

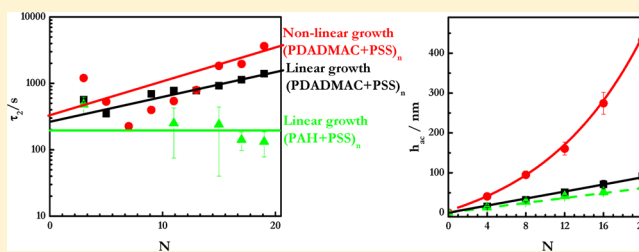
Growth of Polyelectrolyte Layers Formed by Poly(4-styrenesulfonate sodium salt) and Two Different Polycations: New Insights from Study of Adsorption Kinetics

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ABSTRACT: We report an experimental study on the growth and adsorption kinetics of polyelectrolyte multilayers (PEMs). PEMs composed of poly(diallyldimethyl ammonium chloride) (PDADMAC) and poly(sodium 4-styrenesulfonate) (PSS), and of poly(allylamine hydrochloride) (PAH) and PSS polyelectrolyte pairs were built and studied via dissipative quartz crystal microbalance (D-QCM) and ellipsometry. The results have pointed out that the growth trend of PEMs may be controlled by the assembly conditions that modify the layer structure and subsequently the film features. The study of adsorption kinetics of the layers suggests that, even though interdiffusion may take place during the growth of PEMs, it does not determine the growth mechanism. Analysis of the mechanical properties allows confirmation of the scenario proposed for the explanation of the PEMs growth. Independent of growth type, the adsorption kinetics of the layers is a bimodal process. The results here presented allow us to rule out any correlation between growth mechanism and adsorption dynamics.



1. INTRODUCTION

Since the first study by Decher et al.,¹ the layer-by-layer (LbL) self-assembly technique has been widely used in the field of interfacial engineering for the fabrication of functional coatings.² These are useful in a wide range of applications within different areas of nanotechnology (interfacial phenomena, colloids, and nanomaterials).^{3,4} However, to fabricate these functional films with controlled structures and physicochemical properties, it is necessary to know how different variables may affect the building process (polymer charge density and concentration, ionic strength, solvent quality for the polyelectrolytes, pH, and/or temperature).^{5,6}

In recent years, experimental and theoretical efforts in the field of LbL films have been focused on study of the growth mechanism of the layers and on the adsorbed amount, as well as on potential applications of these systems.⁴ Despite the extensive research in this field, many aspects still remain unclear.^{5,7} Among these, there is an important lack of knowledge on the adsorption kinetics of the layers^{8,9} and how it is related to the growth process and to the structure and final properties of the films obtained.

Two types of growth regimes (thickness versus number of layers) have been described for polyelectrolyte multilayers (PEMs): linear and nonlinear (usually known as exponential).⁶ It is commonly accepted that the physical origin of the nonlinear mechanism is the existence of internal reorganization processes (diffusion of polymers within the film). The reorganization has been usually associated with diffusion of at

least one of the polyelectrolytes between the bulk of the multilayer and the film–solution interface, driven by a Donnan equilibrium.^{10–12} However, in the case of linear growth, interactions at the film–solution interface control the growth of the film instead of the Donnan potential. Recently, Haynie et al.¹³ have revisited these classical models and have suggested alternative explanations for nonlinear growth. Even though it does not necessarily rule out the existence of diffusion, they pointed out that interdiffusion is not the only cause responsible for the nonlinear mechanism, and they opened the question whether interdiffusion may also exist in PEMs that grow linearly. It is expected that some information about the processes involved in adsorption of layers, and especially about the existence of interdiffusion, can be obtained from analysis of the adsorption kinetics of different layers of the PEM.^{14,15}

One of the first kinetic models for layer adsorption in PEMs was proposed by Raposo et al.,¹⁶ who considered the adsorption as a bimodal process, including an exponential decay and an Avrami-like process.¹⁷ These two processes are ascribable to a first fast adsorption step and a second slower process due to reorganization of polymer chains in the multilayer,¹⁸ in qualitative agreement with the mean-field calculations of Cohen-Stuart¹⁹ for adsorption of polyelectrolytes onto solid surfaces. More recently, Lane et al.²⁰ explained

