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ORIGINAL CONTRIBUTION

Laser reflectometry to investigate adsorption–desorption of poly(styrene sulfonate) onto polyamide 6.6

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Abstract The adsorption of poly(styrene sulfonate) (PSS) on polyamide 6-6 was investigated using fixed angle laser reflectometry. The appropriate polyamide film thickness for an accurate analysis was first determined theoretically. Polyamide films were further prepared at controlled thickness using dip-coating processes and characterized. The adsorption of PSS was measured at pH 3 on dip-coated films as a function of time and polymer concentration. The adsorption rate at very low polymer coverage revealed diffusion limited adsorption. At and above pH 10, the PSS adsorption/desorption was difficult to evaluate. At and above pH 11.5, the hydrolysis of polyamide produced artifacts that prevent any meaningful measurements. This work showed that reflectometry is an interesting analytical tool in the in situ study of the functionalization of organic materials and to investigate the stability of the films produced.

Keywords Laser reflectometry · PSS adsorption · Polyamide treatment · Stability

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Introduction

The adsorption of polyelectrolytes has a very wide range of applications in formulation processes involved in the synthesis of most functional materials. A considerable knowledge has been gained from extensive theoretical and experimental studies [1, 2]. Experimental tools are either suited for examining a plane interface, which is the case for techniques using the reflection of beams (light, R.X, neutrons, etc.) and electrochemical cells to give some examples or for colloidal systems. In the latter case, investigations proceed generally via batch experiments, i.e., the submicronic solid material in each adsorption experiment is separated after completion of adsorption (via filtration or centrifugation in most cases), and a mass balance of the adsorbing species is performed between the centrifuged and the total amount to calculate the adsorbed fraction. Studying the adsorption of polymers on organic materials brings difficulties, as most analytical tools are sensitive to both the adsorbate and the adsorbed materials, which may result in interferences, superposition of spectra, etc. In addition, in most cases, the polymeric substrate is slightly soluble or release organic residues that also interfere in the adsorption measurement. For this reason, we were interested in examining the potential of laser reflectometry to investigate the deposition of poly(styrene sulfonate) (PSS) on a polyamide substrate. Reflectometry is a powerful technique to investigate the adsorption/desorption properties of polymers as well as the adsorption rate. Most investigations have been done on oxidized silicon wafers to study the adsorption of synthetic polymers [3–5], particles [6–8], surfactants [9, 10], mixture of polymer/surfactant [11] proteins [12–14], but the technique has also been applied using other kinds of substrates such as gold [15, 16], glassy carbon [17], PVI [18], silane-grafted silica wafers [19], polyethylene oxide [20], and modified cellulose [21].

Synthetic polyamides (PA) are widely used, especially for fiber production, although owing their high thermal resistance, they are also extensively used as engineering resins. The field of application is very considerable: textiles, battery manufacturing, motorcars, electricity, sports, membrane filtration [22–24]. Considering the wide interest within the scientific community regarding the surface treatment and functionalization of this material, we investigated the feasibility of using reflectometry to study the adsorption of a polymer on Polyamide 6.6 in aqueous media. Polystyrene sulfonate was chosen as a model polyelectrolyte, as we had formerly obtained data of the adsorption of this polymer on different substrates. In a previous paper, we examined the appropriate conditions for a reliable measurement of PSS on PA 6-6. We showed that the reflectometric signal could be converted into adsorption density with a polynomial relationship [25]. In addition, we measured the adsorption as a function of the PSS concentration in the bulk solution at pH 3, and we found that it varied considerably with the bulk polymer concentration. The present paper reports in more detail the measurement of adsorption and the chemical stability of the interface PA 6-6/PSS/solution. The reflectometric setup and the analytical conditions are those determined by our previous investigation, and they will be recalled briefly in the first section of the paper. In the second part, we will describe the properties of the substrate (PA 6-6 layer) and we will examine its stability at higher pH, as it came out that the degradation of the substrate interfered in the reflectometer output with the polymer adsorption measurement. In the third part, we will comment on the adsorption of PSS at pH 3 in NaCl solutions 10^{-2} M (amount adsorbed and kinetic of adsorption), and finally, we will examine the reversibility and stability of the interface layer upon change of pH between pH 3 and pH 12.

Materials and substrate preparation

Materials and procedures

Sodium poly(styrene-sulfonate), henceforth abbreviated PSS, with a molecular weight of 10,000 g/mol was synthesized by Rhodia (Bevaloid 6794). The substrate was a polyamide 6.6-covered silicon wafer. A silicon wafer—625±15 μm thick, 150 mm in diameter and orientation 100—was obtained from ACM (Villiers St Frederic 78640, France). The following cleaning procedure was used: immersion in a Piranha solution (mixture containing 2 parts sulfuric acid to 1 part hydrogen peroxide 30%), rinsed in Milli Q water and finally dried in a stream of nitrogen. Deposits of the polyamide film on silicon were attempted by spin and dip coatings (see below) using solutions of polyamide 6-6 (Rhodia, France) in 2,2,2-trifluoroethanol (Alfa Aesar). The thickness of the deposits was determined with an ellipsometer (Gaertner L 117) using the wavelength He–Ne laser (632.8 nm).

