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Displacement of adsorbed functionalized polystyrene-*block*-butadiene copolymers by small molecules

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Abstract This work deals with the displacement of end-anchored copolymers by the addition of solvent displacer. The adsorption behavior of functionalized polystyrene-*block*-polybutadiene diblock copolymers from dilute solution in toluene using silicon wafers as solid substrates is investigated by means of null-ellipsometry. The desorption phenomena are observed by adding displacers of

low molecular weight to the mixture. The displacers used are tetrahydrofuran (THF) and acetone. The critical composition of the binary solvent mixture at which the desorption is complete, is determined experimentally.

Key words Adsorption – displacement – functionalized diblock copolymer – ellipsometry

Introduction

Polymer adsorption is a subject of large technological interest in fields concerned, for instance, with stabilization of colloidal dispersions [1], chromatography [2], protective coating and biocompatibility of polymers [3]. The desorption phenomena are also very important for a number of practical applications such as the separation of polymers by adsorption chromatography [2], the tailoring of surface coatings or the recovery of substrates.

The energy involved in the adsorption of a polymer segment from solution onto a substrate surface was first defined by Silberberg [4] in terms of the adsorption energy parameter χ_s^{po} :

$$\chi_s^{po} = [f_{ps} - f_{os} + 1/2(f_{pp} - f_{oo})]/kT, \quad (1)$$

where f_{ps} , f_{os} , f_{pp} , f_{oo} represent the interaction energies polymer/substrate, solvent/substrate, polymer/polymer and solvent/solvent, respectively; k is the Boltzmann constant and T is the temperature.

Polymer adsorption occurs when the segmental adsorption energy χ_s^{po} exceeds a certain critical value χ_{sc} , which involves a balance between the interaction energies

f_{ps} and f_{os} and express a conformational entropy loss. When f_{ps} is larger than f_{os} adsorption takes place. However, if a displacer is added to the system, as the composition of the mixture changes the adsorbed amount of polymer decreases. At a critical composition ϕ_{crit} of the binary solvent system the polymer is totally desorbed. Displacement or desorption of a preadsorbed polymer from a dilute solution on a given substrate occurs when a solvent is added to the system, whose interactions with the surface are stronger than the interactions between the polymer segment and the surface, or when the interactions between polymer and displacer are stronger than those between polymer segment and substrate.

In previous works [5, 6], we presented the adsorption of functionalized diblock polystyrene-*block*-polybutadiene diblock copolymers from solution in toluene onto silicon wafers. The polar functional groups, urazoles, are attached to the small butadiene block. In toluene polystyrene and polybutadiene do not adsorb on the substrate, but only the polar functional groups. The adsorbed chains can be envisaged as end-anchored chains (brushes). In this work, the displacement of the end-adsorbed polystyrene-*block*-polybutadiene copolymers with different molecular weights in toluene from silicon wafers are presented. Tetrahydrofuran

and acetone are used as displacers and the measurements are performed by means of null-ellipsometry.

Experimental

Materials

Polystyrene-*block*-polybutadiene, P(S-*b*-B), was synthesized by anionic polymerization [7], the molecular characteristics are shown in Table 1. The small polybutadiene blocks were functionalized by means of a reaction with 4-(3,5-dioxo-1,2,4-triazolidin-4-yl) benzoic acid, also called 4-urazoyl benzoic acid (urazoles). These functional groups, react preferentially with the polybutadiene blocks. After the functionalization the polybutadiene blocks carry on average six functional groups per chain. The samples are denoted by P(S-*b*-B)31 and P(S-*b*-B)318.

Reagent grade toluene, tetrahydrofuran (THF) and acetone (Riedel-de H  en) were 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 $n = 3.88 - i0.018$) [8] and a top layer of SiO_2 ($n = 1.4625$) typically 160 nm thick. They were rinsed in the standard manner [5, 6, 9] prior to use.

