Macromolecules **1997,** *30,* 6095−6101

Kinetics of Adsorption of Poly(*o*-methoxyaniline) Self-Assembled Films

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Received February 19, 1997; Revised Manuscript Received July 2, 1997[⊗]

ABSTRACT: The kinetics of adsorption of poly(*o*-methoxyaniline) (POMA) via self-assembly has been investigated using UV−vis spectroscopy. Though experimental conditions, including type of substrate, affect the amount of polymer adsorbed, adsorption of the first POMA layer on glass substrates was shown to occur in two stages, reaching saturation within a few minutes. The first stage is represented by a first-order kinetics with characteristic times of 5−10 s. The second stage also has an exponential behavior with $t^{1.5}$ and characteristic times of hundreds of seconds, which was valid for all substrates when the shift in the polaronic band in the beginning of adsorption was taken into account. The $t^{1.5}$ within the exponential is believed to indicate a diffusion-controlled growth of small domains formed during the first stage of adsorption. The appearance of small domains and their subsequent growth are consistent with scanning electron micrographs obtained at distinct time periods of adsorption. When a POMA layer was made to adsorb on an already formed POMA/poly(ethenesulfonic acid) self-assembly multilayer, the adsorption process became faster as the number of bilayers already deposited increased.

Introduction

The self-assembly (SA) technique has become very popular over the last few years, as it allows the fabrication of ultrathin, organized multilayers of polymeric materials. It was originally developed by Decher[1,2] for polyelectrolytes and later extended to doped, conjugated polymers by Rubner.[3,4] Among the many advantages of the SA technique are the ease of film fabrication, as it does not require sophisticated equipment and is low in cost. In this context, it is an extremely promising alternative to the Langmuir−Blodgett (LB) technique[1] for applications in which control at the molecular level is desired. A variety of materials have been used for building SA multilayers (see ref 3, for example), from which an equally wide variety of supramolecular structures have been fabricated, including hybrid systems of LB/SA multilayers deposited on the same substrate.[5] In addition to the technological interest in the use of SA polymeric films in devices, such as LEDs[6,7] and displays,[6] a number of issues more akin to fundamental science are also worth of investigation. In particular, the phenomena associated with adsorption of the polymeric molecules onto the substrate and the kinetics that governs such adsorption process have not as yet been fully understood.

In this work, we have tried to address the kinetics of adsorption and for that we employed SA monolayers and multilayers containing poly(*o*-methoxyaniline) (POMA). POMA was chosen not only because the expertise for preparing and characterizing this material is available in our group but also because POMA LB films display electroactivity similar to conventional films of parent polyaniline.[8] In a previous work we showed that alternated layers of POMA and a polyanion (poly(ethenesulfonic acid) (PVS))[9] can be deposited on glass and on glass coated with indium tin oxide (ITO) substrates. It is shown here that adsorption depends on the type of substrate employed and its kinetics comprises two distinct processes.

Materials and Methods

Self-assembled (SA) films were obtained from polymeric solutions of poly(*o*-methoxyaniline) (POMA) and poly(ethenesulfonic acid), which at the pH = 3 used in the experiments are cationic and anionic, respectively. The films were adsorbed on hydrophilized glass, Teflon FEP (tetrafluorethylenepropylene), and ITO (indium tin oxide) substrates. The hydrophilized glass substrates were prepared using two procedures (I and II). In procedure I, microscope glass slides were treated with a H_2SO_4/H_2O_2 (7:3) bath for 1 h and a $H_2O/H_2O_2/NH_3$ (5:1:1) bath for 30 min, after which the glass slides were washed exhaustively with pure water. Procedure II consisted of washing the hydrophilized slides obtained by procedure I with a toluene bath for 2 min, a toluene/methanol (1:1) bath for 2 min, and a methanol bath for 2 min. Finally, the glass slides were, as in the former case, exhaustively washed with pure water. For the sake of simplicity, we shall refer to glass I and glass II as the hydrophilized glass obtained by procedures I and II, respectively.

Poly(*o*-methoxyaniline) was synthesized with ammonium peroxydisulfate in a 1.0 M HCl aqueous solution at 0 °C. The monomer to oxidant ratio was 4:1. The resulting precipitated polymer was filtered and washed with a 1.0 M HCl solution. Aqueous solutions were then obtained by dissolving the polymer in acetonitrile and subsequently in pure water (acetonitrile/water (1:49)). The processing with acetonitrile was necessary for rendering POMA soluble in an aqueous solution. Poly(ethenesulfonic acid) (Aldrich Chemical) solutions were prepared by dissolving the polymer in pure water. The initial concentration of the solutions of POMA and PVS was 10^{-2} M. However, since POMA solutions were filtered, the final concentration was about 10^{-3} M. We observed that even in these latter solutions some precipitation occurs after longer periods of time. The final pH of the aqueous solutions of POMA and PVS was adjusted to 3 with a 1.0 M HCl solution.

