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Adsorption of di- and triblock copolymers with functionalized butadiene–styrene blocks from dilute solution

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The adsorption behaviour of functionalized polystyrene-*block*-polybutadiene diblock copolymers, P(S-*b*-B), and polybutadiene-*block*-polystyrene-*block*-polybutadiene triblock copolymers, P(B-*b*-S-*b*-B), from dilute solutions in toluene onto silicon wafers was investigated by means of null-ellipsometry. Polar 4-(3,5-dioxo-1,2,4-triazolidin-4-yl) benzoic acid groups (urazole groups) were attached randomly to the butadiene blocks. The PS blocks and the PB blocks adsorb not on the substrate surface, but only on the polar functional groups. It was verified that the adsorbed amount does not depend on the number of functional groups nor on the degree of polymerization of the polybutadiene block within the investigated range. The adsorption isotherms for the di- and triblock copolymers are compared. The plateau value obtained for the diblock copolymers is nearly 50% higher than that for the corresponding triblock copolymers. This difference is explained based on different conformational states of the adsorbed chains, in particular by loop formation of the triblock copolymers. The adsorption kinetics reveals two regimes: a Fickian behaviour at the beginning and a slower process after the formation of a dense surface coverage.

(Keywords: adsorption; kinetics; block copolymers)

Introduction

The adsorption behaviour of polymers is a subject of technological interest. The formation of a homogeneous polymeric film on a solid surface through adsorption has many applications in colloidal dispersions[1] and in the development of biocompatible materials[2]. Much effort has been made in order to predict theoretically or to determine experimentally the best conditions to obtain dense adsorbed polymeric layers, which successfully fulfil these requirements.

In a previous work[3] we have investigated the adsorption behaviour of functionalized polystyrene-*block*-polybutadiene, P(S-*b*-B)u, from dilute toluene solutions onto silicon wafers by means of ellipsometry. Functional urazole groups, denoted by u, are statistically attached to the short butadiene end blocks. The PS blocks and the PB blocks do not adsorb on the substrate surface, but on the polar functional groups. PS and PB are readily soluble in toluene, while the polar functional groups are essentially insoluble in this solvent. It was shown that the adsorbed amount achieved at equilibrium for diblock P(S-*b*-B)u does not depend on the number ($m = 2, 4, 6, 8$) of functional groups attached to the short butadiene blocks, but on the length of the PS block. Chains with longer PS blocks provide lower grafting density, and a linear correlation between the latter and the inverse of the degree of polymerization of PS was observed. This can be understood to result from a balance between adsorption energy and repulsive forces resulting from steric effects. The fact that neither the number of functional groups nor the size of the PB block influence the adsorbed amount was explained with a 'zipper' model, based on the assumption that each functional group adsorbs independently from the next adsorbing site, since there are flexible non-functionalized PB sequences situated in between. It is the aim of this work to compare the adsorption isotherms and the adsorption kinetics of functionalized P(S-*b*-B) diblock and P(B-*b*-S-*b*-B) triblock copolymers with practically the same molecular weights and the same number of functional groups.

Experimental

Polystyrene-*block*-polybutadiene diblock, P(S-*b*-B), and polybutadiene-*block*-polystyrene-*block*-polybutadiene triblock, P(B-*b*-S-*b*-B), were synthesized[4] by anionic polymerization. Molecular weights were determined by light scattering (*Table 1*). The polydispersity (M_w/M_n), determined by gel permeation chromatography (eluent tetrahydrofuran) after calibration with PS standards, lies between 1.1 and 1.07. The PB content in the diblock and triblock copolymer chains was determined by nuclear magnetic resonance (^{1}H n.m.r.) at 200 MHz in $CDCl_3$. A few butadiene repeat units were reacted with 4-(3,5-dioxo-1,2,4-triazolidin-4-yl) benzoic acid[4–6]. These polar groups are statistically attached to the PB end blocks as urazole groups.

The diblock P(S-*b*-B) and triblock P(B-*b*-S-*b*-B) copolymers were functionalized with different numbers of urazole groups per chain. They are denoted here as P(S-*b*-B)*num* and P(B-*b*-S-*b*-B)*num*, where *n* indicates the molecular weight and *m* the number of urazole units.

