Adsorption kinetics of end-attaching triblock copolymers

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Ellipsometry is used to obtain the first measurements of the adsorption kinetics and adsorption isotherm of a doubly end-attaching polymer. A triblock copolymer of poly(ethylene oxide)–polystyrene–poly(ethylene oxide) is adsorbed onto silicon dioxide from toluene; only the polar-end blocks adsorb. At short times, the kinetics of adsorption follow Fickian behaviour. At small bulk concentrations, the surface saturation is approached monotonically but as the bulk concentration is increased an 'overshoot' in the adsorbed amount is observed. The adsorbed amount of triblock copolymer is less than the amount found for a corresponding diblock copolymer. This difference is attributed to the presence of triblock copolymers adsorbed in a loop-like conformation.

(Keywords: polymer brushes; adsorption kinetics; end-functionalized polymers)

INTRODUCTION

The formation of single-polymer chain layers on solid surfaces through adsorption is a subject of technological importance. For example, adsorbing polymers are used for the stabilization or flocculation of colloidal dispersions[1] and to attain adhesive properties[2]. In general, many uses of polymeric thin-film materials are known in a wide variety of applications such as micro-electronics and opto-electronics[3]. Films which maintain the necessary properties while being as thin as possible are desirable in such cases. The use of end-attaching polymer chains holds considerable promise for the construction of ultra-thin films if the relevant parameters can be identified and subsequently controlled. This raises fundamental questions as to the structure of the adsorbed polymer layer formed under a given set of conditions.

We report here on the adsorption of an end-attaching triblock copolymer of poly(ethylene oxide)–polystyrene–poly(ethylene oxide) (PEO-PS-PEO) under good solvent conditions onto a selective surface. The copolymer consists of relatively short PEO end-blocks and a much longer PS middle-block. Adsorption takes place from toluene, which acts as a good solvent for both types of blocks in the copolymer. A silicon wafer covered with a silicon dioxide layer is used as the surface and thus only the polar PEO block adsorbs; the PS block is left dangling in solution. The use of triblock copolymers in which both ends can adsorb creates the possibility of radically different conformational states for the adsorbed polymer chains. *Figure 1* illustrates schematically the expected conformational possibilities for end-attaching triblock copolymers. When both ends of the same molecule adsorb, a 'loop' is created. If only one end adsorbs, a 'tail' is created whereby a short PEO block remains in solution. In the present study, null-ellipsometry is employed to obtain the first measurements of the adsorption kinetics and adsorption isotherm of a triblock copolymer with short end-groups capable of double end attachment.

EXPERIMENTAL

Materials

The triblock copolymer used in this study was purchased from Polymer Laboratories and has the molecular characteristics shown in *Table 1*; also shown in this table are the characteristics of a previously investigated diblock copolymer[4,5] from the same source, which will be used for comparison purposes. Reagent-grade toluene (Riedel-de Haën) was distilled over sodium metal and passed through a Millipore filter prior to use. Silicon wafers (supplied by Wacker-Chemitronic,

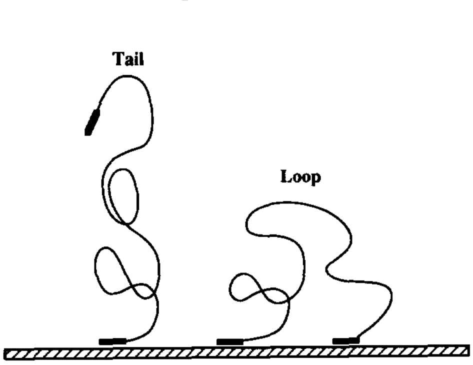

Figure 1 Schematic representation of possible conformational states available for end-attaching triblock copolymers. When both ends adsorb, a closed loop with the surface is formed; if only one end adsorbs, a potentially adsorbing block is left dangling in solution

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Table 1 Molecular characteristics of the polymers used in the adsorption studies

Material	M_w/M_n	PEO (wt%)	Block length (PS units)	Block length (PEO units)
PEO-PS-PEO-45	1.07	7.6	435	80 (2 × 40)
PS-PEO-80	1.15	5.0	730	90

Burghausen) with a well-defined oxide layer (1370 Å) and a mirror-polished finish were used as substrates.