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qualitatively the adsorption kinetics of polyelectrolyte multilayers by considering three different steps, which is in accordance with Brownian dynamic simulations for adsorption of neutral polymers onto solid surfaces.²¹ It is possible to associate the first two steps of this last model with the fast process of bimodal mechanisms (diffusion + adsorption through a Coulombic or steric barrier).²² This would be in agreement with the fact that the fast process is found to be not purely diffusive. This latter is correlated to differences between the bulk and the area close to the surface: attractive electrostatic interactions between the surface and the polyelectrolyte chains in solution induce the attachment of polyelectrolyte chains, creating a barrier to the adsorption of newly arrived chains. This hinders the pure diffusive attachment of molecules near the surface, with polymer adsorption being governed by an intricate balance between diffusion and the created barrier.

In our previous work,¹⁴ we pointed out that the time during which a polymer was allowed to adsorb has an important influence on the internal structure of PEMs. Results obtained by the combination of structural characterization and evaluation of the adsorption kinetics of polyelectrolyte layers allowed us to propose an adsorption scenario in two steps: the adsorption time of the first process, τ_1 , corresponds to the adsorption time that allows the formation of stratified multilayers. For adsorption times larger than τ_1 , internal reorganizations in the film may take place, which, depending on the polyelectrolytes and on the assembly conditions, may lead to nonlayered structures. The present work analyzes the effect of assembly conditions on adsorption kinetics of polyelectrolyte multilayers, searching for possible correlations between changes in the assembly conditions (polymer nature, ionic strength I , and polymer concentration C) and the existence of different types of reorganization processes during the PEM building process, and therefore the effect of reorganization on different growth mechanisms of PEMs. For this purpose we have studied the effect of ionic strength and polyelectrolyte concentration (polycation concentration) on the adsorption kinetics of PEMs, as well as its dependence on the number of layers for PEMs composed of poly(allylamine hydrochloride) (PAH) or poly-(diallyldimethylammonium chloride) (PDADMAC) with poly-(sodium 4-styrenesulfonate) (PSS). These two classical systems^{23,24} are interesting because they have been considered as paradigmatic models of the two types of growth mechanisms. (PAH+PSS)_{*n*} multilayers show linear growth under a broad range of experimental conditions.²³ On the contrary, the (PDADMAC+PSS)_{*n*} system is extremely sensible to assembly conditions (ionic strength, temperature, etc.), and can present either linear or nonlinear growth.^{25,26} In both case, the index n indicates the number of adsorbed bilayers.

The results of the present work point out that there is no direct correlation between internal reorganization of polyelectrolyte chains along the structure of the multilayer and growth mechanism. An important result is that interdiffusion can exist in linear growth PEMs, thus ruling out the traditional correlation between interdiffusion and nonlinear growth. This allows one to explain the growth mechanism as a consequence of the specificity of interactions between the polymers and of their conformations, instead of being a consequence of the adsorption dynamics of the chains, because interdiffusion may occur in both linear and nonlinear systems.

2. MATERIALS AND METHODS

2.1. Chemicals. The sodium salt of poly(4-styrenesulfonate) (PSS) was used as polyanion. The PSS molecular mass was 70 kDa. The polycations used were poly-(diallyldimethylammonium) chloride (PDADMAC), with a molecular mass in the range 200–350 kDa, and poly-(allylamine) (PAH), with a molecular mass of 17 kDa. All the polymers were purchased from Sigma–Aldrich and used without further purification. The ionic strength of the solutions was controlled by adding NaCl (Sigma–Aldrich, purity >99.9%). The water was of Milli-Q quality (Millipore RG model). All the experiments were done at 298.1 ± 1 K.

