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Diblock Copolymer Adsorption from the Aqueous Micellar Phase to Solid Surfaces: Real Time Monitoring by ATR Spectroscopy in the Mid-Infrared

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Summary: Attenuated Total Reflectance (ATR) in the mid-infrared is employed to monitor the adsorption of poly(tert-butyl styrene - b - styrene sulfonate), PtBS-PSS, copolymers with a small hydrophobic head as well as of an analogous poly(styrene sulfonate), PSS, homopolymer on germanium and Au-plated germanium surfaces from aqueous NaCl solutions. The surface density of the adsorbed polyelectrolyte is monitored via the growth of characteristic infrared absorptions of the sulfonated ring at 1036- and 1008 cm^{-1} in the 2nd derivative mode. These probe bands do not exhibit shifts or changes in bandshape over very prolongued adsorption experiments. Pronounced differences in the kinetics of adsorption are observed between the PSS homopolymer and the PtBS-PSS copolymers in agreement to previous investigations by phase-modulated ellipsometry on similar systems. Adsorption of the diblocks above the critical micelle concentration is found to involve a sequence of diffusion, micellar relaxation and brush-limited processes.

Keywords: adsorption; attenuated total reflectance; micelles; polyelectrolyte; poly(tert-butyl styrene - b - styrene sulfonate)

Introduction

Surface modification of solids by adsorption of organic molecules from solution is often used to modify the wettability, friction, adhesion, corrosion or optical properties of the surface. It therefore finds numerous technological applications and sustains a continuing research effort. Among the various experimental techniques employed to study the thickness and structure of the

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adsorbed layer, those applicable *in situ* are suitable for shedding light to the dynamics of the adsorption and the possible mechanisms involved. Infrared spectroscopy is one of these techniques.[1] It is employed mostly in the Attenuated Total Reflectance mode (ATR) where the substrate is the surface of a transparent, high-refractive-index lightguide in contact with the solution, and the evanescent infrared radiation penetrates into the sample by a fraction of the wavelength.[2] Althougth ATR is a surface technique and improves the contrast between the adsorbed species and the solvent, the penetration depth of the infrared beam inside the sample is still much larger than the thickenss of the adsorbed layer.[3-4] Therefore, distinguishing from the solvent background and quantifying in real time the signal due to the adsorbed layer is not trivial. In addition, the time scales involved require often a temporal resolution of a few seconds in the early stages of adsorption, and a long-term stability of hours, even days to record equilibrium.

In this work, we employ ATR in the infrared to study the adsorption of the aqueous micellar phase of poly(tert-butyl styrene - b - styrene sulfonate), (PtBS-PSS), copolymers with a short hydrophobic block on germanium and Au-plated germanium surfaces, in comparison to an analogous (PSS) polyelectrolyte solution. The goal of this study is twofold: First, to compare the capabilities of ATR in monitoring the adsorption kinetics from an aqueous micellar system with the results of a recent very thorough investigation by the Tirrell group.[5-7] And second, to examine whether the various adsorption processes that are known to operate over different time scales can be identified through variations of the vibrational spectrum.

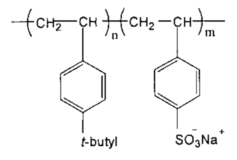
Experimental

The diblock PtBS-PSS copolymers were prepared by a two-step procedure. In the first step, a PtBS-PS precursor was synthesized by anionic "living" polymerisation under argon atmosphere, in THF at –40 °C, using sec-butyl lithium as initiator. The precursor polymers were purified by fractional precipitation and characterized by size exclusion chromatography and ^{1}H NMR. In the second step the samples were modified to PtBS-PSS by sulfonation in concentrated sulphuric acid. The degree of sulfonation of the PS blocks was quantitative as determined by elemental analysis. The samples were then neutralized and purified by dialysis against deionised water and freeze dried. Their molecular characteristics are given in Table 1. They are both highly asymmetric (n<<m), and are similar to those described in refs 5-7, except for their higher

molecular weight, and polydispersity (1.13-1.14 instead of 1.03-1.1). The PSS homopolymer was purchased from Polysciences.

