qquad (A.1)$$

$F_B{}^S$ being the free energy of the layer per unit surface.

We make here a blob description of the brush from the work of Alexander.[10] When the external pressure π_{ex} vanishes, each chain can be viewed as a fully extended chain of excluded-volume blobs of size $D = a\sigma^{-1/2}$. Each blob contains $g_D = (D/a)^{5/3} \sim \sigma^{-5/6}$ monomers.

The thickness of the layer is

$$L = \frac{N_B}{g_D}D \sim N_B\sigma^{1/3} \qquad (A.2)$$

Each blob having an energy k_BT, the free energy of the layer per unit surface is

$$G_B{}^S = \sigma a^{-2}\frac{N_B}{g_D}T \sim TN_Ba^{-2}\sigma^{11/6} \qquad (A.3)$$

When the external pressure π_{ex} does not vanish, the blobs are not deformed only if $\pi_{ex} < T/D^3$ and the effect of the external pressure is negligible in (A.1). When $\pi_{ex} > T/D^3$, the grafted layer forms a semidilute solution of concentration $c = (N_B\sigma/La^2)$ where the osmotic pressure $\pi = T/a^3(ca^3)^{9/4}$ balances the external pressure π_{ex}. This gives the thickness of the adsorbed layer:

$$L = aN_B\sigma\left(\frac{\pi_{ex}a^3}{T}\right)^{-4/9} \qquad (A.4)$$

The free energy $G_B{}^S$ scales as

$$G_B{}^S \sim \pi_{ex}L \sim TN_B\sigma a^{-2}\left[\frac{\pi_{ex}a^3}{T}\right]^{5/9} \qquad (A.5)$$

This crosses over smoothly to the results at zero external pressure when $\pi_{ex} \sim T/D^3$.

When we study copolymer adsorption in equilibrium with a reservoir, the external pressure π_{ex} is the osmotic pressure of the dilute solution of free chains $\pi_{ex} = Tc_b/N_B$ which is always much smaller than T/D^3; the external pressure π_{ex} has thus always a small contribution which can be neglected.

In a force measurement appratus one brings together two grafted layers at a distance $2L$. It can be shown[22] that

the two brushes do not interpenetrate. If the distance L is smaller than the equilibrium distance L_{eq} given by eq A.2 the force between the two layers is extremely small. In order to obtain a distance L smaller than the equilibrium distance L_{eq} one must apply a finite pressure π_{ex}. The relation between the measured force and the distance is given by eq A.4

$$\pi_{ex} = \frac{T}{a^3}\left(\frac{N_B\sigma}{La^2}\right)^{9/4} \quad (A.4a)$$

This holds for $L_{min} \ll L \ll L_{eq}$, L_{min} being the minimum distance obtained when the chains are collapsed on the surface: $L_{min} = N_B\sigma a$.

When L becomes close to L_{min}, the pressure π_{ex} increases strongly and cannot be described by equation A.4a. We use a Flory model for the potential G

$$\frac{G}{T} = L\left(\frac{1}{a^3} - c\right)\log(1 - ca^3) + \chi c(1 - ca^3)L + \frac{\pi_{ex}L}{T} \quad (A.6)$$

where χ is the FLORY interaction parameter and the concentration c is related to L by $c = N_B\sigma/La^2$. Minimization with respect to L gives a pressure which diverges with distance as L approaches L_{min}

$$\pi_{ex} = -\frac{T}{a^3}\log\left(1 - \frac{L_{min}}{L}\right) \quad (A.7)$$

and crosses over smoothly to (A.4a) when $(L - L_{min})/L_{min} = 1$.

Appendix B: Grafted Layer in a Spherical Geometry

Grafted polymer layers on a sphere have been studied in detail by Daoud et al.[16-23] The junction points are on the core of the micelle with a surface density σ; the radius of the core is R_M.

In the absence of external pressure the grafted layer may be described in terms of blobs quite similarly to the planar case. The size of the blob, however, depends on the distance from the center of the micelle (Figure 4).

$$\xi(r) \sim \frac{r}{R_M}\sigma^{-1/2}a \quad (B.1)$$

Each blob has excluded-volume statistics and contains g monomers

$$g(r) \sim \left(\frac{\xi}{a}\right)^{5/3} \sim \left(\frac{r}{R_M}\right)^{5/3}\sigma^{-5/6} \quad (B.2)$$

The local concentration is

$$c(r) \simeq \frac{g(r)}{\xi^3(r)} = \left(\frac{r}{R_M}\right)^{-4/3}\sigma^{2/3}a^{-3} \quad (B.3)$$

Each micelle contains $p = \sigma 4\pi R_M^2 a^{-2}$ chains. The total number of B monomers is thus

$$N_B p = \int_{R_M}^{R_M+L} 4\pi r^2 c(r)\, dr$$

This determines the thickness of the grafted layer L

$$L = R_{FB}(\sigma R_M^2)^{1/5} = R_{FB}p^{1/5} \quad \text{if } L \gg R_M$$
$$= N_B a\sigma^{1/3} \quad \text{if } L \ll R_M$$
$$(B.4)$$

In the last case there is no effect of the spherical geometry and the result is the same as for the planar geometry (Appendix A). From now on, we restrict the study to B

chains long enough that $L \gg R_M$.