Experimental techniques

Null-ellipsometry was used to measure the adsorbed amount of P(S-*b*-B)31 and P(S-*b*-B)318. The measurements were performed with a self-built, computer-controlled null ellipsometer in a vertical polarizer-compensator-sample-analyzer (PCSA) arrangement described elsewhere [5, 6, 9]. A He-Ne laser ($\lambda = 632.8 \text{ nm}$) was used as the light source and the angle of incidence was fixed at 70.0° , which is the angle that provides for our system best sensitivity. Using a motorized linear polarizer (P) and a compensator (C), a state of elliptical polarization is generated, which after reflection, becomes linear polarized light. The reflected light is extinguished by an analyzer (A), which in

fact is a second polarizer. The intensity of reflected light passing through the analyzer is detected by a photomultiplier and the computer control of polarizer and analyzer allows the automated search for the null settings. The null setting for the polarizer yields the ellipsometric angle Δ ($\Delta = 2P + 90^\circ$) and for the analyzer the ellipsometric angle Ψ ($\Psi = A$). Δ and Ψ contain information respectively, about the relative phase shift and attenuation of the component waves perpendicular (s -wave) and parallel (p -wave) to the plane of incidence.

Assuming a multilayer model formed by an adsorbed homogeneous isotropic polymer film on a silicon wafer and in contact with a dilute polymer solution, the unknown film thickness d_1 and refractive index n_1 can be calculated from the ellipsometric angles using the following relation [10]:

$$e^{i\Delta} \tan \Psi = R_p/R_s = f(n_k, d_k, \lambda, \phi), \quad (2)$$

where R_p and R_s represent the overall reflection coefficient for the basis p - and s -waves. They are a function of n_k and d_k , which refer to the indices of refraction and the thickness of each layer in the model (polymer solution, adsorbed polymer, SiO_2 and Si), the wavelength λ and the angle of incidence ϕ .

The amount of adsorbed polymer A (mg/m^2) can be calculated from the following equation:

$$A = \frac{d_1(n_1 - n_0)}{(dn/dc)} = d_1 c_1, \quad (3)$$

where n_1 and d_1 are the polymer layer parameters obtained from the ellipsometric measurements, n_0 is the index of refraction of the solution measured with an Abbe refractometer, dn/dc is the increment of refractive index determined with a differential refractometer and c_1 is the average polymer concentration within the layer. The small differences in the indices of refraction of the substrate, polymer and solution, make difficult an independent determination of n_1 and d_1 . However, the product $n_1 d_1$ does not depend on the adopted later model and on the concentration profile near the wall [9].

Solutions of P(S-*b*-B)31 were prepared in toluene. A freshly rinsed silicon wafer (1 cm^2) was fixed in a support inside the measuring glass cell, which was built with windows fixed at 70.0° [5, 6, 9]. Then distilled toluene was added to the cell and the ellipsometric angles Δ and Ψ were measured. After this a small volume of concentrated polymer solution was added to the cell and stirred for 2 min. Subsequently, every 24 s a pair of ellipsometric angles was recorded. After about 1 h, when constant values of Δ and Ψ are observed, the equilibrium in the adsorption process is achieved. Subsequently, small amounts of displacers are added to the measuring cell and the solution is gently

Table 1 Molecular characteristics of the polymers used. M_w values were determined by means of light scattering, the polydispersity with gel permeation chromatography and the styrene to butadiene ratio was obtained by nuclear magnet resonance (200 MHz – ^1H -NMR) in CDCl_3

Sample	M_w (g/mol)	M_w/M_n	N_S	N_B
P(S- <i>b</i> -B)31	31 000	1.07	282	32
P(S- <i>b</i> -B)318	318 000	1.1	2996	118

stirred continuously during the whole experiment. The stirring magnet is placed beneath the sample at the bottom of the cell and at the sample surface there is only a very weak current. For an adequate treatment of the ellipsometric results, after each addition of the displacer a small aliquot of the solution is taken off and its index of refraction is measured by means of an Abbe refractometer. All measurements are performed at 20.0 °C.

Results and discussion

In previous works the adsorption behavior of functionalized polystyrene-*block*-polybutadiene from dilute solutions onto silicon wafers was presented [5, 6]. Toluene is a good solvent for both blocks, but a poor solvent for the functional groups. However, in the very dilute range where the adsorption experiments are carried out, no aggregation is detected by measurements of dynamic light scattering. The PS and the PB blocks do not adsorb on the silicon wafers, but the polar urazole groups do. The energy gain due to the favorable interactions between the functional groups and SiO₂ is estimated to be about 10 *kT* [11], which is high enough to compensate the entropic losses. Adsorption experiments of functionalized P(S-*b*-B) from dilute solutions in tetrahydrofuran (THF) instead of toluene onto silicon wafers were also tried [5]. No adsorption was observed. This can be qualitatively explained on the basis of Eq. (1) in terms of competitive interactions. THF is a good solvent for both blocks, PS and PB, and for the functional groups. The energy involved in the adsorption of molecules of THF on the SiO₂ surface and the favorable interactions between THF and the functionalized P(S-*b*-B) overcome the energy involved in the adsorption of functional groups on the SiO₂ surface.