All solutions were prepared at a polymer concentration of 100ppm (0.1mg/ml) in doubly distilled water with 0.5M NaCl. This concentration is well above the critical micelle concentration (cmc).[7] The solutions were left to equilibrate for at least 10 days at room temperature, and then studied without further treatment.

Table 1. Molecular characteristics of the polymers in this study

	**PtBS$_n$-PSS$_m$**	**n**	**m**	**M$_w$/M$_n$**
	PtBS$_{41}$-PSS$_{830}$	41	830	1.13
	PtBS$_{51}$-PSS$_{3789}$	51	3789	1.14
	PSS$_{1712}$	-	1712	1.10

n, m is the degree of polymerization of the corresponding blocks.

The infrared data were collected at 4 cm^{-1} resolution on a Fourier transform instrument (Bruker Equinox 55) equiped with a temperature stabilized thermoelectric (DLATGS) detector. Data were collected at room temperature over the 650-5000 cm^{-1} range, with Blackman-Harris apodization (3-term) and a zerofilling factor of 2. The interferometer was operating at 70 scans/min, allowing for the fast acquisition of spectra (10-15 s/spectrum) during the early stages of the experiments. To minimize the effects of varying water vapour and CO_2 concentration in the sample compartment, the latter was equiped with P_2O_5 and NaOH traps and kept 12h before as well as during the experiment under a continuous flow of dry nitrogen. The derivative spectra were calculated by the Savitsky-Golay algorithm (9-point smoothing) of the Bruker Opus software.

A standard 6-reflection vertical cell by Specac was employed for the ATR measurements of liquids. This cell accepts a 2x3 cm^2, 45° parallelogram crystal and has two independently filled reservoirs confined by stainless steel plates and 200 μm thick poly(isoprene) spacers. The inner surfaces of the steel plates have been gold coated to eliminate corrosion by the saline solutions. Data collected during the first ca. 1 min after the onset of each experiment correspond to a partially filled cell and have been discarded. Germanium (n_I=4.0) was used as the internal reflection element of the liquid ATR cell. Prior to each experiment, the Ge crystal was sonicated for 15 min in ethyl acetate, dried, then immersed in a dilute (1:5) HF solution to remove the oxide layer[8] and rinsed thoroughly with doubly distilled water. Alternatively, selected adsorption experiments were performed on Ge crystals coated by thermal evaporation with 1 nm of Cr and 4 nm of Au.[9] Finally, the ATR spectra of the powdered polymers were measured on a single reflection diamond cell (n_I=2.1, Durascope by SensIR).

Results and Discussion

Immediately after the introduction of any aqueous polymer solution into the ATR cell, a subtle but systematic spectral evolution is observed. This evolution, is due to the formation of the adsorbed layer on the Ge surface. Figure 1 shows the absorption spectum recorded by the 6-reflection Ge/ATR cell 1h after the introduction of a 100 ppm $PtBS_{41}$-PSS_{830} solution in H_2O/0.5M NaCl. This spectrum is ratioed by the reference spectrum of the cell filled with neat H_2O/0.5M NaCl, and