Polyamide coating

The polyamide coatings on silicon were attempted by spin- and by dip-coating procedures. Spin-coating deposits were made at different rotation speeds for 60 s with an acceleration of 500 rpm/s. The deposit thickness is theoretically related to the experimental parameters as follows [26]:

$$h = kc_0^2/f^{1/2} \tag{1}$$

k depends on the solvent, c_0 is the polymer concentration, and f is the rotation speed (revolutions per second). Two deposition series with different polymer concentrations (10 and 15 g/l) were made at different speeds. The measured thickness vs ln(f) showed the expected linear dependency with slopes between −0.52 and −0.55 (Fig. 1). However, as thickness heterogeneities were detected over some 3 mm on each side of the wafers, the use of dip coating was finally preferred.

Dip-coating experiments were performed by immersing the silicon wafers in trifluoroethanol solutions for about 15 s and withdrawing them at a constant rate with a traction machine. Figure 2 presents the coating thickness vs withdrawal rate (v) for polyamide concentrations of 10 and 15 g/l. Results correspond well to the Landau–Levich relationship which reads [27]:

$$h = 0.94\frac{\eta^{2/3}}{\gamma_{LV}^{1/6}(\rho g)^{1/2}}v^{2/3} \tag{2}$$

with h being the coating thickness, η the viscosity (Pa.s), ρ the specific gravity, and γ the surface tension of the solution. Slopes in Fig. 1 are 0.59 and 0.60, which is very close to the theoretical value (0.666). Homogeneous deposits were obtained over nearly the entire wafer surface (heterogene-

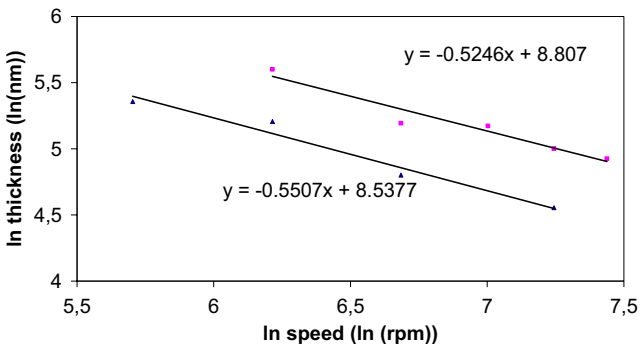

Fig. 1 Spin coating deposition of polyamide. ln(thickness) vs rotation rate. PA solution concentration: *filled triangle* 10 g/l, *filled square* 15 g/l

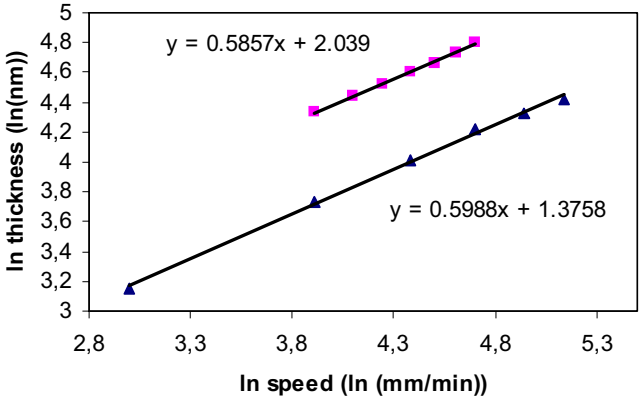

Fig. 2 Polyamide deposit thickness vs. withdrawing rate using dip coating. PA solution concentration: *filled triangle* 10 g/l, *filled square* 15 g/l

ities appeared only within 1–2 mm at the bottom of the 1× 4-cm wafers); this procedure was therefore used throughout the study. The deposit thickness was chosen to produce an optimum accuracy of the reflectometric signal, which was determined theoretically (see below) using a previous calculation model described [28].

Reflectometry

The reflectometer constructed in the laboratory is similar to that of Dijt et al. [29]. Details of the apparatus were given in a former report [15]. The polarized laser beam reflected by the surface in the cell is decomposed in the two parallel (p) and perpendicular (s) components with respect to the incidence plane. The respective intensities (I_p and I_s) of the two components are measured with photodiodes, and the reflectometric signal S is calculated from

$$S = \frac{I_p}{I_s} = f\frac{R_p}{R_S} \tag{3}$$

R_p and R_s are the parallel and perpendicular reflectivity coefficients, respectively; they are calculated at the interface [27] using an appropriate optical model. f is an instrument coefficient that takes into account the optical and detection efficiencies.

The reflectometer output ($\Delta S/S_0$, see below) was related to the surface excess of the polymer (Γ) using a new approach described by Dejeu et al. [25]:

$$\frac{S-S_0}{S_0} = \frac{\Delta S}{S_0} = \frac{(R_p/R_s) - (R_p/R_s)_o}{(R_p/R_s)_o} = f(\Gamma) \tag{4}$$

S_0 and S are the values of the signal defined in 3 before (baseline) and in the course of the adsorption experiment respectively. The f function depends on several experimental parameters: the wavelength of the laser beam (632.8 nm), the thickness and the refractive index of the PA 6-6 layer on the silicon substrate (n=1.53), the refractive index increment of the polymer solution (dn/dc), and the refractive index of the adsorbed layer (n_{ads}). The latter may be calculated from the De Feijter relationship [30]:

$$n_{ads} = n_s + \frac{dn}{dc}\frac{\Gamma}{d_{ads}} \tag{5}$$

n_s is the refractive index of the polymer solution, d_{ads} is the thickness of the polymer deposit. The refractive index increment of the polymer solution (dn/dc) was measured for each solution using a differential refractometer (Mettler Toledo RE50). dn/dc was 0.2374 cm^3/g at 20 °C for PSSNa solutions at pH 3.