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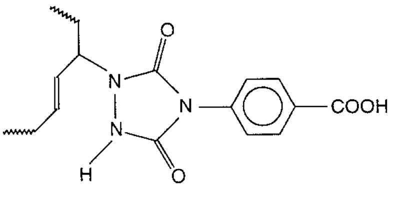
Table 1 Molecular characteristics of the functionalized diblock and triblock copolymers and geometrical parameters of the adsorbed layers. The molecular weight M_w was determined by means of light scattering (LS). N_S and N_B are the degrees of polymerization of the styrene and the butadiene blocks, respectively. The increment of refractive index, dn/dc, was measured in toluene at 20.0°C. A is the adsorbed amount from ellipsometric measurements; σ gives the surface density ($\sigma = AN_{\mathrm{Avogadro}}/M_w$); D_{inter} denotes the experimental average interchain spacing ($D_{\mathrm{inter}} = 1/\sigma^{0.5}$); D_{over} corresponds to the calculated chain spacing needed for unperturbed coils on the surface to begin to touch ($D_{\mathrm{over}} = 3.297N_S^{0.595}$; ref. 17) and $\gamma = D_{\mathrm{inter}}/D_{\mathrm{over}}$ is the parameter which indicates chain stretching

Sample	M_w^{LS} (g mol^{-1})	N_S	N_B	dn/dc (ml g^{-1})	A (mg m^{-2})	σ (chains nm^{-2})	D_{inter} (nm)	D_{over} (nm)	γ
P(B-*b*-S-*b*-B)41u10	41 000	350	84	0.095	1.69	0.025	6.3	10.8	0.58
P(S-*b*-B)39u10	39 000	350	50	0.096	2.62	0.04	5	10.8	0.46
P(S-*b*-B)31u6	31 000	282	32	0.095	2.75	0.054	4.3	9.46	0.46
P(S-*b*-B)31u4	31 000	282	32	0.095	3.35	0.065	3.9	9.46	0.41



Functionalized polybutadiene sequence

Reagent grade toluene (Riedel de Häen) was distilled over sodium metal and filtered through a Millipore filter (0.2 μm) prior to use. Silicon wafers, kindly supplied by Wacker-Chemitronics, Burghausen, were used as substrates. They are composed of Si (index of refraction $n = 3.88 - i0.018$)[7] and a top SiO_2 layer typically 1500 Å thick ($n = 1.462$), determined through ellipsometric measurements. The refractive index increment, dn/dc, was determined by means of a differential refractometer at 20.00°C (*Table 1*).

Null-ellipsometry was employed to measure *in situ* the adsorption of P(S-*b*-B)*num* and P(B-*b*-S-*b*-B)*num* from dilute solutions in toluene onto silicon wafers. Details of this technique and the ellipsometer are given elsewhere[3,8]. A He–Ne laser ($\lambda = 632.8$ nm) was used. All adsorption measurements were made in a specially built glass cell (Hellma), which has stress-free entrance and exit windows fixed at an angle of 70.0° with respect to each other. The freshly cleaned silicon wafer was fixed in a support and placed in the cell. The cell was filled with *ca.* 80 ml of pure solvent, kept at a constant temperature of 20.0 ± 0.1°C by a thermostat, and the ellipsometric angles Δ and Ψ were measured. Then a small volume of the concentrated polymer solution was added and stirred for 2 min. Subsequently, every 24 s a pair of ellipsometric angles, Δ and Ψ, was recorded. Measurements were performed over 3 h. After at least 1 h (depending on concentration), constant values of the ellipsometric angles were obtained, indicating that equilibrium in the adsorption process had been achieved[3].

Considering the adsorbed polymer film as a homogeneous layer, the index of refraction and thickness of the adsorbed polymer film, n_1 and d_1, can be obtained from ellipsometric measurements by standard procedures[3,8,9]. Although a separate determination of n_1 and d_1 may be difficult owing to the small differences between the indices of refraction of the substrate, polymer and solution, the product $n_1 d_1$ is an invariant of the adopted layer model with a homogeneous polymer layer. Simulations reveal that the adsorbed amount A, determined by means of monochromatic ellipsometry, does not depend on the particular concentration profile near the wall (step, parabolic or exponential)[8].

Results and discussion

Toluene is a good solvent for butadiene and styrene blocks, but it is a non-solvent for the urazole groups. Therefore the presence of micelles in solution is expected at higher concentrations. From dynamic and static light-scattering measurements at concentrations of 0.6 to 30 mg ml^{-1} it is concluded that at these concentrations micelles are present in equilibrium with isolated free chains[4], while the number of micelles decreases significantly at lower concentrations. In the concentration range where the adsorption experiments are performed, within the sensitivity of the light-scattering detector no micelles could be detected, although we cannot completely exclude the presence of a very small number of micelles at these dilute concentrations. At the dilute solution conditions, where the ellipsometry experiments are performed, we thus can assume, to a good approximation, that adsorption is dominated by free chains adsorbing on the SiO_2 surface.