The adsorption isotherms obtained for P(S-*b*-B)31 and P(S-*b*-B)318 are reported in a previous work [5] and shown in Fig. 1. The adsorption plateaus lie at 3.0 mg/m² and 1.0 mg/m² for the two materials, respectively.

After the adsorption equilibrium was achieved (ca. 1 hour), small amounts of THF were added consecutively to the system. The addition of just 2 ml of THF to the 60 ml of solution of P(S-*b*-B)31 in toluene already caused some desorption and the adsorbed amount decreases from 3.0 mg/m² to 2.64 mg/m², as shown in Fig. 2. This is a very fast process compared to our data acquisition time. Adding consecutively small volumes of THF, the adsorbed amount decreased, until the desorption is complete. This is better depicted in the displacement isotherm in Fig. 3. The critical composition at which the total desorption occurs is denoted as ϕ_{crit} and corresponds to a volume fraction of THF equal to (0.16 ± 0.02) in the solvent mixture. In the literature [12–15], we could only find reports about

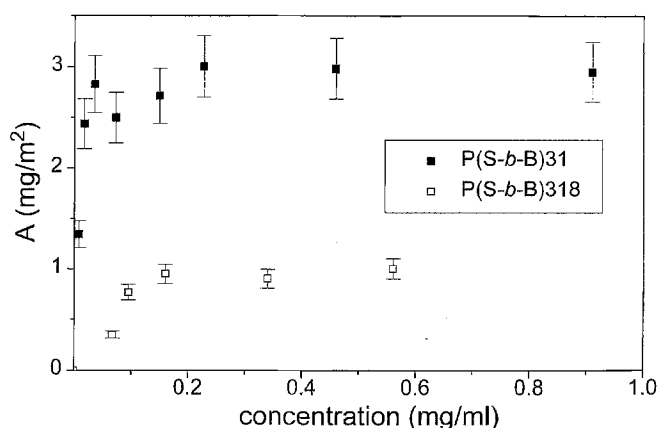


Fig. 1 Adsorption isotherms for the diblock copolymers P(S-*b*-B)31 (■) and P(S-*b*-B)318 (□) in toluene at 20 °C obtained from ellipsometry. The data are from ref. [5]

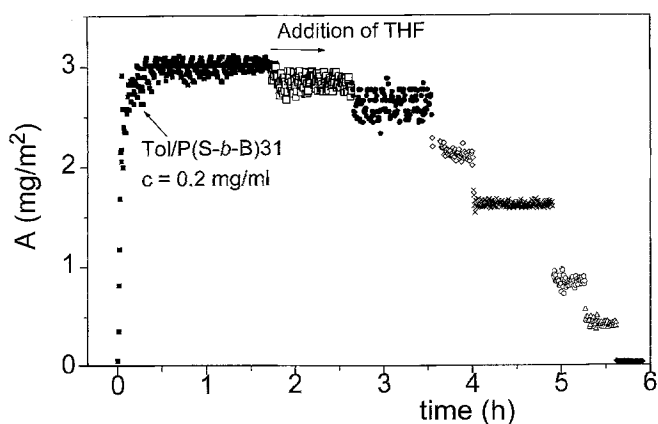


Fig. 2 Adsorbed amount of P(S-*b*-B)31 in toluene onto SiO₂ surface as a function of time and of the volume of THF added to the mixture: (·) 0 ml; (□) 1.0 ml; (●) 2.0 ml; (◇) 3.0 ml; (×) 5.0 ml; (○) 7.0 ml; (△) 9.0 ml and (◆) 11.0 ml

displacements of homopolymers by addition of solvents. To our knowledge, this is the first report on the displacement of end-anchored polymer chains by addition of solvents.

In order to verify the effect of the chain length on the ϕ_{crit} , displacement isotherms were also measured with a higher molecular weight copolymer, carrying the same number of urazoles. The displacement isotherm obtained for P(S-*b*-B)318 in toluene by addition of THF is presented in Fig. 4. Although it has a higher molecular weight than P(S-*b*-B)31, the critical volume ϕ_{crit} is practically the same, $\phi_{crit} = (0.20 \pm 0.02)$, if the experimental errors are considered. The (near) independence of ϕ_{crit} on the chain length is also observed for the displacement of homopolymers. [12, 15].