Calculation of the reflection properties with and without the adsorbed layer [i.e., (R_p/R_s) and $(R_p/R_s)_0$, respectively] was done using a procedure described previously [31]. $\Delta S/S_0$ was calculated using relation 4, and for the system PA 6-6/PSSNa, we found that a polynomial relationship of the second order was appropriate to relate Γ with $\Delta S/S_0$ [25]:

$$\Gamma = \frac{1}{2a}\left(-b \pm \sqrt{b^2 + 4a\left(\frac{\Delta S}{S_0} - c\right)}\right) \tag{6}$$

a, b, and c follow from a fit of this equation with the calculated response of the reflectometer to the adsorbed amount [25, 32]. These coefficients depend on the refractive index of the solutions. The sign ± is the same as that of b, which means that the adsorbed amount increases with $|\Delta S/S_0|$.

The choice of the PA layer thickness should be the best compromise between a high signal sensitivity to the polymer uptake and the lower sensitivity to thickness heterogeneities. The appropriate range was between 50 and 150 nm [25]. Additional characterization of the PA 6-6 layer was done to determine the appropriate substrate thickness more precisely.

Characterization of the polyamide coating

Coatings were analyzed using IR spectrometry, wetting angle, scanning electron microscopy (SEM), atomic force microscopy (AFM), and streaming potential measurements.

Infrared analysis

Fourier transform infrared-attenuated total reflectance spectra (IRFT NEXUS 470, Thermo Nicolet; not shown) revealed similar bands as those reported by Elzein et al. [33–35]. They were attributed to the elongational vibration of C–N and secondary amine (1,531 cm^{-1}), amide vibration (1,625.7 cm^{-1}),

vibration of symmetrical CH_2 (2,850.7 cm^{-1}), asymmetrical CH_2 (2,926.3 cm^{-1}) and bonded NH (3,285.8 cm^{-1}).

Wetting angle measurements

Measurements of the wetting angle of water and CH_2I_2 (GBX Digidrop) were consistent with results in the literature (Table 1) [36]. The slight difference in the case of water was attributed to the enrichment of oligomeric polar groups at the polyamide/water interface and possibly to some effect of the surface roughness.

SEM and AFM

SEM images showed no significant difference between 60 and 115 nm deposits. AFM images (Stand Alone Smena, NT-MDT) did, however, show that the 60-nm deposits presented a lower roughness (rms=6.3 nm) than the 115 nm (rms=12 nm; Fig. 3).

In the end, a deposit approximately 60 nm thick was chosen for an appropriate compromise. The uncertainty regarding the measurement of thickness was estimated at about 3 nm, which makes a variation of As about 6%. Practically, the polyamide film was made by dip coating from a solution containing 15 g/l of PA 6-6 with a withdrawal rate of 30 mm/mn.

Streaming potential

Streaming potential measurements (EKA, Anton Paar) were done on PA 6-6 fibers (9 μm thick and 9 mm long). The material was introduced in a cylindrical cell and first equilibrated in a KCl 10^{-3} M solution for 46 h. The pH was modified from the original value (pH 5.6) to either pH 11 or pH 3 by addition of KOH or HCl, respectively. The pH dependence of the streaming potential (Fig. 4) showed an isoelectric point about pH 4.8. The shape of the streaming potential curve was typical of a surface containing the NH_2 and COOH groups and resembled other measurements performed with polyamides [37, 38]. Assuming the intrinsic ionization p*K*as 9.85 and 4.8 for the following equilibria:

$$NH_3^+ \longleftrightarrow NH_2 + H^+ \quad (7)$$

Table 1 Wetting angle of water and diiodomethane on polyamide-coated silicon

Solvent	Measurement	Literature [36]
H_2O	64.12±1.4	72
CH_2I_2	34.9±1.5	35

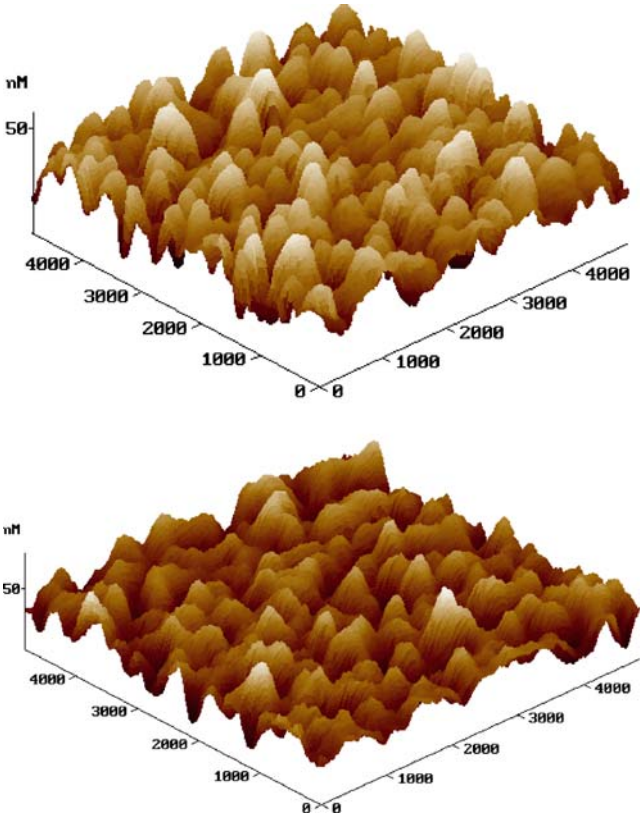

Fig. 3 AFM picture of dip-coated polyamide films; **a** 60 nm, **b** 115 nm

$$COOH \longleftrightarrow COO^- + H^+ \quad (8)$$

and referring to a former study [38], the ratio between the densities of NH_2 and COOH groups on the polyamide surface was estimated to be about 2. The electrokinetic curve lead to the choice of pH 3 for the adsorption experiments of PSS to create favorable electrostatic interactions.

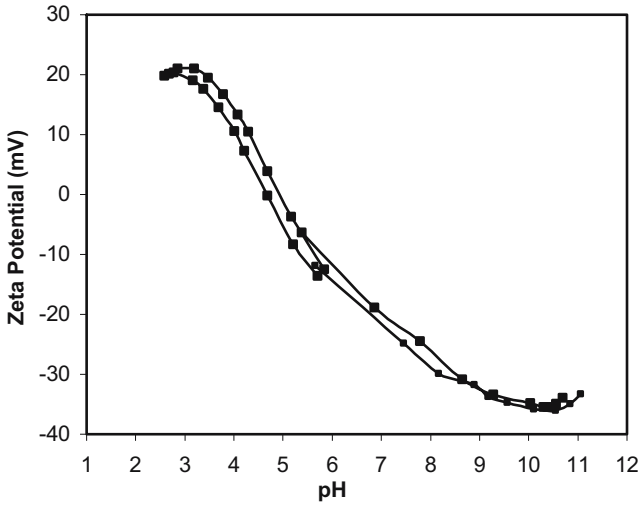

Fig. 4 Streaming potential vs pH of the polyamide fibers

Stability of the substrate (PA 6-6 layer)

In the course of the adsorption measurements, we found that the PA 6-6 layer was profoundly altered at higher pH, which subsequently interfered with adsorption in the reflectometric signal. Therefore, we shall first report on the stability of the substrate.

To evaluate the stability of the PA 6-6 substrate, we flowed polymer-free solutions at different pH, starting with a solution at pH 5.5 and subsequently at pH 11, 11.5, and 12. After each alkaline flow, the solution at pH 5.5 was circulated again. The output of these experiments (Fig. 5) showed a positive and very steep drift upon introduction of all alkaline solutions, the higher pH, the greater the increase. There was, however, a difference between pH 11 where the output was the same at each successive step and pH 11.5 and pH 12 where the output increased continuously and regularly at each alkaline step, merging approximately to the same output value after four sequences.

Another series of experiments was done by alternately flowing polymer-free solutions at pH 12 and pH 5.5, 7.6, or 9 with NaCl 10^{-2} M to maintain the ionic strength. Results (Fig. 6) showed an output trend similar to that in Fig. 5 at pH 12, but the return to the baseline depended on the pH of the alternate solution.

At pH 5.5, the baseline exhibited a slight negative drift at each repeated step. At pH 7.6, the baseline increased incrementally, and at pH 9, there was only a very slight difference between outputs at pH 12 and pH 9. In addition, output at pH 12 increased continuously during the flow of the solution, whereas it was stationary in the course of each alternate rinse at pH 9. Note that outputs were quantitatively similar in Figs. 5 and 6 at pH 12. There was quite a regular increase in output for alternate solutions at pH 12 (as in Fig. 5), where-

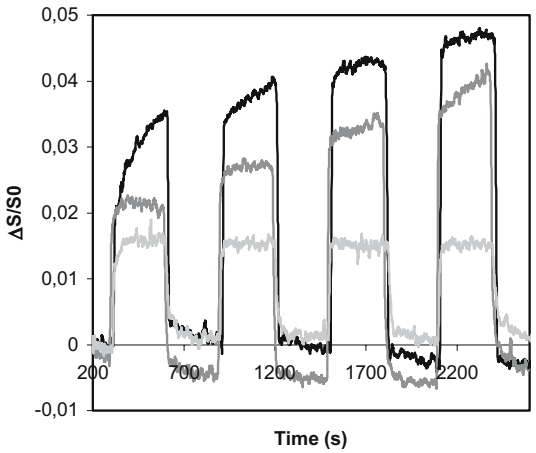

Fig. 5 Reflectometric output from the polyamide substrate (*PA*) upon rinses at different pH and alternate returns to pH 5.5. (*light gray*) pH 11, (*dark gray*) pH 11.5, (*black*) pH 12

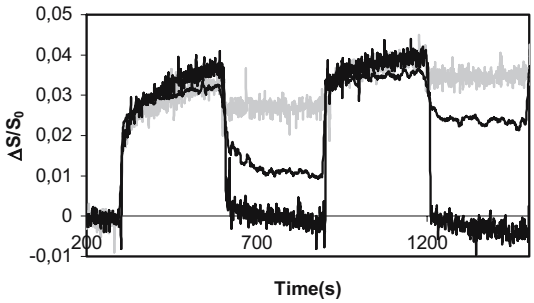

Fig. 6 Reflectometric output from the polyamide substrate (*PA*) upon alternate rinses at pH 12 and solutions at different pH. Alternate solution pH (*black*) 5.5, (*light gray*) 7.6, (*dark gray*) 9

as they were stationary at pH 9 but increased stepwise at each alternation.