SA bilayers were built according to the following procedure: (a) the substrate was immersed in the cationic polyelectrolyte solution during the time required for a complete layer to be adsorbed; (b) the substrate was rinsed in a HCl aqueous solution with the same pH of the former solutions; and (c) the substrate was immersed in the anionic polyelectrolyte. Pure water was supplied by a Millipore system comprising reverse osmosis followed by ion exchange and filtration steps (Milli-Q, Millipore GmbH). The self-assembled films were characterized by UV−vis spectroscopy using a Hitachi U-2000 spectrophotometer, scanning electron micros-

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[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1997.

S0024-9297(97)00228-3 CCC: $14.00

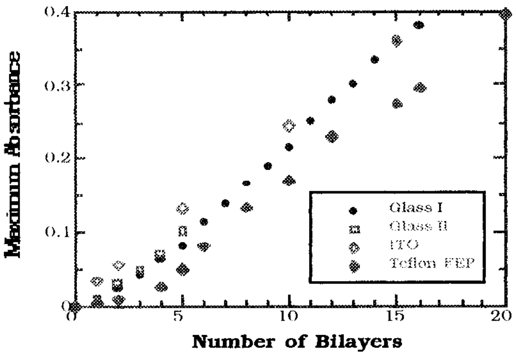

Figure 1. Maximum absorbance versus number of bilayers of POMA/PVS self-assembled films adsorbed on Teflon FEP, ITO, glass I, and glass II.

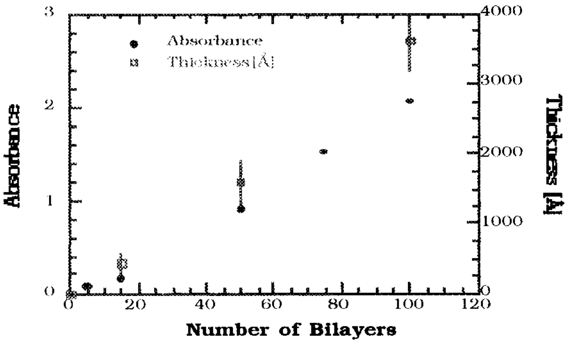

Figure 2. Maximum absorbance and thickness as a function of the number of bilayers of POMA/PVS self-assembled films adsorbed on glass II.

copy (SEM) (Zeiss DSM 960), atomic force microscopy (TopoMetrix TMX 2010), and profilometry (Taylor-Hobson Talystep). Samples observed through SEM had their surface covered with gold, and the voltage of the electron beam was 10 kV. All experiments were conducted at room temperature in the range 23 ± 4 °C.

Results and Discussion

Fabrication of SA Films. Doped POMA in solution or in the form of films produced by casting[10] and the LB technique[11] displays a band in the UV−vis spectra peaking at 750−950 nm. This is the so-called polaronic band.[12] Such behavior was also observed for SA films from doped POMA and PVS, since PVS does not absorb in this wavelength range. The absorbance at the peak (at λ_{max}) was then used to monitor the buildup of multilayers, as illustrated in Figure 1. POMA/PVS bilayers were deposited on glass, coated glass with indium tin oxide (ITO), and Teflon substrates, and the amount of POMA deposited is seen to depend on the type of substrate. The time of substrate immersion in each solution was 3 min, and the substrates were dried after washing with the HCl aqueous solution. One can see that the data follow straight lines within experimental error, indicating that each deposited bilayer contributes an equal amount of deposited polymer, which demonstrates the formation of multilayers of POMA and PVS. The first data points for Teflon FEP, however, do not follow a linear plot. This may have occurred because the immersion time used (3 min) was not sufficient for complete coverage of the substrate, as it became clear from subsequent studies of the kinetics of adsorption. Teflon FEP is hydrophobic and as a consequence only a small amount of POMA could be attached to the surface. When the Teflon substrate is immersed in the PVS solution, PVS molecules could be adsorbed on the POMA film and on the uncovered surface. So the available surface for the next POMA layer to be adsorbed is larger. When this process is completed, the POMA/PVS film grows linearly. Adhesion is also poor on Teflon substrates, with the SA films being easily detached when a sealing tape is peeled from it. This is not the case for the SA films deposited onto glass substrates.