2.2. Dissipative Quartz Crystal Microbalance. A dissipative quartz crystal microbalance (D-QCM) from KSV (Model QCM Z-500, Finland) was used. The quartz crystals, AT-cut, were cleaned with piranha solution (70% H₂SO₄/30% H₂O₂) over a period of 30 min and then thoroughly rinsed with pure water. The characteristic frequency of quartz crystal in vacuum was $f_0 \sim 5$ MHz. A self-assembled monolayer of the sodium salt of 3-mercaptopropanesulfonic acid was initially built on the surface of the gold electrode of the quartz crystal, in order to obtain a charged substrate.²⁷ D-QCM provided the impedance spectra of the crystal for the fundamental resonance frequency and for its odd overtones, ν , up to the 11th (central frequency $f_{11} = 55$ MHz). The data have been analyzed by use of the model proposed by Johannsmann et al.²⁸

2.3. Ellipsometry. An imaging null-ellipsometer from Nanofilm (Model EP3, Germany) was used; all the experiments were carried out on a solid–liquid cell at a fixed angle of 60°. Silicon wafers (Siltronix, France) were used as the substrates. In order to obtain the ellipsometric thickness h_{op} and the refractive index n_f of the layers, a four-layer model has been used, as in a previous work.²⁷

2.4. Layer-by-Layer Assembly. The multilayers were built from polyelectrolyte solutions of different concentrations and ionic strengths, I , obtained by use of NaCl. Adsorption of the layers was studied until a steady state was reached, as was evidenced from the absence of changes in D-QCM or ellipsometry signals during a time period longer than 10 min. Between the adsorption of successive layers, multilayers were rinsed with the solvent used for preparing the polyelectrolyte solutions. The rinsing process removed the polymer chains that were not strongly adsorbed. All experiments were performed under static conditions, without any stirring in the adsorption cell. The filling process of the measurement chamber took a few seconds and sometimes led to an abrupt shift on the signal that may be considered as an artifact, resulting from the injection process. These were not taken into account in the analysis of the adsorption process.

3. RESULTS AND DISCUSSION

3.1. Multilayer Growth: Ionic Strength and Polyelectrolyte Concentration Effects. Figure 1 shows the effect of ionic strength, I , on the assembly of (PDADMAC+PSS)_{*n*} and (PAH+PSS)_{*n*} multilayers; some of these data have been presented in our previous publication and are reproduced here for the sake of comparison.²⁷ In both systems, the effect of I on the thickness of the film can be easily explained by considering the influence of this parameter on the conformation of the polyelectrolyte in solution. The increase of I reduces the effective charge density of the polyelectrolytes, thus screening the electrostatic repulsion between the charged

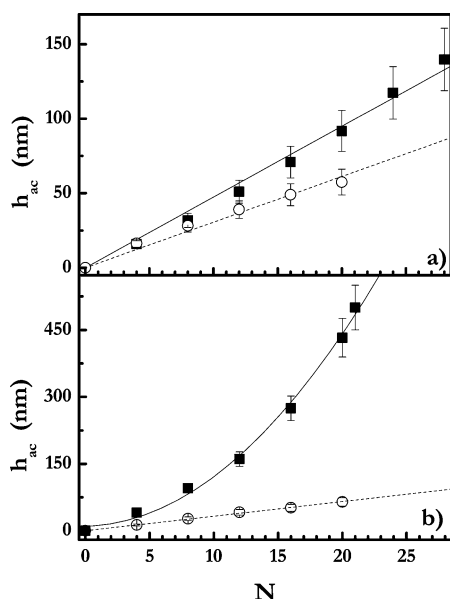


Figure 1. Effect of I on the growth of PEMs, as h_{ac} vs N , for multilayers of (■) (PDADMAC+PSS)_{*n*} and (○) (PAH+PSS)_{*n*}. (a) $I = 100$ mM; (b) $I = 500$ mM. The lines are guides for the eye.

groups of the chains. The effect of I on effective charge density of the polyelectrolytes is strongly dependent on the characteristics of the polyelectrolyte chains; in particular the screening parameter, $\chi = (e^2/ekTnb)$, plays a major role, where nb is the distance between adjacent charges on the polymer chain with values of 5.2 and 2.7 Å for PDADMAC and PSS, respectively,²⁶ and 2.8 Å for PAH;²⁹ e is the electron charge and ϵ is the solvent dielectric constant. This leads to adsorption of the polyelectrolyte in a more coiled conformation,³⁰ forming fuzzy layers, with the subsequent increase in thickness of the layer. Similar changes were observed when the polymer concentration was increased (see Figure 2) for a constant I . The above explanation considers only structural factors related to the polyelectrolyte conformation; further considerations about the growth of PEMs can be found in the literature.^{6,27,31}