The results above can be explained by the degradation of the polyamide substrate in very alkaline media at and above pH 11.5. It is our opinion that the hydrolysis of the polyamide layer at higher pH formed new carboxylic groups that increased the uptake of sodium counterions. Both the degradation of the layer and the binding of sodium ions caused an increase in the refractive index, hence, an increase in the reflectometer output. Obviously, chemical alterations at higher pH were irreversible, which explains the systematic increase in output when returning to lower pH. This can explain why the output increased continuously during the flow at pH 11.5 and pH 12, as the substrate was being hydrolized, contrary to the stationary output during the flow of solutions at pH below 11.5 due to the chemical stability of PA 6-6. It can also explain why output increased incrementally at pH 9, after treatment at pH 11.5 or 12, as the substrate was loaded with a higher amount of counterions. Finally, when returning to pH 5.5, the negative drift of the output certainly resulted from a change in the refractive index and/or a change in the substrate thickness caused by the chemical alteration taking place at pH 12.

The extent and rate of polyamide degradation was measured by performing a continuous flow of the polymer-free solution at pH 12 after recording a baseline at pH 5.5 (Fig. 7).

The output showed an instantaneous increase in $\Delta S/S_0$ from 0 to 0.04 followed by a progressive increase and a sudden break. Using the optical model, we estimate that the refractive index at the first increase (due to hydrolysis and sodium insertion) changed from 1.54 to 1.546, assuming a constant thickness. This increase would correspond to 10 wt % NaOH in the PA 6-6 layer. The intermediate drift in Fig. 7 resembled quantitatively that in Figs. 5 and 6 with a maximum $\Delta S/S_0$ value of about 0.13 at the break. The latter value corresponds to a refractive index between 1.561 and 1.554 with a film thickness between 60 and 62.5 nm, respectively. The break indicated that the polyamide layer was

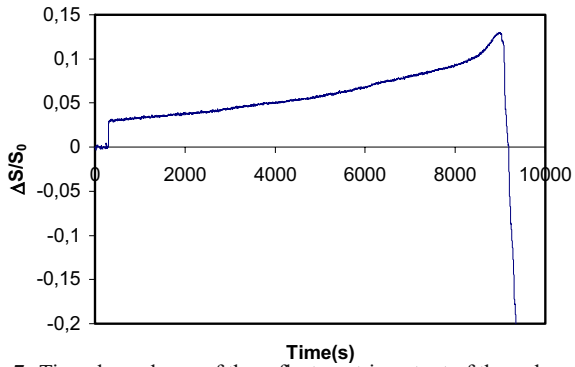

Fig. 7 Time dependence of the reflectometric output of the polyamide substrate in a solution at pH 12, NaOH 10^{-2} M

totally destroyed, which was confirmed under the microscope (not shown).

Polyamide hydrolysis has been reported in several papers in acidic [39, 40] neutral [41] and basic media [42]. In the latter case, the following reactions were proposed:

$$(\mathrm{I})\mathrm{P}-\mathrm{CO}-\mathrm{NH}-\mathrm{P}'+\mathrm{H}_2O \rightarrow [\mathrm{P}-\mathrm{COOH}\mathrm{H}_2\mathrm{N}-\mathrm{P}']_{\mathrm{cage}} \quad (11)$$

$$(\mathrm{II})[\mathrm{P}-\mathrm{COOH}\mathrm{H}_2\mathrm{N}-\mathrm{P}']_{\mathrm{cage}} \rightarrow \mathrm{P}-\mathrm{CO}-\mathrm{NH}-\mathrm{P}'+\mathrm{H}_2\mathrm{O} \quad (12)$$

$$(\mathrm{III})[\mathrm{P}-\mathrm{COOH}\mathrm{H}_2\mathrm{N}-\mathrm{P}']_{\mathrm{cage}} \rightarrow \mathrm{P}-\mathrm{COOH}+\mathrm{H}_2\mathrm{N}-\mathrm{P}' \quad (13)$$

Our experiments showed that hydrolysis did not occur reversibly, which means that the carboxylic + amine groups formed in reaction (I) did not reverse (reaction II) but more likely produced smaller segments (reaction III) that eventually detached, which lead to the final destruction of the layer (Fig. 7). At higher pH, the carboxylic group was totally ionized, with Na^+ ions in place of the protons in reactions I to III above. At pH 11.5 to 12, reactions I and III progressed continuously, producing new carboxylate groups and mobile oligomeric fragments that detached from the substrate. When switching to a lower pH, the carboxylate/carboxylic ratio and the bound Na^+ content followed from equilibrium at this pH, which is also reminiscent of the journey at higher pH. Figure 6 shows actually that the lower the pH of the rinse (9, 7.6, and 5.5), the lower the output, which is consistent with a higher $COOH/COO^-$ ratio (less Na^+ ions). Conversely, at pH 9, all carboxylic groups ionized and were neutralized with Na^+ counterions. As seen experimentally, at pH close and above the p*K*a of the carboxylic group (p*K*a≈ 6), we expect a higher output that increases with the rinse time at pH 11.5–12 due to a higher amount of COO^- Na^+.