The adsorption of POMA by self-assembly on a variety of substrates is important insofar as it demonstrates that different engineering strategies may be used for producing superstructures. Glass coated with indium tin oxide (ITO) is now widely used for cyclic voltammetry studies as well as in applications where a transparent electrode is required, such as for building light emitting diodes.[6,7] That highly stable polymers like Teflon may be coated with SA films is also of interest. As the results demonstrated, adequate experimental conditions must be identified for each class of substrate. In subsidiary experiments, POMA layers were adsorbed on aluminum slides. Adhesion proved to be the strongest among the films observed, probably due to H-bonding, as the Al_2O_3 layer on top of the aluminum surface contains Al−OH groups.

The drying procedure between adsorption of either cationic or anionic layers is necessary for building uniform self-assembled layers, especially for the first few bilayers. For the attempts to grow multilayers by simply alternating immersion into the polymer solutions and washing in between, consecutive adsorption procedures (without drying) failed to produce a linear increase in absorbance with the number of layers, in particular for the first three or four deposited layers.

The thickness of SA POMA/PVS films with various bilayers was measured with a profilometer. As shown in Figure 2, the maximum absorbance and the thickness of self-assembled POMA/PVS films on glass II increase linearly with the number of bilayers, which is further indication of formation of a uniform multilayer structure. The thickness per POMA/PVS bilayer is ∼35 Å, but this value may change when experimental conditions are altered. Such changes in thickness have also been observed by Ferreira and Rubner for poly(thiophene-3-acetic acid) (PTAA)/poly(allylamine) (PAH) multilayers.[13]

The in-plane conductivity of POMA/PVS multilayers, as measured using the four-probe van der Pauw technique, is of the order of 10^{-4} S/cm. Though no attempt has been made to measure the transverse conductivity in the samples produced for this work, it is known that such a conductivity is normally much lower than the in-plane conductivity, analogous to what has been observed for Langmuir−Blodgett films from conducting polymers.[14] Because of the layer-by-layer structure of an LB film, the anisotropy may be so large as to allow for in-plane conductivities that are 8−10 orders of magnitude higher than the transverse ones.[14]

Kinetics of Adsorption of the First POMA Layer. The kinetics of adsorption of conducting polymers in self-assembled films has been discussed by Ferreira and Rubner[13] for poly(thiophene-3-acetic-acid) (PTAA). They observed that in the first 3 min of adsorption, the amount of adsorbed polymer increased with $t^{1/2}$, thus suggesting that adsorption could be diffusion controlled as in a Langmuir−Schaefer type adsorption.[13] However, the calculated effective diffusion coefficient for various polymer concentrations varied over four orders of magnitude which prompted them to conclude that the

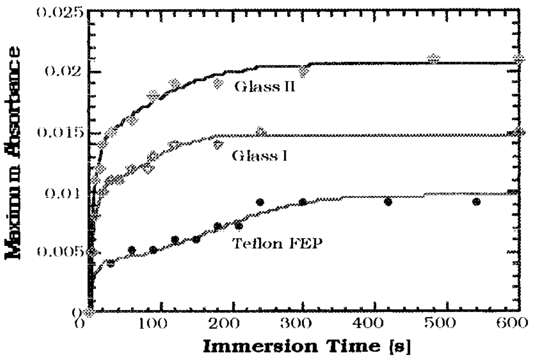

Figure 3. Maximum absorbance versus immersion time for the first layer of POMA deposited onto various substrates. The solid lines represent the fitting using eq 1 with the parameters of Table 1.

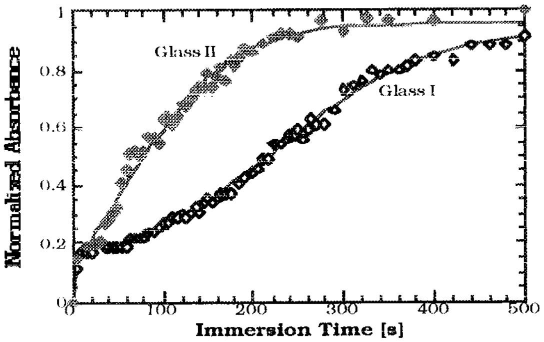

Figure 4. Absorbance versus immersion time for the first POMA layer adsorbed onto glass I and glass II substrates. Points were taken every 5 s. The solid lines represent the fitting using eq 1 with the parameters of Table 1.

Langmuir–Schaefer relationship is not valid for PTAA in the time regime accessible by UV–vis experiments. Our data for POMA cannot be explained by a $t^{1/2}$ dependence even for the first minute of immersion, as a very sharp increase occurs in the initial stage. In fact, the curves in Figure 3 for adsorption of the first POMA layer onto distinct substrates indicate the probable existence of a two-step process during adsorption, as discussed later. Other interesting features are observed in the figure: (i) Under the experimental conditions adopted, saturation of the UV–vis absorbance is achieved within 5 min of immersion for all substrates. A deviation of about 30% was observed in the saturation value for distinct substrates prepared under the same conditions. Similar deviations were obtained by Avlyanov et al.[15] (ii) For Teflon FEP a smaller value of saturation was obtained, indicating a less effective POMA uptake as discussed before. (iii) A small kink is apparent in all curves.