Dynamic light scattering was used to check for the existence of micelles in solution; a description of the apparatus and procedure employed can be found in the literature[6]. No micelles were detected at a concentration of 2.0 mg ml^{-1}, which is more than four times the highest concentration used in our experiments. The apparent diffusion coefficient and hydrodynamic radius were found to be 8.06×10^{-7} cm^2 s^{-1} and 46 Å, respectively.

Adsorption experiments

Ellipsometry was used to measure film thickness and refractive index as a function of time during the adsorption process. The type of apparatus employed and the method of data reduction have been described previously[4] and so are only sketched here.

The trapezoidal sample cell was constructed by Hellma and had entrance and exit windows fixed at 70.0°. A clean silicon wafer was placed in the cell, which was then filled with 60 ml of freshly distilled and filtered toluene. A thermostat provided thermal control so that all runs were performed at 20.0±0.1°C. Upon establishment of the baseline signal, 20 ml of polymer solution (pre-cooled to 20°C) was injected into the glass cell and the ellipsometric angles were monitored with time. Control experiments with toluene and pure PS showed no indications of adsorption.

The technique of null-ellipsometry was used. With a motorized linear polarizer (P_1) and a compensator it is possible to generate a state of elliptical polarization which, when reflected, becomes linearly polarized light; such light can be extinguished by a second motorized linear polarizer (P_2). The intensity of light passing through the second polarizer may be monitored using a photodiode while computer control of the polarizers allows an automated search for the null settings. Readings on the polarizers yield the ellipsometric angles Ψ and Δ: $\Psi = P_2$ and $\Delta = 2P_1 + 90°$. These angles contain information about the relative attenuation and phase shift of the component waves perpendicular (s-wave) and parallel (p-wave) to the plane of incidence[7].

The unknown film thickness, d_1, and index of refraction, n_1, can be found assuming that the polymer film is a homogeneous layer. The relationship between the ellipsometric angles and the film parameters can be expressed in functional form as:

$$e^{i\Delta} \tan \Psi = R_p/R_s = F(n_k, d_k) \qquad (1)$$

where, n_k and d_k refer to the indices of refraction and the thicknesses of each layer present which is denoted by subscript k (i.e. solution, polymer, silicon dioxide and silicon). R_p and R_s represent the overall reflection coefficients for the basis p- and s-waves. Measurement of the two independent quantities Ψ and Δ allows the solution of the only two unknowns, the polymer layer thickness, d_1, and index of refraction, n_1. The amount of adsorbed polymer (mg m^{-2}) can be calculated from:

$$A = d_1 c_1 = d_1(n_1 - n_0)/(dn/dc)_0 \qquad (2)$$

where n_0 represents the index of refraction of the polymer solution and $(dn/dc)_0$ is the change in the refractive index of the solution with polymer concentration. Although a separate determination of n_1 and d_1 is difficult due to the small differences in index of refraction of the polymer and solution, the product $n_1 d_1$ is an invariant of the adopted layer model. The adsorbed amount, A, also proves insensitive towards which type of concentration profile near the wall is assumed — step, parabolic or exponential[4] — and we therefore focus our attention on this quantity in the following discussion.

RESULTS

The adsorption behaviour of the triblock copolymer is shown in *Figure 2*. A Fickian regime is found at short times where the adsorbed amount increases linearly with the square root of time. Solution of the diffusion equation subject to the appropriate boundary conditions yields an error function. Subsequent differentiation with respect to the spatial variable yields an expression for the flux to the adsorbing surface. Integration of this flux with respect to time gives the adsorbed amount:

$$A(z=0, t) = \frac{2c_0}{\sqrt{\pi}} \sqrt{D_{AB} t} \qquad (3)$$

where D_{AB} is the diffusion coefficient of the polymer in solution and c_0 is the uniform bulk concentration of the solution. The straight lines shown in *Figure 2* are calculated according to equation (3) using the diffusion coefficient measured via dynamic light scattering (8.06×10^{-7} cm^2 s^{-1}). This analysis of the early time adsorption behaviour thus involves no adjustable parameters.