It has been checked that homopolymers PB and PS in dilute toluene solution do not adsorb on the SiO_2 surface[3,8], in contrast to the functionalized P(S-*b*-B)u and P(B-*b*-S-*b*-B)u. Considering an abundant presence of free chains of P(S-*b*-B)u or P(B-*b*-S-*b*-B)u in the concentration range 0.008–0.55 mg ml^{-1}, the following model can be drawn. The polar urazole groups attached to the butadiene groups stick to the SiO_2 surface. In the case of the diblock P(S-*b*-B)u copolymers, the stickers (functional groups) at the PB block adsorb on the SiO_2 surface, while the PS block dangles in the solution, forming a brush-like layer (*Figure 1*). In the case of triblock P(B-*b*-S-*b*-B)u copolymer, the functional groups are attached to both PB end blocks. In this case there are two possible conformational states for the adsorbed chains: (i) both ends adsorb on the SiO_2 surface, while the PS block tends to form a 'loop' in the solution, or (ii) only one end adsorbs on the SiO_2 surface, whereas the PS block and the other functionalized PB block dangle in the solution (*Figure 1*).

The adsorption isotherms obtained for P(S-*b*-B)39u10 and P(B-*b*-S-*b*-B)41u10 are plotted in *Figure 2*. In both cases the adsorbed amount of polymer increases as the concentration rises, reaching a plateau value where the adsorbed amount is independent of the polymer concentration. Such behaviour is typical of a Langmuir isotherm. The plateau value obtained for P(S-*b*-B)39u*m* (2.6 mg m^{-2}) is *ca.* 50% higher than that observed for the P(B-*b*-S-*b*-B)41u10 (1.7 mg m^{-2}). Since the diblock and

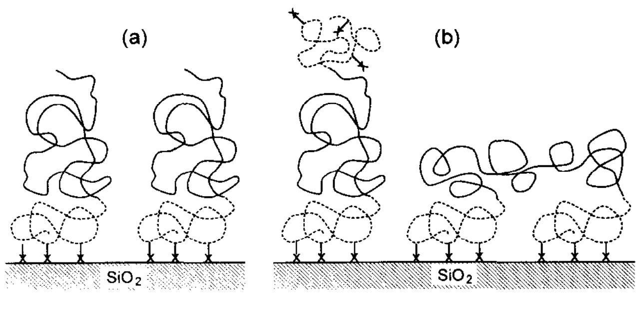


Figure 1 Schematic representation of the possible conformational states assumed by the adsorbed chains. (a) Diblock copolymers: the chains form a dense layer with brush-like chain conformations. (b) Triblock copolymers: the adsorbed chains form a significant amount of loop conformations

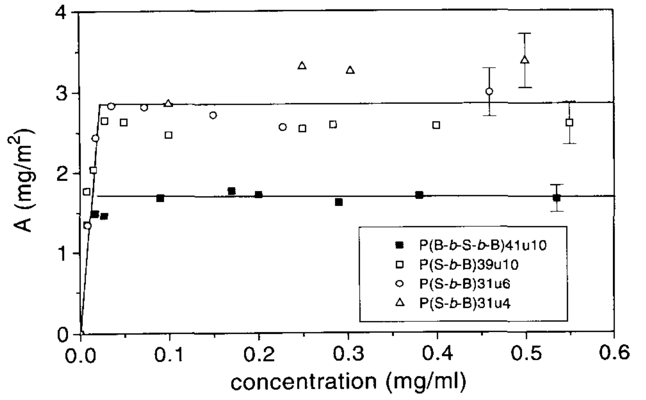


Figure 2 Adsorption isotherms obtained for P(S-*b*-B)39u10, P(S-*b*-B)41u10, P(S-*b*-B)31u4 and P(S-*b*-B)31u6 at a temperature of 20.0°C