In order to make a more detailed analysis of the mechanisms responsible for the kinetics of adsorption, we had to check the existence of a kink (or even a plateau) in Figure 3. Since this could only be confirmed if measurements were taken at shorter intervals, further experiments were conducted with data being collected every 5 s of immersion. After each immersion the substrate was washed with a HCl aqueous solution and then dried by blowing nitrogen gas. Resolution in time improved considerably, as illustrated in Figure 4, which shows the POMA first layer normalized adsorption kinetics on glass I and II substrates. It should be noticed that the absorbance saturation values for glass I substrates are lower (0.06) than those for glass II (0.1), indicating a more effective polymer adsorption in the latter case. The results revealed for glass II a slight kink after the initial, sharp increase in absorbance, while a plateau was observed for glass I. Another major difference to be noted is the magnitude of the absorbance saturation values obtained (0.06 for glass I and 0.1 for glass II), in comparison with the results shown in Figure 3 (0.015 for glass I and 0.02 for glass II) which means that the amount of material adsorbed is approximately 4–5 times that of Figure 3 for the same time period and substrate.

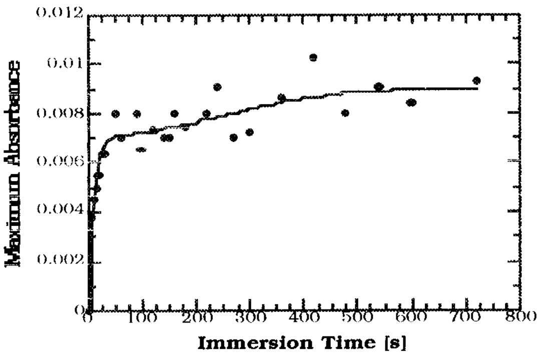

Figure 5. Maximum absorbance versus immersion time for the first layer of POMA adsorbed on glass I substrates. Each point represents the average from four distinct substrates, which explains the large dispersion. The solid line is the fitting obtained with eq 1 and the parameters shown in Table 1.

It is clear then that interrupting the adsorption process every 5 s allows more material to be adsorbed. One may wonder now whether the plateau only appeared because of this large number of interruptions. This was checked by carrying out an experiment in which 100 slides of glass I were employed for POMA adsorption. Groups of four samples were immersed during a given time period, which varied from 5 up to 700 s. Therefore, each substrate was submitted to only one drying procedure for the UV–vis spectra to be taken. The points in Figure 5 represent the absorbance average for each group. The absorbance is again much lower than in Figure 4 since the samples were not submitted to repeated drying procedures. Because the substrate surfaces are bound not to be identical, a dispersion of ca. 30% was observed in the absorbance value. The trend for a two-step adsorption process, including a plateau after the initial, steep rise in absorbance, is nevertheless apparent in the figure. One may thus conclude that the plateau is indeed a real effect, regardless of the interruptions for drying the sample.

Two possible explanations may be proposed for the remarkable increase in the POMA adsorbed amount when adsorption is interrupted several times. (a) As the hydrophilized substrate is immersed into the polymeric solution, POMA and water molecules are adsorbed on the substrate surface. Where water molecules are adsorbed, POMA molecules may find it difficult to adsorb, and therefore substrate coverage may not be complete. When the substrate is taken off the solution and dried, the sites created by removing water molecules become available for further POMA adsorption in the next immersion. Saturation values are then expected to be higher when data are collected more frequently. (b) Another possibility is that the substrate + POMA system is being affected by the washing solution, through altering the doping state and/or the polymer conformation.

In an attempt to fit the absorbance vs time data we tried several model equations but failed when using a

Table 1. Parameters Used in Equation 1 for Fitting the Experimental Data of Figures 3−5

substrate	figure	k_1	τ_1 (s)	k_2	τ_2 (s)	n
glass I	3	0.011 ± 0.001	7 ± 1	0.004 ± 0.001	110 ± 10	2.24
	4[a]	0.011 ± 0.001	5 ± 2	0.045 ± 0.001	280 ± 50	2.24
	5	0.007 ± 0.001	10 ± 2	0.002 ± 0.001	300 ± 100	2.24
glass II	3	0.014 ± 0.001	8 ± 1	0.006 ± 0.001	120 ± 20	1.5
	4[a]	0.016 ± 0.001	4.6 ± 0.1	0.080 ± 0.002	117 ± 4	1.5
Teflon FEP	3	0.004 ± 0.001	7.8 ± 0.1	0.005 ± 0.001	220 ± 20	2.24