The adsorption behaviour beyond the Fickian regime displays a fascinating phenomenon with increasing bulk concentration. In *Figure 3* the adsorbed amount is plotted against time for three different bulk concentrations,

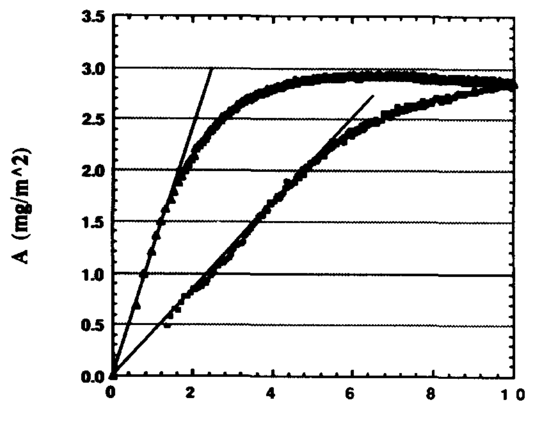

Figure 2 Short time adsorbtion behaviour for end-attaching triblock copolymer. The linear increase in the adsorbed amount with the square root of time is indicative of Fickian diffusion. Solid lines correspond to calculations based on equation (3): □, $c = 0.005$ mg ml^{-1}; △, $c = 0.025$ mg ml^{-1}

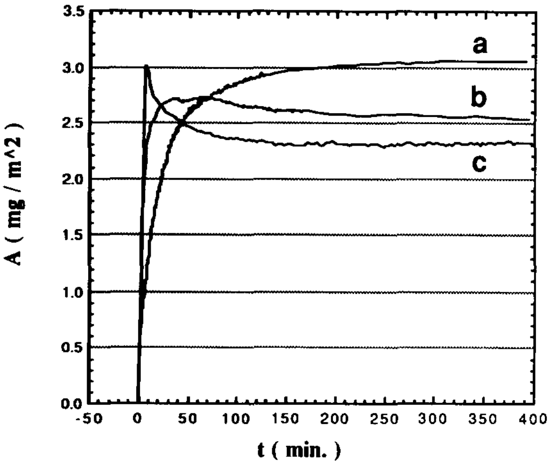

Figure 3 Development of overshoot phenomenon with increasing concentration of polymer in solution. Less saturation adsorption is seen with increasing bulk concentration: a, $c=0.005\ \mathrm{mg\,ml^{-1}}$; b, $c=0.025\ \mathrm{mg\,ml^{-1}}$; c, $c=0.081\ \mathrm{mg\,ml^{-1}}$

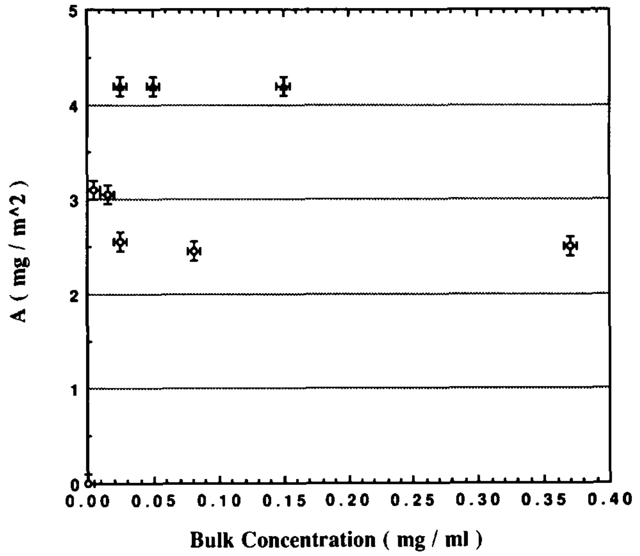

Figure 4 Measured adsorption isotherms for PEO-PS-PEO-45 triblock copolymer (○, M_w 45 000) and PEO-PS-80 diblock copolymer (▲, M_w 80 000) on a silicon oxide surface. Both isotherms were measured at 20°C under identical conditions. Although the molecular weight of the triblock is lower than that of the diblock, less triblock polymer is adsorbed