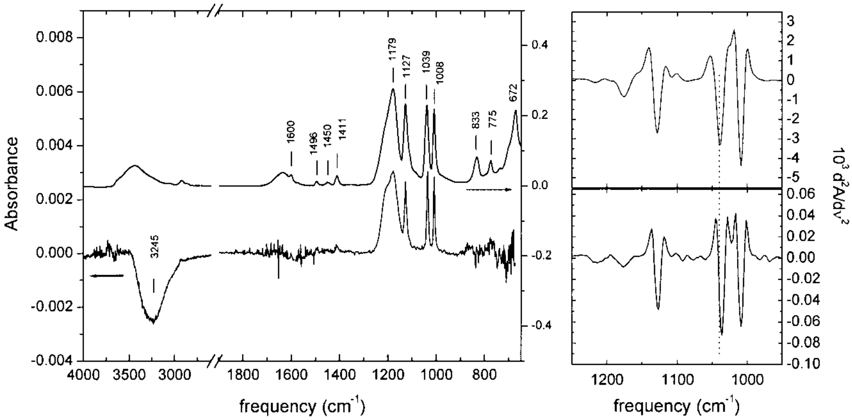


Figure 1. *(left)* ATR absorption spectra of $PtBS_{41}$-PSS_{830} powder (top) and interface on Ge (bottom) obtained ca. 1h after the onset of the experiment. The concentration was 100 ppm in 0.5M NaCl/water, and the interface spectrum is referenced by the solvent. *(right)* Detail of the same spectra in the 2nd derivative mode, multiplied by 10^3

therefore exhibits positive and negative peaks due to the enrichment and depletion of the Ge/liquid interface in polymer and water, respectively. In the same Figure 1, we show for comparison the single reflection diamond ATR spectrum of the neat PtBS$_{41}$-PSS$_{830}$ powder over the same frequency range. Although most features of this latter spectrum can be discerned in the ATR spectrum of the Ge/liquid interface, it is evident that only those in the 950-1250 cm^{-1} range are strong enough to be of diagnostic value for the vibrational characterization of the adsorbed layer.

Five bands, common to both spectra, can be identified: a broad doublet centered at ca. 1180 cm^{-1}, as well as three sharp bands at 1128-, 1036- and 1008 cm^{-1}. All are typical of para-substituted PSSNa with very high degree of sulfonation.[10] Of these bands, the doublet at ca. 1180 cm^{-1} and that at 1036 cm^{-1} are identified as the asymmetric and symmetric stretching modes of the $-SO_3^-$ Na^+ species, respectively.[11-12] The features at 1128- and 1008 cm^{-1} have been assigned to in plane vibrations of the para-sulfonated aromatic ring.[11] An alternative assignment of the 1127 cm^{-1} band to a stretching mode of the non-ionized $-SO_3H$ groups [13] is not supported by our findings.

Despite the strong resemblance of the powder and adsorbed layer spectra in Figure 1, subtle differences can be observed in the exact position of the frequency maxima and bandwidths. The differences in peak maxima could be due to the different internal reflection elements employed (diamond and Ge, respectively). However, the narrowing of the bands in the spectrum of the interface, is suggestive that the PSS blocks in the adsorbed layer are more ordered than in the neat powder.

An estimate of the surface excess density, Γ, corresponding to the ATR spectrum of the adsorbed layer in Figure 1 can be advanced based on the early work of Tompkins.[14] Adsorption is assumed to yield a step composition profile, with polymer concentration $C=C_i$ up to distance $z=t$ from the solid surface, and $C=C_s$ for z bigger than t, where t is the (time dependent) thickness of the adsorbed layer. Then, the measured absorption per reflection (A/N) will involve two terms, one originating from the adsorbed layer, and the other from the remaining solution,

$$\frac{A}{N}=\frac{2d_e}{d_p}\varepsilon\left[C_i\int_0^t \exp\left(\frac{-2z}{d_p}\right)dz+C_s\int_t^\infty \exp\left(\frac{-2z}{d_p}\right)dz\right] \qquad (1)$$

where ε is the extinction coefficient, and d_p ,d_e are the penetration depth and effective penetration depth defined by Harrick.[15] Since t is much smaller than d_p , the first integral is approximately equal to t, while the second integral is equal to $d_p/2$. Then, Equation 1 can be simplified to give the surface excess, $C_i t = \Gamma$, as follows

$$\frac{A}{N} = \frac{2d_e}{d_p}\varepsilon\Gamma + d_e\varepsilon C_s \qquad (2)$$

One limitation of this approach in the case of aqueous solutions is the significant uncertainty in measuring small values of A/N against the very strong and broad features of the solvent. This problem can be solved in part by referencing the spectra against the solvent, but uncertainties due to small changes in the slope of the baseline remain, especially over very long acquisition times. For this reason, we have applied Equation 2 to the absolute intensity of $d^2A/d\nu^2$ (ν: frequency in cm^{-1}) at ν_{max}, thereby defining a suitable extinction coefficient, ε''. This modification is equivalent