[a] Note that the fitting was obtained with the maximum absorbance vs time data instead of the normalized maximum absorbance shown in Figure 4.

single function. The behavior is surely not characteristic of a first order kinetics process (exponential behavior) nor is it characteristic of a diffusion-controlled adsorption ($A \sim t^{1/2}$). The data can, nevertheless, be fit if two exponential functions are superimposed. Indeed, if we use

$$A = k_1\left(1 - \exp\left(-\frac{t}{\tau_1}\right)\right) + k_2\left(1 - \exp\left(-\left(\frac{t}{\tau_2}\right)^n\right)\right) \quad (1)$$

where A is the absorbance (taken as proportional to the amount of adsorbed material), k_1, k_2 and n are constants, and τ_1 and τ_2 are the characteristic times, reasonable fittings are obtained, as demonstrated by the full curves shown in Figures 3−5. The first exponential corresponds to a first-order kinetics with a very short characteristic time (approximately 5−10 s). The second process cannot be first-order because the increase in absorbance that follows the plateau has an upward inflexion. Rather, it was represented by a so-called Johnson−Mehl−Avrami function with t^n in the exponential and with characteristic times ranging from 100 s to 350 s. Table 1 shows the parameters used for fitting the data of Figures 3−5. The only major difference in the parameters is that adsorption is most concentrated in the first process when there are no repeated drying procedures ($k_1 > k_2$), whereas the opposite is true for the data in Figure 4.

The two-step process of adsorption was to be expected since the first one should correspond to the polymer molecules being driven toward the substrate by electrostatic attraction while the second process corresponds to the rearrangement of polymer molecules on the substrate. This behavior is in accordance with results obtained by Motschmann et al.[16] and Haidara et al.,[17] who observed intermediate plateaus in the adsorption kinetics of polystyrene (PS)−poly(ethylene oxide) (PEO) copolymer onto a silicon wafer and a nonionic alkylpoly(oxyethylene) surfactant on a methyl-terminated surface, respectively. These transitions were also related to structural rearrangements on the adsorbed surface. What is intriguing in the results presented here is the time scale of the first process (5−10 s), during which polymer molecules are unlikely to suffer changes other than collapsing onto the surface. Yet, this is the order of magnitude of the characteristic time for the first process. On the other hand, the first-order kinetics nature of the first process has a simple physical meaning while the second process requiring a t^n in the exponential has no straightforward meaning. According to Machlin,[18] the t^n within the exponential may be related to a process of diffusion-controlled growth for domains (islands) of adsorbed material. Values of n ranging from 1.5 to 2.5 would be suitable for all domain shapes growing from small dimensions and a decreasing nucleation rate.[18] When the substrate is glass II, the experimental data are fitted with a sum of a pure exponential with a constant time of about 5−10 s and an exponential of $t^{1.5}$. In this case, the process should be associated with a diffusion-controlled growth with domains growing from small dimensions and zero nucleation rate.[18] That is, nucleation was entirely restricted to the first adsorption process, with the domains growing in the second step.

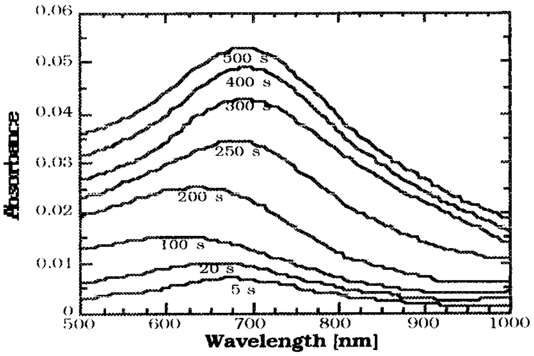

Figure 6. UV−vis absorbance spectra of adsorbed POMA on glass I for various time periods of immersion.

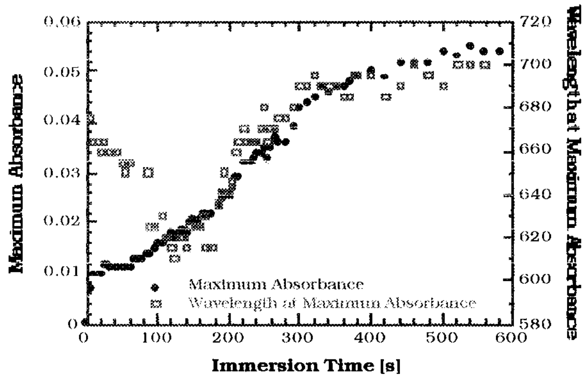

Figure 7. Absorbance and wavelength at maximum absorbance of adsorbed POMA on glass I as a function of immersion time.