Acetone also acts as a displacer to the system formed by toluene, P(S-*b*-B)31 and the SiO₂ surface. The

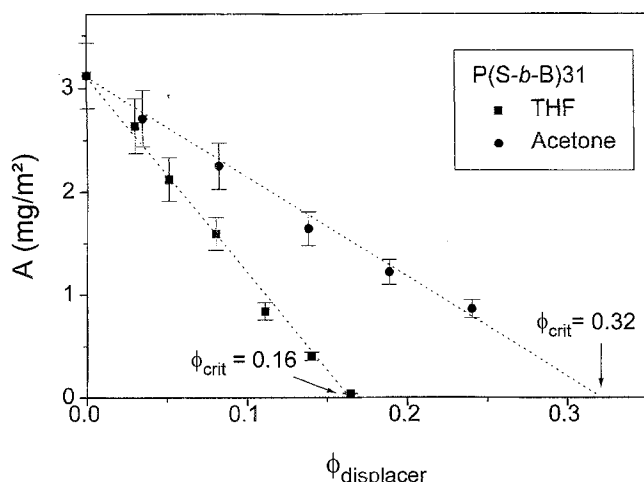


Fig. 3 Displacement of P(S-*b*-B)31 in toluene from SiO₂ surface by the addition of THF (■) and acetone (●) measured at 20 °C. The dotted lines represent fits with a linear regression for the determination of the critical concentration ϕ_{crit} where the total displacement takes place

consecutive addition of small quantities of acetone provokes a decrease of the adsorbed amount, until the critical composition ϕ_{crit} at which total desorption is achieved. The displacement isotherms obtained for both displacers THF and acetone are shown in Fig. 3. When acetone is used as a displacer, ϕ_{crit} is 0.32 ± 0.03 and thus larger than that observed with THF. Since THF and acetone are both polar solvents and adsorb on SiO₂ with approximately the same strength [16, 17], the difference observed in the ϕ_{crit} may be due to the fact that THF is a better solvent for the functional urazole groups on the polymer than acetone.

The displacement of the functional groups adsorbed on to the SiO₂ surface by THF or acetone molecules can be qualitatively explained in terms of adsorption energy. The energy involved in the adsorption of one molecule of THF or acetone from toluene on the SiO₂ surface and the

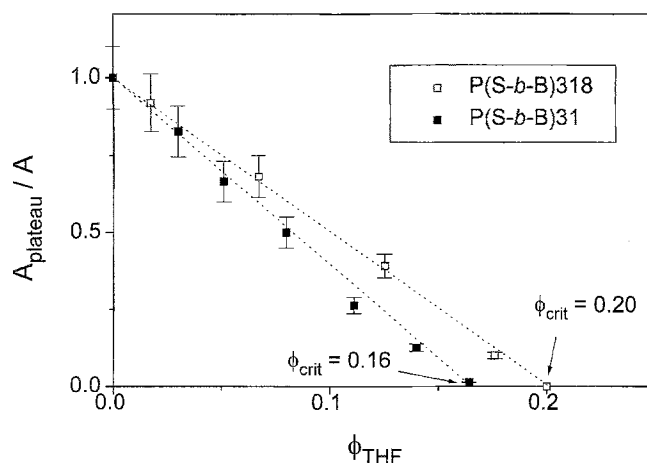


Fig. 4 Displacement isotherms of P(S-*b*-B)31 (■) and P(S-*b*-B)318 (□) in toluene from SiO₂ surface by the addition of THF, measured at 20 °C. A_{plateau} denotes the mean adsorbed amount in the plateau region of the adsorption isotherms. The dotted lines represent fits with a linear regression

favorable interactions between THF or acetone and the functionalized P(S-*b*-B) overcome the energy involved in the adsorption of one functional group from toluene on the SiO₂ surface.

The results presented here show total and partial displacement of end-anchored polymer chains by a very simple method, namely the addition of stronger solvent. Such experiments provide the possibility of tailoring surface coverages and of recovering substrates. It might also offer other applications like controlled release and controlled colloidal coagulation which still have to be explored further.

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