triblock copolymer chains have almost the same molecular weights, the difference observed in the adsorbed amount must be due to different conformational states (*Figure 1*). The adsorbed chains in 'loop' conformation occupy more lateral space, and therefore less adsorbing sites on the surface are available. This is also demonstrated in terms of the stretching parameter γ (refs 10, 11), which is determined from the ratio of the average interchain spacing D_{inter}, determined experimentally from the adsorbed amount, and the calculated interchain spacing D_{over}, expected for unperturbed chains[3]. The value of $\gamma \sim 0.5$ indicates significant chain stretching. Comparing the γ values obtained for the given materials, the triblock P(B-*b*-S-*b*-B)41u10 adsorbed chains ($\gamma = 0.58$) are clearly less stretched than the diblock P(S-*b*-B)39u10 adsorbed chains ($\gamma = 0.46$) (*Table 1*). Similar experimental results are also found for the adsorption of P(S-*b*-EO) and P(EO-*b*-S-*b*-EO) block copolymers (PEO = poly(ethylene oxide)) from dilute solutions in toluene onto silicon wafers[10,11]. Force balance experiments with P(VP-*b*-S-*b*-VP) triblock copolymers[12,13] (PVP = poly(vinyl pyridine)) show a significantly different behaviour with respect to force–distance profiles as compared to corresponding diblocks, which is attributed to loop formation; the adsorbed amount was not measured. These findings are also supported by theoretical predictions from Evers and co-workers[14], where a lower adsorbed amount for the mid-adsorbing triblock copolymer BAB is predicted as compared to an AB diblock copolymer with the same total number of non-adsorbing segments B.

The plateau values obtained for P(S-*b*-B)31u4 and P(S-*b*-B)31u6 copolymers are the same, if the experimental error is considered. These values are practically identical to that obtained for P(S-*b*-B)39u10, although in this sample the PB blocks are longer and carry still more functional groups than in P(S-*b*-B)31u4 or P(S-*b*-B)31u6 copolymers. Moreover, in all three cases the chains show comparable stretching parameters γ. These findings reinforce the previously proposed model[3] that for functionalized diblock copolymers AB, where the A block is statistically functionalized and only the functional groups adsorb, the size of the non-adsorbing B block plays the main role in adsorption due to repulsion between the dangling chains, whereas the size of the non-adsorbing functionalized A block, as well as the number of stickers attached to this block, do not influence the adsorbed amount.

The adsorption kinetics at short times are shown in *Figure 3*. The triblock P(B-*b*-S-*b*-B)41u10 and diblock P(S-*b*-B)39u10 show quite similar behaviour. At short times, the adsorbed amount increases linearly with the square root of time, typical of a Fickian regime. Solution of the diffusion equation, subject to appropriate boundary conditions, yields an error function for the concentration profile[8]. Subsequent differentiation with respect to the spatial variable yields an expression for the flux to the adsorbing surface. The integration of this flux with respect to time t leads to an expression of the adsorbed amount at the surface as a function of time:

$$A(t) = \frac{2c_0}{\sqrt{\pi}}\sqrt{Dt} \tag{1}$$

where D is the diffusion coefficient of the polymer in solution and c_0 is the initial bulk concentration.

From the slopes of the straight lines shown in *Figure 3*, it is possible to obtain the diffusion coefficients D. The values of D obtained for solutions of P(B-*b*-S-*b*-B)41u10 and P(S-*b*-B)39u10 at the same concentrations are practically the same, $2.4 \times 10^{-7}\,\text{cm}^2\,\text{s}^{-1}$ and $2.84 \times 10^{-7}\,\text{cm}^2\,\text{s}^{-1}$, respectively. This is a very reasonable result, since both materials have comparable molecular weights. For the triblock P(B-*b*-S-*b*-B)41u10, a concentration dependence on the D value has been observed.

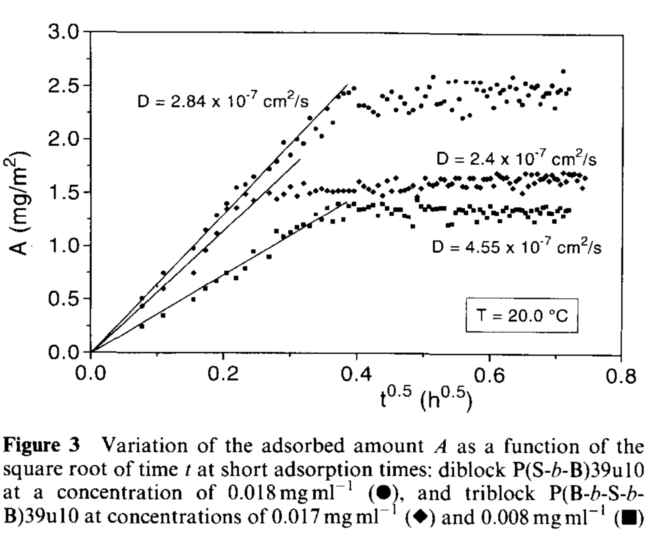


Figure 3 Variation of the adsorbed amount A as a function of the square root of time t at short adsorption times: diblock P(S-*b*-B)39u10 at a concentration of $0.018\,\text{mg}\,\text{ml}^{-1}$ (●), and triblock P(B-*b*-S-*b*-B)39u10 at concentrations of $0.017\,\text{mg}\,\text{ml}^{-1}$ (◆) and $0.008\,\text{mg}\,\text{ml}^{-1}$ (■)