At and below pH 5.5, sodium ions have no effect on the baseline, as most carboxylic groups are protonated. As said earlier, the slow and continuous decrease in the baseline is attributed to the progressive destruction of the PA 6-6 layer.

Adsorption measurements

Adsorption experiments were made by first circulating the solvent for 5 min at the pH and salt concentration of the subsequent polymer solution to record the baseline (S_0). The polymer solution was then introduced until the reflectometric signal was stationary.

Adsorption isotherm

Figure 8 presents an example of the variation with time of the output of the reflectometer ($\Delta S/S_0$) for the adsorption of PSS on PA 6-6 at pH 3 and polymer concentration 0.2 g/l.

All curves drawn at different polymer concentrations could be divided into three principal sections. At the start of adsorption (low polymer coverage), the output increased linearly with time, then the adsorption rate decreased progressively to reach a plateau value that depended on the polymer concentration (Table 2). The shape of the kinetic curves is typical for polymer adsorption. The initial slope is generally determined by a diffusion-limited adsorption process (see below), whereas the adsorption rate decreases close to saturation due mostly to electrostatic interactions in the case of ionized polymers [43]. Adsorbed amounts were calculated using relation 6. Plateau values varied significantly with polymer concentration, which was not expected, as, for a given sample of a "clean" polymer, there should be no influence of the bulk concentration in the electrostatic saturation of the substrate. If we examine Table 2 more carefully, we note that values at lower concentrations (about 0. 3 mg m^{-2}) were similar to other measurements, such as the adsorption of PSS on BaSO4 (0.25 mg m^{-2}) [44], PSS on hematite (0.6 mg m^{-2}) [45], and alumina (0.4 to 0.6 mg m^{-2}) [46], whereas the increase to 4.1 mg m^{-2} at higher

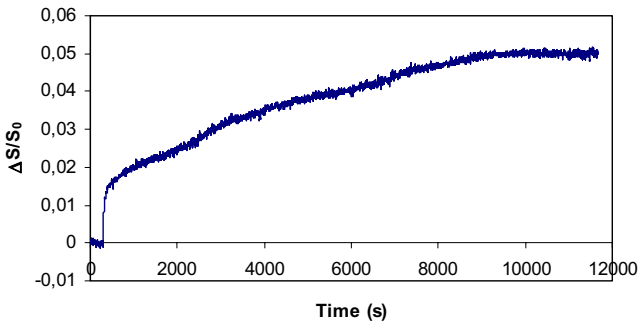

Fig. 8 Time dependence of the reflectometric output upon flowing a PSS solution (100 mg/l, pH 3)

concentrations is illogical in terms of surface occupancy for charged polymers (12 monomer units per nm^2). Polyelectrolyte adsorption is generally limited at the neutralization of the charge of the substrate [2]. Practically, the zeta potential of a saturated layer of adsorbed species does not exceed ±40 mV, which creates an electrostatic barrier preventing additional molecules to reach the surface [43]. We attribute the excessive uptake of polymer to the formation of complexes between PSS and cationic polyamide segments protruding from the surface or accessible by diffusion into the substrate. We will see below that the kinetic measurements support this hypothesis.

Adsorption rate

The time dependence of the reflectometric signal at the start of the experiment reflects the rate of adsorption of isolated molecules at low surface coverage [43]. In Fig. 9, adsorption rates are plotted as a function of the polymer concentration in the solution and show a strong increase with the solution concentration up to a constant value (1.6×10^{-8} kg/m^2 s^{-1}) at and above 0.2 g/l. Interestingly, rates at lower PSS concentrations (up to 2 mg/l, insert in Fig. 9) exhibit a linear variation, which is to be expected for a diffusion-controlled adsorption process [43, 47]:

$$\frac{d\Gamma}{dt} = kC_b \tag{9}$$

Γ is the uptake of polymer (mg/m^2), C_b is the bulk concentration, and k is a rate constant that depends on experimental variables [48, 49]:

$$k = 0.776\nu^{1/3}R^{-1}D^{2/3}\overline{\alpha}^{1/3}\mathrm{Re}^{1/3} \tag{10}$$

The different parameters in this equation and their numerical values in our experiments are ν the Kinematic viscosity of the solution (about 0.8×10^{-3} m^2.s^{-1} at 25 °C), R the inlet capillary radius (0.6 mm), D the diffusion coefficient of the polymer (5.62×10^{-11} m^2/s), $\overline{\alpha}$ an adimensional parameter that depends on the flow intensity close to the stagnation point (3.88), and Re the Reynolds number (8.5). Values of parameters in parentheses lead to k=5.6×10^{-5} m/s, which is very close to the experimental value found from the slope in Fig. 9 (5×10^{-6} m/s).