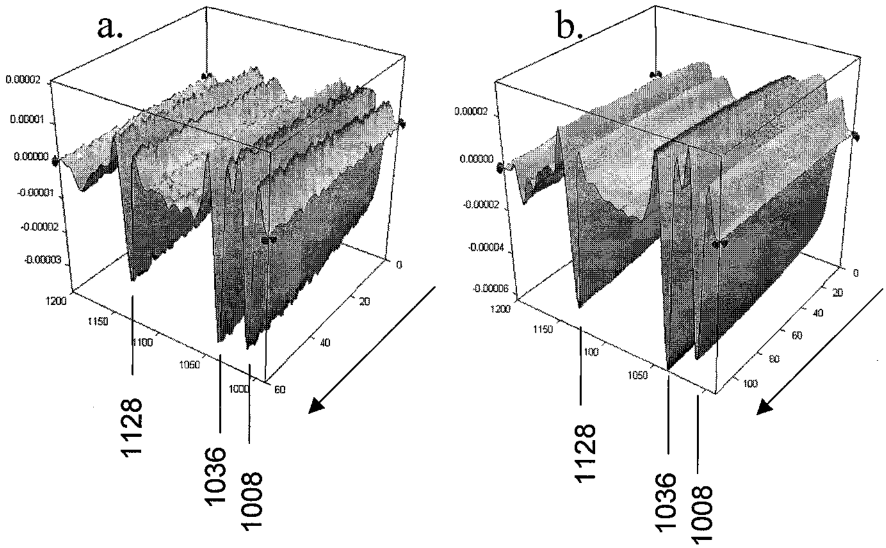


Figure 2. Second derivative spectral evolution (back to front) recorded during the adsorption of $PtBS_{41}$-PSS_{830} (100 ppm, 0.5M NaCl) on Au-plated Ge during: (a.) the first hour of the experiment recorded every minute, and (b.) the whole 5-day experiment, depicted every hour

to Equation 2, provided that both the frequency and width of the probe band remain fixed. A representative time sequence of the 2nd derivative spectra recorded during the 5-day adsorption experiment of $PtBS_{41}$-PSS_{830} (100 ppm, 0.5M NaCl) on Au-plated Ge is shown in Figure 2.

The estimation of Γ in Equation 2 requires the calculation of ε'' from transmission data. In our case, the 100 ppm solution of $PtBS_{41}$-PSS_{830} measured in a ZnSe liquid transmission cell with an optical path of 10±2 μm, was found to exhibit $d^2A/dv^2 \approx 10^{-5}$ at 1036 cm^{-1}. Substituting this value to the Beer-Lambert relationship one obtains an estimate of $\varepsilon'' \approx 10^{-3}$ dm^2/mg, suitable for calibrating the intensity of d^2A/dv^2. Obviously, the accurate application of the Beer-Lambert law would require a series of measurements at various polymer concentrations and optical paths, but this is in the present case nearly impossible due to the very high extinction coefficient of water. However, this estimate of ε allows us to predict that the value of d^2A/dv^2 corresponding to the second term of Equation (2) is in the order of $6x10^{-7}$ per reflection, i.e. ca. $3.6x10^{-6}$ for a six-reflection ATR cell. Note that the absolute intensity of the interface spectrum in Figure 1 is higher by a factor of ca. 20, and therefore originating almost exclusively from the adsorbed layer term of Equation 2. Despite the fact that this spectrum represents an early stage of the adsorption process, the value of Γ calculated on the basis of the first term of Equation 2 is of the order of 0.6 mg/m^2. [16]

Based on the above broad-brush calibration, we show in Figure 3 the time dependence of the adsorption density for the diblock polymers $PtBS_{41}$-PSS_{830} and $PtBS_{51}$-PSS_{3789} as well as the homopolymer PSS_{1712} over the first 24 hours. In the absence of a hydrophobic head, adsorption leads quickly to a low surface density layer ($\Gamma<0.1$ mg/m^2) with a hint for an overshoot at ca. 120 min. The presence of a small (<1.5%) hydrophobic block in $PtBS_{51}$-PSS_{3789} results in considerably enhanced adsorption density reaching an equilibrium value of 0.5 mg/m^2 ca. 5 h after the onset of the adsorption experiment. This pronounced effect of the hydrophobic head to the surface density of the adsorbed layer and the kinetics of adsorption arises from the relatively hydrophobic nature of the substrate [7].