The free energy density is $F = kT/\xi^3$; the layer free energy is

$$F_B{}^S = \int_{R_M}^{R_M+L}\frac{T}{\xi^3}4\pi r^2\, dr = Tp^{3/2}\log\frac{L}{R_M} \quad (B.5)$$

The effect of a finite external pressure may be discussed following the same procedure as in Appendix A. Blobs are not deformed as soon as $\pi_{ex} < T/\xi^3$. This defines a characteristic radius

$$R_e = R_M\sigma^{1/2}\Big/\left(\frac{\pi_{ex}a^3}{T}\right)^{1/3}$$

If $r < R_e$ the structure of the grafted layer is given by eq B1-B3. If $r > R_e$ the concentration is roughly constant as in the planar case

$$c_e a^3 = \left(\frac{\pi_{ex}a^3}{T}\right)^{4/9}$$

The conservation of monomers in the grafted layer leads to a thickness L

$$L = \frac{(pN_B)^{1/3}}{\left(\dfrac{\pi_{ex}a^3}{T}\right)^{4/27}}a \quad (B.6)$$

when the pressure π_{ex} is larger than a critical value π_c

$$\pi_{ex} > \pi_c = N_B{}^{-9/5}p^{9/10}\frac{T}{a^3} \quad (B.7)$$

This critical value π_c is much larger than the pressure at the overlap concentration $c^* \sim N_B{}^{-9/5}$ ($p \gg 1$). The effect of the external pressure might thus be neglected here, the concentration of free chains being always smaller than c^*.

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Adsorption of Polybutadienes with Polar Group Terminations on the Solid Surface. 1. Infrared Study at the Silica Surface

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ABSTRACT: Adsorption of polybutadiene terminated with a very polar functional group (T-PBR) on a silica surface from carbon tetrachloride solution has been investigated by using IR spectroscopy and compared with normal polybutadienes (PBR). Carbon tetrachloride is a good solvent for polybutadiene. The adsorbed amount, A, the surface coverage θ of the silanol groups, and the bound fraction of a polymer chain p were measured. A marked difference in adsorption behavior between T-PBR and PBR polymers was observed. T-PBR has an A and θ twice as large as those for PBR, while the p value was approximately the same for both polymers. From the chemical structure of the terminal group we can qualitatively interpret the difference in the adsorption behavior by taking into account the preferential adsorption of the terminal polar functional groups over the double-bond groups in polybutadiene chains onto the silanol groups of silica surface.

Introduction

The loop–train–tail conformation is generally accepted as a structure of flexible polymer chains adsorbed on flat, cylindrical, and spherical surfaces if there is no specific interaction between polymer and surface.[1-4] Tail portions of adsorbed polymer chain are considered to be random-flight chains attached on a surface with one end, and they play an important role in understanding the behavior of flexible polymer chains at surfaces and interfaces. In particular, the large layer thickness of the adsorbed polymer chains is believed to be mainly governed by the tail portions in both theoretical and experimental sides. Moreover, the tail portions of adsorbed chains not only act as a steric stabilization moiety for colloidal particles but also can serve as bridges between different particles in flocculation of colloidal dispersions.[5]

Tail formation on the solid surface in adsorption experiments is available by use of (1) a polymer terminated with a single specific functional group, which strongly interacts with surface sites of the adsorbing surface, or (2) a block copolymer in which one block adsorbs in train conformation and the other block adsorbs negligibly. The two methods described above contain some demerits: (1) A polymer chain adsorbed with one anchored terminal group may desorb from the surface under good solvent conditions as the result of repulsive interaction of dangling tails caused by the excluded volume effect if the bond strength between the terminal group and a surface site is not very strong. (2) One adsorbed block may not behave as one long train part without loop formation.

However, there are a few successful examples. Hadzi-ioannou et al.[6] recently have measured surface forces between 2-vinylpyridine–styrene block copolymers adsorbed on mica surfaces; the 2-vinylpyridine block adsorbs

strongly on a mica surface with a flattened conformation, while the styrene block is not adsorbed directly to a mica surface at all. Some block copolymers were used as polymer monolayers at the air–water interface where one block (uncharged block) lays flat on the interface and the other block (charged block) is extended into water.[7,8]

On the other hand, there are some adsorption studies of polymers terminated by a polar group, which adsorbs preferentially over functional groups in the main polymer chains.[9-11] They used low molecular weight fractions, i.e., $M_n \sim 2 \times 10^3$. The effect of terminal functional groups on adsorption was definitely observed as expected. For high molecular weights of polymers with terminal groups, a definite effect of terminal functional groups on adsorption behavior has not been recognized. In this study we investigate the effect of a terminal functional group with strong adsorbability on polymer adsorption behavior by using well-characterized samples for both adsorbate and adsorbent. Adsorption measurements of high molecular weight ($\sim 10^5$) polybutadienes terminated with bis(p-diethylamino)phenyl)methanol onto the silica surface were performed by using IR spectroscopy in carbon tetrachloride, which is a good solvent for polybutadiene, in comparison with adsorption of normal polybutadiene. The reason why these adsorption experiments are done under good solvent conditions is as follows: under good solvent conditions both the adsorbed amount and surface coverage are usually much smaller than those under poor solvent conditions at the same polymer concentration; thus, it is expected that the differences in adsorbed amount as well as surface coverage between polymers terminated and those not terminated with functional groups will be emphasized by the preferential adsorption of terminal groups.

Experimental Section

Materials. Polybutadiene (PBR) and polybutadiene terminated with bis(p-(diethylamino)phenyl)methanol (T-PBR) were kindly supplied from Nippon Zeon Co., Ltd. The chemical

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