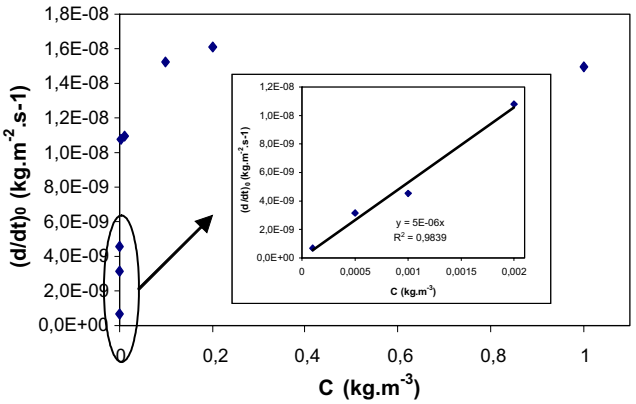

Fig. 9 Initial (low coverage) adsorption rate from experimental data (Fig. 5) vs PSS bulk concentration. Polymer concentration between 0 and 1 g/l. *Insert*, lower concentration domain (up to 2 mg/l)

Therefore, the rate of adsorption in the initial stage of our experiments satisfies the convective diffusion equation. At higher coverage, the rate decreased, and eventually, the adsorption reached a stationary value. At low polymer concentration, in the range of a diffusion limited process, the entire adsorption process took less than several minutes, which is well in line with most experimental and theoretical values found in experiments with the reflectometric cell [7, 21]. Oppositely, the timescale in the second adsorption regime at higher polymer concentration (see Fig. 8 for concentration 0.2 g/l) was much larger than usual (up to a few hours). The existence of a slow process met with the range of an excessive polymer uptake, which is a support to the hypothesis that a slow physicochemical process followed the prompt adsorption of PSS. The latter phenomenon was not investigated further in the present research.

Alternate PSS adsorption/desorption experiments on PA 6-6

Due to the degradation of the polyamide layer, we were not able to study PSS adsorption at a higher pH. Therefore, we used the following procedure to examine the reflectometric response of the polyamide/PSS system at different pH: the polymer was first adsorbed at pH 3 using a 15-mn flow of polymer solution at 10 mg/l (corresponding to the plateau adsorption 0.24 mg/m^{-2}, Table 2). Polymer-free solutions at different pH, NaCl 10^{-2} M,

Table 2 Value of the reflectometric signal and surface excess corresponding for different PSS concentration

C (ppm)	1	10	100	200	1,000	2,000	5,000	10,000
$\Delta S/S_0$	0.011	0.014	0.028	0.05	0.12	0.18	0.18	0.18
Γ (mg/m^2)	0.17	0.24	0.63	1.08	2.7	3.9	4.1	4.1

were then flowed into the cell for 15 mn, and the polymer solution at pH 3 was again circulated. The two successive experiments (adsorption and rinse) were repeated several times. Figure 10 summarizes the measurements that used rinsing solutions in the 5.5 to 12 pH range. Note that in all cases, PSS was adsorbed at pH 3 (Fig. 10a–f) and that the only difference was the pH of the rinse.

A complex behavior was observed depending on the pH of the rinse. Up to pH 10, the rinse caused a decrease in output ($\Delta S/S_0$) attributed to a partial desorption of PSS, as the flow of a new polymer solution at pH 3 nearly restored the initial output, i.e., the polymer released during rinsing reabsorbed. For rinse solutions at and above pH 11 (Fig. 10d–f), the output was meaningless in terms of adsorption–desorption phenomena, as rinsing with the polymer-free solution caused an increase in output, whereas no increase in adsorption was to be expected. Several experiments were performed to understand this phenomenon.

Remembering the results in the study of the stability of the PA 6-6 substrate to the adsorption–desorption measurements in Fig. 10, we may read the output rather clearly. Upon rinsing at pH 5.5, part of the adsorption layer formed at pH 3 detached due to the decrease in the positive charge of PA 6-6 (shown by the decrease of streaming potential in Fig. 4). It is