Increasing further the relative length of the hydrophobic head (ca. 5% in $PtBS_{41}$-PSS_{830}) results in even higher surface densities approaching 1 mg/m^2, but the system does not reach equilibrium after 24 h. Instead, over the period from 4-24 hours, the surface density appears to be increasing linearly with time at a rate of $1x10^{-4}$ mg/m^2min (see Figure 3).

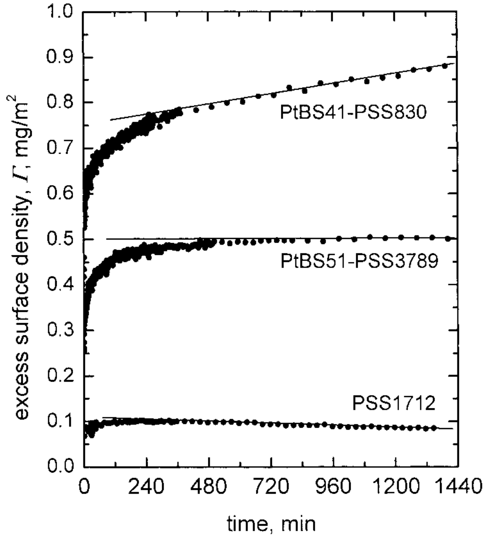


Figure 3. Real time monitoring of the density of the adsorbed layer over 24 hours. In all cases, the polymer concentration was 0.1 mg/ml in 0.5M NaCl/water, and the substrate was Ge

The same contrasting behavior between the diblocks and the homopolymer has been reported recently on the basis of phase-modulated ellipsometry experiments on similar systems.[7] Two polymers with composition $PtBS_{15}$-PSS_{440} and PSS_{500} (100 ppm in 0.3M NaCl/water) were found to yield similar Γ (~1.2 mg/m^2) at long times on hydrophilic silicon surfaces. In contrast, the same systems adsorb very differently on silicon, subjected to surface modification by octadecyltriethoxy silane (OTS). On these hydrophobic surfaces, PSS_{500} yields very quickly a low density interface ($\Gamma \approx 0.3$ mg/m^2), while the presence of the hydrophobic block in $PtBS_{15}$-PSS_{440} reduces the initial rate of adsorption, but enhances considerably the final value of Γ (>2.5 mg/m^2). These differences have been associated with the presence of micelles in the solution of the diblock. These are thought to adsorb directly on OTS modified silicon, albeit with rate limited by the potential barrier induced by the hydrophilic corona. Once attached to the hydrophobic silicon, the micelle undergo relaxation and expose their core to the surface. On the contrary, the adsorption of the micelle on the hydrophilic silicon surface does not occur directly, but via chain expulsion.[13]

Within the range of the substrates studied by Toomey, [13] the cleaning procedure employed here renders the surface of the Ge ATR elements rather hydrophobic. This is due to the leaching of the oxide layer by the HF treatment, and is confirmed by the fact that the as-treated surface was not wetted by water. Therefore, the observed tenfold increase in the long time adsorption density of $PtBS_{41}$-PSS_{830} vs. PSS_{1712} reported here is not surprising.

The long time kinetics of adsorption for the $PtBS_{41}$-PSS_{830} system are shown in Figure 4. The d^2A/dv^2 changes are recorded for both the 1036 cm^{-1} $\nu_{sym}(SO_3^-)$ and 1008 cm^{-1} ring bands, and for two substrates: bare Ge and the more hydrophilic Au-plated Ge.