Wavelength Shift in the Polaronic Band. Wavelength shifts in the polaronic band in UV−vis spectra may be associated with changes in the doping level of POMA, consistent with the work by MacDiarmid and collaborators[12,19] who showed that the polyaniline absorption band shifts to higher wavelengths when the doping state goes from emeraldine base to emeraldine salt. A shift of this kind is shown in Figure 6 where the UV−vis absorbance spectra are plotted for different immersion times of glass I substrates into a POMA solution. The effect is more clearly visualized if one plots both maximum absorbance and wavelength at maximum absorbance as a function of immersion time, as in Figure 7. In fact, one can observe that λ_{max} is seen to decrease during the first fast process, indicating dedoping. It is interesting to note that when the plateau is complete, λ_{max} rises in much the same way as the maximum absorbance itself. Therefore, POMA not only recovers its initial doping level but may also become

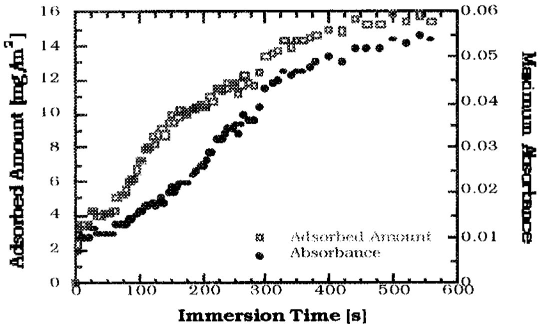

Figure 8. Estimated adsorbed amount per unit area and maximum absorbance versus immersion time.

Table 2. Parameters Used in Equation 1 for Fitting the Experimental Data of Figure 8 and Also the Data on the Estimated Adsorbed Amount of POMA from Figure 5

data from	k_1 (mg/m^2)	τ_1 (s)	k_2 (mg/m^2)	τ_2 (s)	n
Figure 8	3.8 ± 0.2	4 ± 2	12.3 ± 0.2	214 ± 7	1.5
Figure 5	2.2 ±0.2	10 ± 3	0.6 ± 0.2	200 ± 70	1.5

more heavily doped than in the beginning. Dedoping was unlikely to arise from the handling process, since measurements were carried out immediately after removing and drying the substrate from the polymeric solution. It was probably caused by interaction between the adsorbed polymer and the substrate. Indeed, this is corroborated by a shift in λ_{max}, which is also observed when multilayer films are adsorbed on a glass substrate (results not shown here). As the number of layers is increased, λ_{max} is shifted toward higher wavelengths as the substrate effect becomes increasingly less important, until it reaches a steady state value.

The shifts observed may alter the kinetics curves since the extinction coefficient associated with each peak could vary during adsorption. In order to check this hypothesis, the time dependence of the estimated amount of polymer should be obtained. For that, two extinction coefficients were determined from calibration curves of absorbance versus concentration carried out on POMA aqueous solutions for pH = 3 and pH = 4.5. The maximum absorbances occur at about 750 and 650 nm, for pH = 3 and pH = 4.5, respectively. Using Beer's law the extinction coefficients for these POMA solutions were calculated to be $(1.7 \pm 0.1) \times 10^4$ g^{-1}cm^2 (pH = 3) and $(1.0 \pm 0.1) \times 10^4$ g^{-1}cm^2 (pH = 4.5). Assuming that the extinction coefficient is the same for POMA molecules in aqueous solutions and molecules adsorbed on a solid substrate, and also that in a first approximation the extinction coefficient varies linearly with the wavelength of maximum absorbance, the amount of polymer adsorbed per unit area could be estimated. Figure 8 shows the results obtained as a function of immersion time. It can be readily seen that the overall behavior is maintained, including the plateau after the initial, fast increase in absorbance.

The kinetics of the adsorbed amount shown in Figure 8 for a glass I substrate approaches that obtained with glass II for the kinetics of the UV–vis absorbance (Figure 4). Table 2 shows the parameters used in the fitting by eq 1, where n is now 1.5 as for glass II in Table 1. The characteristic times τ_1 and τ_2, on the other hand, are of the same order of those in Table 1 for glass I and II substrates. The plateau region seems to be associated with the dedoping effect. This could possibly be explained by the decrease in the positive charge density within the polymer upon dedoping; the electrostatic driving force for adsorption will decrease, having a quenching effect on the adsorption increase.