$c=0.005$, 0.025 and $0.081\ \mathrm{mg\,ml^{-1}}$. A clearly definable 'overshoot' in the adsorbed amount develops with increasing bulk concentration. The possible existence of the overshoot phenomenon at low concentrations but at a much longer time scale was checked by performing a long-time experiment. For the concentration $c=0.005\ \mathrm{mg\,ml^{-1}}$, an experiment lasting in excess of 4000 min (~3 days) showed some evidence of passing through a maximum; the adsorbed amount decreased slightly from the value reached by 400 min.

The measured adsorption isotherm for the triblock material is shown in *Figure 4*. It is seen that for the lowest achievable bulk concentrations (extremely low bulk concentrations contain a high amount of uncertainty due to adsorption onto the glass walls of the cell) the triblock isotherm is essentially flat. This is a result of the relatively high sticking energy of the end-groups; the rise from the zero bulk concentration to the plateau value is extremely sharp. Increasing the bulk concentration further leads to a peculiar behaviour: less polymer is adsorbed at higher bulk concentrations, so there is the possibility of a surface phase transition at a critical bulk concentration. The adsorbed amount under identical conditions for the diblock material described in *Table 1* is also plotted in *Figure 4* for comparison. It is important to note that the adsorbed amount of triblock copolymer is less than the adsorbed amount of diblock polymer, even though the molecular weight of the diblock is greater than the triblock. These findings have important implications which are discussed in the next section.

DISCUSSION

Review of diblock behaviour

Prior to discussing the results on triblock adsorption, it is instructive to recapitulate the main results previously found for end-attaching diblock materials under the same conditions. It was previously shown that: (1) pure PS does not adsorb onto the silicon dioxide surface from toluene at the concentrations studied; (2) lower molecular weight of the non-adsorbing PS block leads to a higher total adsorbed amount; and (3) two time-scales govern the kinetics of adsorption, a Fickian regime at early times and an exponential process associated with free chain penetration of the brush at later times[4].

Results for triblock behaviour

The fact that a Fickian diffusion regime exists in the case of triblock adsorption is easily understood. All of the adsorption experiments were carried out in the dilute regime well below the critical concentration for chain overlap. Thus the molecules are isolated in solution and diffuse independently. Transport of material to the surface is limited by the arrival of these molecules. This situation holds true until the surface reaches a high enough coverage such that arriving chains begin to interact with chains already on the surface. Close examination of *Figure 2* reveals that the deviation from Fickian behaviour occurs at approximately the same surface coverage for both bulk concentrations. Using this approximate value ($1.9\ \mathrm{mg\,m^{-2}}$) for the adsorbed amount of polymer, the area available for each polymer chain can be calculated and therefore the interchain spacing can be determined. The value found is 63 Å, which may be compared with the value of 69 Å for the Flory radius of gyration of the PS block in toluene[8].

The overshoot phenomenon implies that the region in the immediate vicinity of the surface becomes temporarily overpopulated with polymer chains. It is probable that this process reflects the conformational rearrangements of polymer molecules at the surface. Molecules which adsorb at early times and low surface coverage have a relatively non-distorted conformation, but after the surface coverage exceeds the point where each chain occupies roughly its radius of gyration, the polymer chains must be distorted and stretched in the surface layer. The free energy of the system may be decreased through the realization of the enthalpy of adsorption, and this driving force causes chains to adsorb. As the adsorbed layer increases in concentration, the initially adsorbed chains are subjected to new topological constraints which may lead to a large stretching energy. If a chain is too highly distorted, its conformation represents a non-equilibrium state and it will detach from the surface. The enthalpic heat of adsorption is balanced against the entropic stretching at equilibrium.