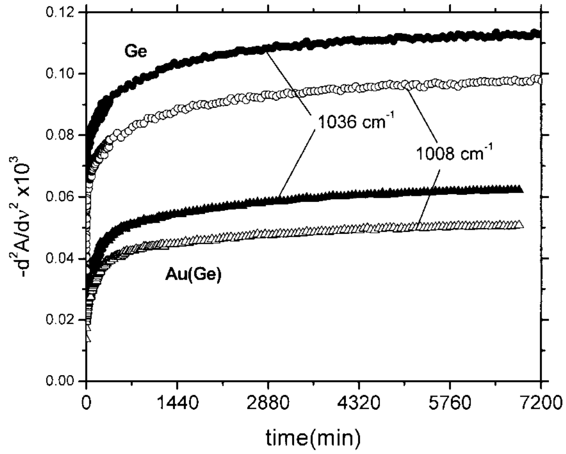


Figure 4. Long term spectral evolution of $PtBS_{41}$-PSS_{830} (0.1mg/ml in 0.5M NaCl/water) on Ge, and Au-plated Ge. The instensities of both 1036- and 1008 cm^{-1} bands in the 2nd derivative mode are depicted. The data on the Au-plated Ge correspond to the spectra shown in Figure 2

During the whole monitoring period, none of these modes was found to exhibit a significant shift or width change (see Figure 5). This implies that neither probe band is sensing changes in the conformation of the hydrophilic block that could be associated with changing adsorption mechanisms. On the other hand, this also implies that the proportionality between d^2A/dv^2 and Γ implied by Equation (2) is valid over the whole duration of the experiment, and can be employed for a detailed kinetic evaluation of the adsorption process(es).

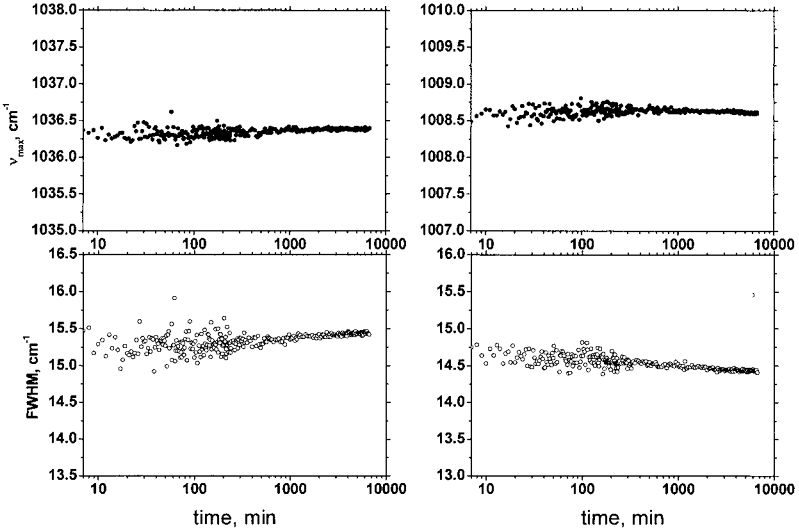


Figure 5. Frequency (top) and FWHM (bottom) of the 1036- and 1008 cm^{-1} probe bands during the 5-day adsorption monitoring of PtBS$_{41}$-PSS$_{830}$ on gold-plated Ge

The excess surface densities, Γ, corresponding to the data of Figure 4 are plotted in Figure 6 *vs.* $t^{1/2}$ for the first 4 h of the experiment, and *vs.* log(t) for the period from 4 hours to 5 days. It is evident that during the first 4-5 minutes, adsorption is dominated by a very fast process that leads to 50-60% of the final coverage! The time necessary for filling the cell, and the relatively low signal to noise ratio of the first data points do not allow for a detailed quantification of this process, which is assumed to be diffusion-limited with values of $d\Gamma/dt^{1/2}$ in the order of 0.2-0.5 $mg/m^2s^{1/2}$. At longer times, from 5 minutes to ca. 4 h, a second process is discerned with adsorption scaling again with $t^{1/2}$, albeit with a much smaller slope ($d\Gamma/dt^{1/2}$ = 1.2(±0.2) and 1.7(±0.2) x 10^{-3} $mg/m^2s^{1/2}$ for Ge and Au-plated Ge, respectively). At the other end of the time window investigated, Γ is found to increase linearly with logt at a rate of ca. 0.1 mg/m^2 per decade (Figure 6). Neither system has reached equilibrium after 5 days. The transition from the t$^{1/2}$ to the logt regimes involves an intermediate range where Γ is proportional to t. This can be best seen in the data on Ge (see also Figure 3).