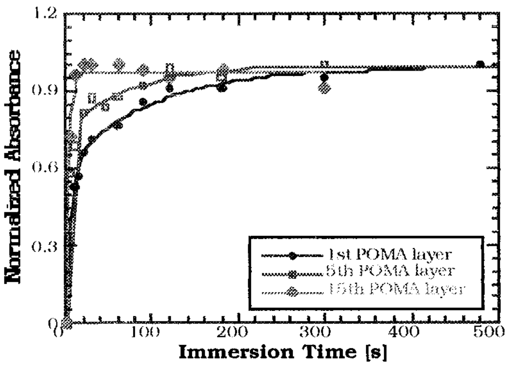

Figure 9. Normalized average absorbance versus immersion time for adsorption of a POMA layer onto an already formed POMA/PVS multilayer with 0, 4, and 14 bilayers. Glass II was used as the substrate.

Data for the adsorbed amount of POMA on glass II substrates are not shown here, since there is very little change in behavior when the peak shift is taken into account. The fitting with eq 1 is also carried out with $n = 1.5$. The same applies to the results in Figure 5 from those substrates immersed into a POMA solution for distinct time periods and submitted to only one drying procedure. As illustrated in Table 2, the data are fitted with eq 1 and $n = 1.5$. Note that because substrates were dried only once, the total amount of adsorbed POMA per unit area (2.8 ± 0.4 mg/m^2) is considerably smaller than that for the sample in Figure 8 (16.1 ± 0.4 mg/m^2). In conclusion, when adsorption data are corrected for the peak shift, eq 1 holds with $n = 1.5$ in all cases. That is to say, during the first kinetics process, most domains (nuclei) are formed, which then grow in the second adsorption process. The differences observed in the adsorbed amount for glass I and glass II proved to be less important than one might have expected, as the kinetics of adsorption has the same nature in the two cases.

Adsorption Kinetics in SA Films. The influence of the substrate was highlighted while discussing adsorption data in the previous sections. Even the process of surface treatment of glass was also shown to have some effect. This has prompted us to analyze in detail the kinetics of adsorption of a given POMA layer on top of an already formed SA multilayer, since in this case substrate effects should be less important. Figure 9 shows normalized absorbance vs time curves for deposition of the 1st, 5th, and 15th layer of POMA onto glass II. It can be seen that the adsorption process becomes faster when the number of layers already deposited is increased. Analogously to the adsorption of the first layer, we were unable to fit the data using only a single function. Indeed, the major features observed for the first deposited layer are present in Figure 9. This is consistent with the results for the poly(thiophene-3-acetic acid)/poly(allylamine) (PTAA/PAH) system investigated by Ferreira and Rubner,[13] for which the kinetics of adsorption was practically independent of the number of layers already deposited. The data can again be fitted by eq 1, as demonstrated by the full curves in Figure 9, though now $n = 1$ in the second exponential. The parameters calculated by fitting the data are shown in Table 3. The first exponential corresponds to a fairly fast process (characteristic time of approximately 5 s), while the second exponential process is slower with a characteristic time of the order of 100 s. The time

Table 3. Parameters Used in Equation 1 for fitting the data of Figure 9

POMA layer	k_1	τ_1 (s)	k_2	τ_2 (s)	n
1	0.62 ± 0.04	7 ± 1	0.37 ± 0.04	100 ± 30	1
5	0.74 ± 0.04	3.8 ± 0.6	0.25 ± 0.04	70 ± 30	1
10	0.72 ± 0.03	4.3 ± 0.5	0.29 ± 0.03	120 ± 30	1
15	0.98 ± 0.03	3.5 ± 0.6			0

constant, τ_2, calculated with these data is within the interval obtained for the values calculated from eq 1, Table 1. These time constants appear to be independent of the number of layers already deposited (probably also independent of the substrate).

The constant k_1 tends to increase with the number of POMA layers, which shows the increasing predominance of the first process. This could be taken as a complete elimination of substrate effects, also indicating that the electrostatic attraction is stronger between POMA and PVS than between POMA and the substrate. Another feature worth attention is the absorbance decay subsequent to saturation. This decay tends to increase with the number of POMA layers and could be associated with polymer desorption but a more detailed study is required to confirm such a hypothesis.

SEM and AFM Measurements. In order to further investigate the buildup process of a polymer layer, substrates of glass I with different immersion times were observed using scanning electron microscopy (SEM) (results not shown) and atomic force microscopy (AFM). In both cases there was evidence that a large number of small domains were formed at very early stages of adsorption. These domains grew as the time of immersion was increased, as can be illustrated by comparison of two AFM micrographs in Figure 10a,b. The differences in these particular figures are enhanced because in Figure 10b the substrate was immersed six times (5 s each immersion), according to the procedures described for obtaining Figure 4. As already discussed, the amount of material deposited under these conditions is considerably larger, as is evident from the micrographs. It is worth mentioning that the small dots taken as evidence of polymer domains do not appear in an AFM micrograph taken with bare glass. Though the number of domains is already very high for 10 s of immersion (Figure 10a), larger aggregates only appear after some time of immersion, which is consistent with the growth of domains predominating in the second stage of adsorption (discussed above).