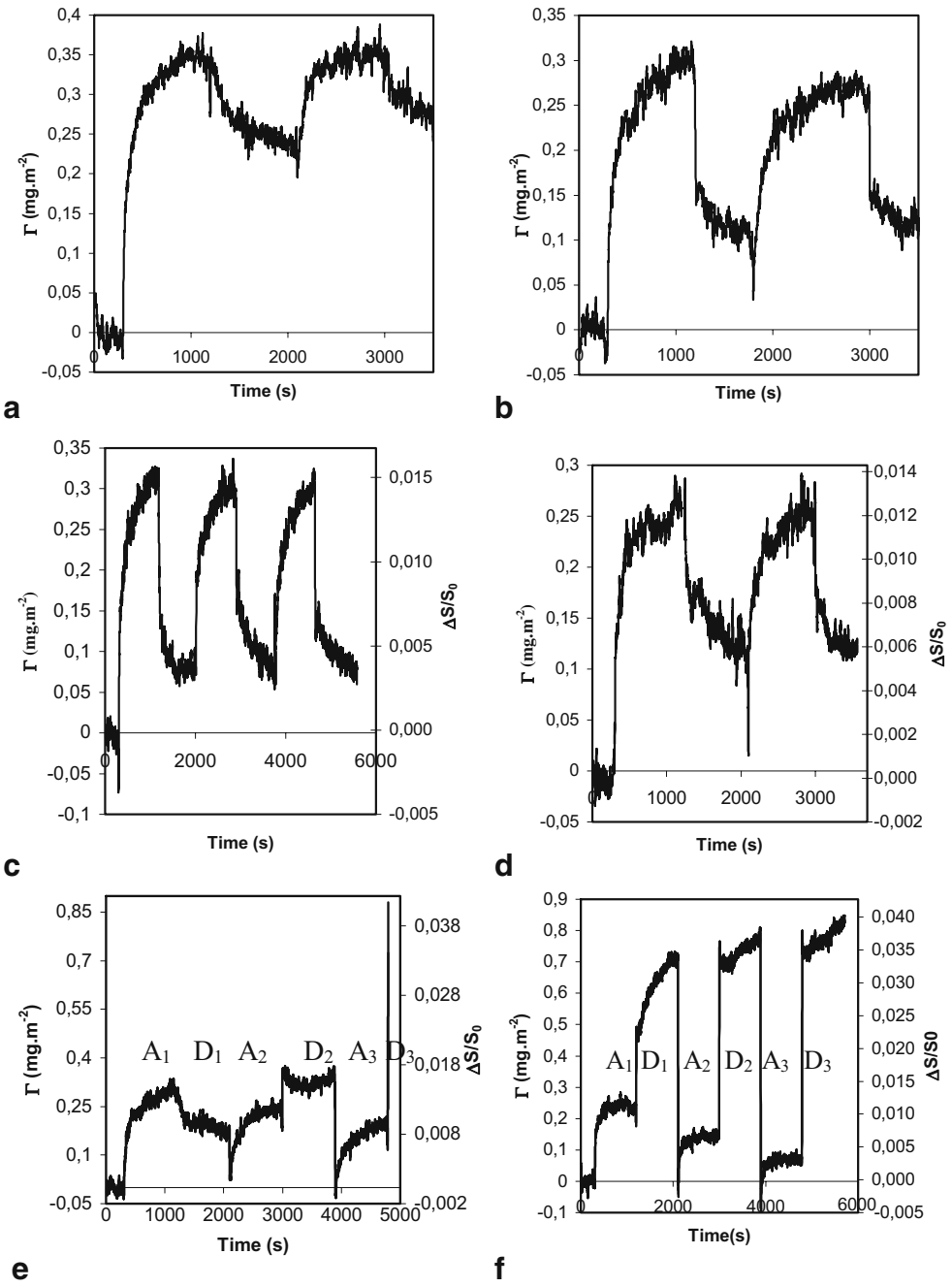

Fig. 10 Reflectometric outputs upon flowing PSS solution (100 mg/l, pH 3) and alternate rinses at different pH. pH of the rinse **a** pH 5.5, **b** pH 9, **c** pH 10, **d** pH 11, **e** pH 11.5, **f** pH 12

known that polyelectrolyte adsorption is approximately limited to the compensation of the surface charge [43]; thus, the polymer in excess of the charge balance desorbed easily upon electrostatic repulsion forces [50]. pH 5.5 is above the isoelectric point, i.e., the surface was in fact slightly negative; the remaining amount of PSS in the film at this pH was stabilized by non-electrostatic interactions, most likely van der Waals and hydrophobic forces. A similar behavior took place when alternating adsorption at pH 3 and rinsing at pH 9 (Fig. 10b) and 10 (Fig. 10c). Interestingly, we noted that the adsorption–desorption reaction was reversible upon change of pH, which is not a common feature with charged polymers. Once the polymer layer was immersed in a solution at and above pH 11.5, the degradation of the polyamide and the uptake of sodium ions modified the reflectometric output in a way that no longer allowed the monitoring of polymer adsorption. Although the different experiments presented in Fig. 10 were no longer useful for studying polymer adsorption at high pH, they reveal a very coherent and reproducible picture of the extent and progress of the deterioration of the polyamide substrate, which may be of interest with respect to other applications and studies.

Conclusion

The aim of this paper was twofold: to study the adsorption–desorption of a charged polymer ($PSS^{-}Na^{+}$) on polyamide 6-6 and to examine the feasibility of using reflectometry as a measuring tool.

PSS adsorbed significantly on PA 6-6 at pH 3, and the adsorption decreased as pH increased. This was due to the decrease and the reversal of the surface charge that turned negative at about pH 5. Some PSS remained adsorbed at pH 7.5 and pH 10, which is attributed to a non-electrostatic contribution to the binding with the surface.

Reflectometry allowed easy examination of the adsorption–desorption properties, showing that a reversible reaction took place when cycling the pH between pH 3 and pH 10. Reflectometry also revealed that PA 6-6 hydrolyzed irreversibly at and above pH 11.5, probably forming oligomeric fragments that detached from the substrate layer.

Finally, the time dependence of the reflectometric signal allowed the determination of the adsorption rate, from which, we found two kinetic regimes depending on the PSS concentration in the solution. A rapid increase in polymer uptake leads to a regular surface coverage about 0.3 mg m^{-2} at low polymer concentration and a slow increase in the output lasting several hours in high polymer concentration solutions. The slow increase in adsorption leads to unexpected values about 4 mg m^{-2}, which was attributed to the formation of complexes between PSS and functional groups at the surface and within the PA 6-6 layer.

Reflectometry proved to be a powerful tool to investigate the interaction between PA 6-6 and PSS, with results that could not be obtained by conventional batch adsorption procedures.

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