The overshoot relaxation appears with increasing bulk concentration; at low concentrations the diffusion of free chains to the wall is the rate-limiting step. When the reservoir concentration of chains is high, the flux of chains to the surface is large and the kinetics are dominated by the actual adsorption process kinetics. Recently, a theory has appeared which describes such an overshoot phenomenon in polymer adsorption by using the concept of a time delay[9]. In this model, a polymer chain must spend a fixed amount of time on the surface in order to undergo conformational rearrangement before desorption can occur. This mechanism is quite general and we expect that for copolymers consisting of small attaching and larger non-attaching blocks the overshoot phenomenon will often be present.

This overshoot time dependence has been observed previously for diblock materials under conditions similar to those used in the present study[10]. A surface phase transition was proposed as the mechanism responsible for the observed behaviour in the diblock system studied. A surface transition caused by surface diffusion and subsequent local clustering of polymer chains has recently been predicted by Monte Carlo simulation techniques[11]. This type of mechanism can explain the lower adsorbed amounts at higher bulk concentrations if the clustering of end-groups brings non-adsorbing blocks near the surface, thus shielding some of the available adsorption sites. If such lateral surface inhomogeneities do develop with increasing reservoir concentration, then it is possible that some adsorbed chains will be displaced, leading to a lower adsorbed amount.

The adsorption isotherm (*Figure 4*) demonstrates the unique behaviour of the triblock material. It was shown previously in the case of diblock copolymers, that the adsorbed amount follows an inverse power law relationship with the molecular weight of the PS block, and is insensitive to relatively small changes in the PEO block size[4]. Based on this finding, if the triblock material were to adsorb only in the 'tail' conformation, the adsorbed amount for the triblock should be greater than for the diblock because the molecular weight of the triblock is lower than that of the diblock. Viewing a triblock chain adsorbed in a 'loop' conformation as equivalent to two diblock chains, each with a molecular weight of one-half that of the triblock, would also imply that the adsorbed amount for the triblock should be greater than for the diblock case. The fact that it is not implies that there is a fundamental difference in the structure of the adsorbed polymer film for the triblock case. Using the lowest plateau value for the adsorbed amount (roughly 2.5 mg m^{-2}) the final interchain spacing can be calculated and is found to be 55 Å, which is less than the Flory radius of gyration of the PS block (69 Å) in toluene. This implies that the chains are in a stretched conformation; a 'brush' structure is present. One possible explanation for the lower adsorbed amount in the triblock case is that chains adsorbed in loop conformations tend to shield available adsorption sites on the surface. Further experiments are needed in order to fully elucidate the observed behaviour.

CONCLUSIONS

Null-ellipsometry has been employed to obtain the first measurements of the adsorption kinetics and adsorption isotherm of end-attaching triblock copolymers. The conditions employed for the adsorption of the polymer were those of a good solvent onto a selective substrate. The copolymer studied consisted of short PEO end-blocks and a much longer PS middle-block. Resolution of the kinetics of adsorption demonstrates that at early times the behaviour is Fickian; the adsorbed amount of polymer increases linearly with the square root of time. As the bulk concentration is increased, a maximum in the adsorbed amount *versus* time appears. This process can be rationalized by the need for conformational rearrangements in the layer of adsorbed polymer chains. The measured triblock adsorption isotherm shows the adsorbed amount decreasing with increasing bulk concentration. The adsorbed amount of triblock polymer is less than would be expected for a diblock material of comparable molecular weight. From these results it can be inferred that at least some of the polymer chains adsorb in a loop-like manner. The structure of polymer brushes formed from the adsorption of end-attaching triblock copolymers is thus shown to be distinct from the structure formed by single end-attaching diblock copolymers.

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