For solutions of P(B-*b*-S-*b*-B)41u10 and P(S-*b*-B)39u10 in toluene at a concentration of $0.6\,\mathrm{mg\,ml^{-1}}$, the diffusion coefficients for the polymer chains, determined by dynamic light scattering (d.l.s.) at 20.0°C, are $1.76 \times 10^{-7}\,\mathrm{cm^2\,s^{-1}}$ and $1.49 \times 10^{-7}\,\mathrm{cm^2\,s^{-1}}$, respectively. These values may, however, already be influenced by a small amount of micelles present at this concentration, which causes a reduction of the c_0 value used in equation (1), since for the adsorption at the silicon wafer the concentration of single chains is important. From d.l.s. measurements it is also shown[4] that the apparent diffusion coefficient depends strongly on concentration. The values of D obtained from the two techniques are, on the other hand, of the same order of magnitude.

The adsorption kinetics can thus be divided into two regimes. At the beginning, the adsorption kinetics are determined by a diffusion-controlled process leading to a surface coverage with small interaction between the molecules. This is consistent with a picture where chains arriving at the surface are instantaneously (on the same timescale of the experiment) adsorbed, and diffusion of those chains to the surface is the rate-limiting step. This essentially unhindered adsorption is, however, only observed when the surface coverage is not very high and when sufficient free adsorption sites are still available. After formation of a dense surface layer, a slower process becomes important, where the penetration of chains through the layer formed by the already adsorbed chains has to be considered. This process is described in several theoretical treatments where limiting expressions are discussed[15,16]. In the latter regime, diffusion to the surface is assumed to be much faster than penetration of the chains through the already existing layer. One can also envisage this process as diffusion across an activation barrier, where the height of the barrier increases with surface density. Newly arriving chains have to push the already adsorbed ones aside, which costs an entropy penalty. Adsorbed chains have to adopt a brush-like conformation when the surface coverage is increased. The maximal adsorbed amount is limited by a balance between the gain in enthalpy by adsorption (adsorption energy) and the entropic contribution due to the distorted chain conformations of the brushy chains. Our experiments are thus in qualitative agreement with this picture. We do not try to interpret the crossover regime in more detail, since a rigorous theoretical description is missing.

It has been discussed previously[3] that adsorption energy in the present case is determined by the adsorption of a single sticker, since it can be assumed that functional groups connected by flexible spacers adsorb essentially independently from each other. The amount of chain stretching can be estimated from the parameter γ (*Table 1*). The diblocks are more extended than the triblock copolymers, which is a clear indication of the different chain conformations. One can assume that triblock copolymers form loops at a significant percentage.

Summary

The adsorption from dilute solutions of a diblock copolymer AB, where the A block is functionalized with adsorbing groups, but neither the A block nor the B block adsorb on the substrate, was investigated. Keeping the size of the non-functionalized and non-adsorbing B block constant, it was verified that the magnitude of the adsorbed amount does not depend on the number of functional groups nor on the size of the functionalized and non-adsorbing A block. This is explained by a previously proposed model[3] where adsorption of the different functional groups at the surface is expected to be independent from each other, since those groups are connected by non-adsorbing flexible sequences. Desorption can thus be envisaged by a 'zipper' process, where one of these groups is always removed from the surface and thus the adsorption energy of a single functional group plays the dominant role. The grafting density scales with N_B^{-1}, N_B being the number of non-adsorbing monomers dangling in solution, which determines the repulsion between neighbouring chains.

The adsorbed amount observed for triblock and diblock copolymers, with identical molecular weights and the same number of functional groups, differs considerably. The diblock copolymers show a plateau value in the adsorption isotherm approximately 50% higher than for the triblock copolymers. Such a difference is expected to be due to different conformational states of the adsorbed chains: the former assumes a brush conformation and the latter, to a large extent, a loop conformation.

The adsorption kinetics can be described as two processes. At short times a diffusion-controlled process is dominant, where the mass transport is governed essentially by the diffusion coefficient of polymer chains in solution. As the grafted layer grows, further adsorption of arriving chains becomes more difficult, owing to the presence of the already adsorbed chains, and the adsorption process becomes slower.

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