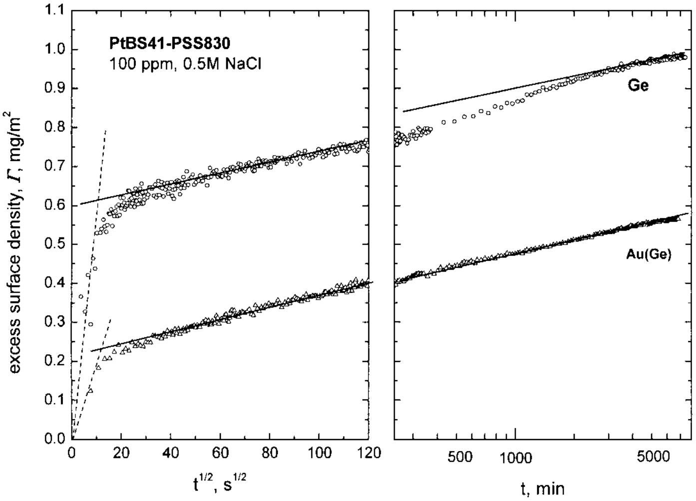


Figure 6. Kinetics of excess surface density of PtBS$_{41}$-PSS$_{830}$ (0.1 mg/ml in 0.5M NaCl/water) on Ge and Au-plated Ge plotted vs. t$^{1/2}$ (0-4h, left) and logt (4h-5 days, right). Dashed lines are guiding the eye, solid lines are least square fits

The kinetics of adsorption of asymmetric *AB* diblock copolymers from the micellar phase in a solvent highly selective for the non adsorbing block *B* and poor for the adsorbing block *A* have been studied by Johner and Joanny. [17] In the absence of direct adsorption of the micelles, the authors predict three distinct kinetic regimes: The fastest adsorption process obeys a t$^{1/2}$ law and is due to the diffusion of free chains. As a result of this process, the solution in the vicinity of the wall is depleted of free chains and the equilibrium between free chains and micelles is broken. Further adsorption leading to brush formation is limited by the relaxation of micelles via the expulsion of free chains and obeys a linear dependence with t. The as formed brush presents a barrier to incoming chains, and a third regime with logt dependence characterizes the very slow approach to equilibrium. These kinetic regimes are qualitatively similar to those deduced from

Figures 3 and 6. The main difference is that the early adsorption of $PtBS_{41}$-PSS_{830} on Ge or Au-plated Ge seems to involve two distinct $t^{1/2}$ regimes with slopes differing by a factor of ca. 200. We tentatively attribute the second $t^{1/2}$ process to direct adsorption of micelles which should not forbidden when the substrate is not ideally hydrophobic but bears a mild hydrophilic character.

Conclusions

We have demonstrated that the real-time monitoring of the adsorption of PtBS-PSS polyelectrolytes from the aqueous micellar phase to germanium is feasible by ATR spectroscopy in the mid infrared, employing a standard liquid cell. Infrared monitoring based on the evolution of the 2nd derivative spectrum of the majority PSS block allowed for the identification of the adsorption mechanisms and was found to reproduce the main findings of phase-modulated ellipsometry. No changes in the packing or conformation of the hydrophilic chains in the adsorbed layer have been detected in this system. However, a judicious selection of polymers as well as a further improvement of the time resolution and/or signal to noise ratio it is anticipated to make such studies entirely feasible.

Acknowledgments

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