Conclusions

The adsorption process via self-assembly of a conducting polymer, POMA, has been monitored by UV−vis spectroscopy. Two stages of adsorption were clearly identified not only for the first POMA layer but also for a layer deposited on top of an already formed POMA/PVS self-assembly multilayer. Because several experimental parameters (e.g., substrate, drying procedure, etc.) affect the kinetics of adsorption, a large number of experiments were conducted to confirm this two-step process. The data have been fitted by an empirical equation comprising an initial, fast first-order kinetics with characteristic times of a few seconds, followed by a Johnson−Mehl−Avrami function with t^n in the exponential and slower characteristic times (hundreds of seconds). The latter function is generally believed to occur in processes of diffusion-controlled growth for domains (islands) of adsorbed material. When the effect of the peak shift is taken into account, the data may be fitted with $n = 1.5$, which means that all nucleation took place in the first stage of adsorption and the domains grew in the second stage. This nucleation and growth mechanism was corroborated by scanning electron and atomic force microscopy observations and was also consistent with atomic force microscopy results for in situ adsorbed polyaniline by Avylanov et al.[15]

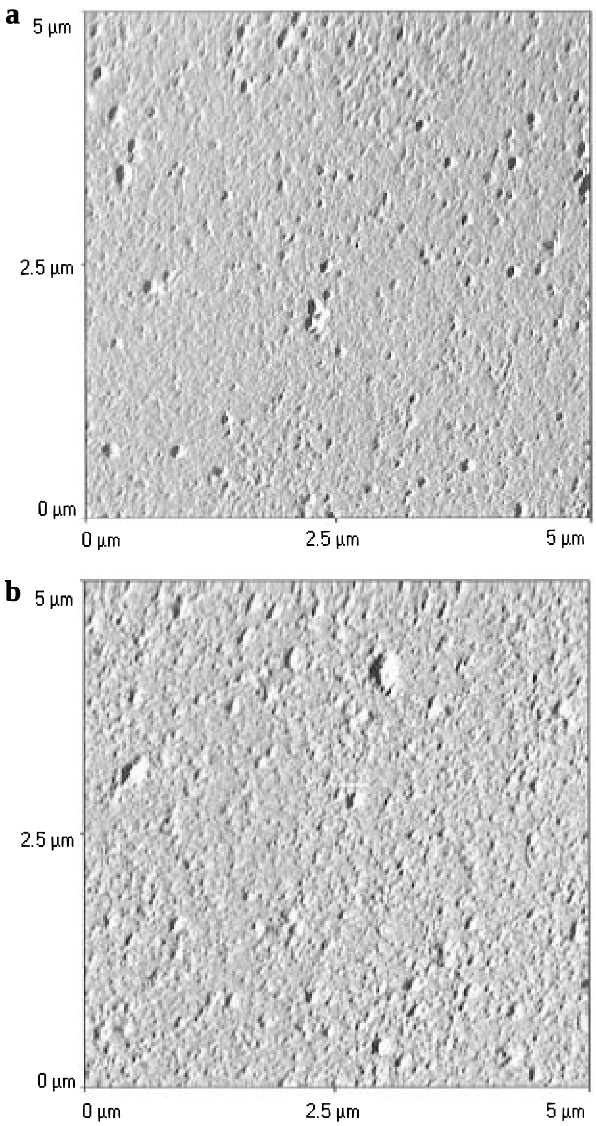

Figure 10. Noncontacting atomic force micrographs of POMA adsorbed on glass I substrates under the following conditions: (a) a single immersion lasting 10 s; (b) six immersions of 5 s each.

As for the generality of the two-step process identified for POMA self-assembly films, the influence of other parameters should be considered. It is widely known that experimental conditions such as the pH, concentration, and ionic strength of the polymeric solution affect the adsorption mechanism. Based on our own work for poly(*o*-ethoxyaniline) (POEA)[20] and the work by Ferreira and Rubner,[13] we may infer that such parameters will affect the amount of POMA adsorption to some extent but the overall behavior, consisting of a two-step process, will probably remain the same.

A particularly important result from the experimental point of view was the influence of the drying procedure between immersions. By frequently interrupting the adsorption process for washing and drying the film, one is able to deposit much thicker layers of POMA, though the possible differences in electrical and optical characteristics of such films are yet to be investigated.

Acknowledgment. The authors acknowledge the financial support from FAPESP and CNPq (Brazil). M.R. is supported by JNICT-PRAXIS XXI (Portugal). They are also grateful to Mr. Rubens Bernardes Filho for the help with the AFM measurements.

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MA970228F