More important than modification of the amount of polyelectrolyte adsorbed is to understand how different assembly conditions affect the growth regime of the PEMs. The results point out clearly the different influence of I on the growth mechanism of the two multilayers studied (Figure 1). For (PAH+PSS)_{*n*}, the thickness grows linearly independent of I , which is in good agreement with the results previously reported by Lavalle et al.²³ However, for (PDADMAC+PSS)_{*n*}, increasing I leads to the transition from linear to nonlinear growth, in accordance with previous studies reported.^{26,27} The threshold for the transition was found at $I \approx 300$ mM, in good accordance with the results reported by McAloney et al.²⁶ The change in concentration of the polycation solution (Figure 2) for a fixed I does not modify the growth regime. Here, we evaluate only the influence of the polycation in assembly of the multilayers because a previous study pointed out that the PSS presents similar adsorption under the different assembly conditions considered.²⁷

To explain the different growth trends of PEMs, several authors have used complex arguments based on interdiffusion of the polyelectrolyte chains across the multilayer. However, the experimental results obtained here may be explained by considering the physicochemical nature of the polyelectrolyte

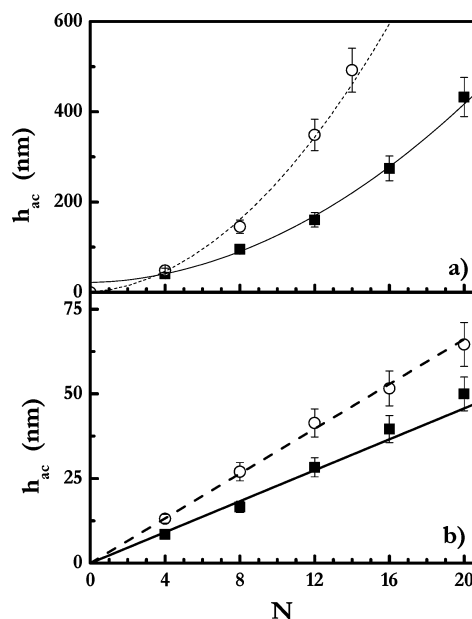


Figure 2. Effect of polycation concentration (PSS concentration is always fixed at 1 mg/mL) on the growth of PEMs, as h_{ac} vs N , for a fixed I of 500 mM. (a) (PDADMAC+PSS)_{*n*}: $c_{PDADMAC} =$ (■) 1 and (○) 7 mg/mL. (b) (PAH+PSS)_{*n*}: $c_{PAH} =$ (■) 1 and (○) 2.5 mg/mL. The lines are guides for the eye.

chains^{6,32} and how these properties are modified by the assembly conditions.²⁷ The fact that PDADMAC and PSS are strong polyelectrolytes whereas PAH is a weak polyelectrolyte is expected to influence the structural characteristics of the assembled layers. PDADMAC is a highly charged polyelectrolyte whose charge density is strongly modified by the assembly conditions.²⁷ On the contrary, PSS and PAH have lower charge densities, and in the particular case of PSS chains, this is almost insensitive to I , pH, etc.²⁷ The high charge density of PDADMAC chains induces a strong electrostatic intrachain repulsion under low ionic strength conditions, and this leads to adsorption of PDADMAC chains in a flat conformation. This does not induce a strong increase in the area accessible to adsorption in each adsorption cycle, which leads to adsorption of similar amounts of polymer in successive deposition cycles^{26,27} that provoke the existence of linear growth of (PDADMAC+PSS)_{*n*} multilayers under low ionic strength conditions. However, the increase of ionic strength for (PDADMAC+PSS)_{*n*} provokes the screening of the intrachain electrostatic repulsions on PDADMAC, which leads to the adsorption of polymer chains in a more coiled conformations. This increases the roughness of the multilayer [in accordance to McAloney et al.,²⁶ the roughness of multilayers of (PDADMAC+PSS)_{*n*} assembled from solutions of $I = 500$ mM is more than 1 order of magnitude higher than that of films assembled from solutions of $I = 100$ mM], and consequently the increase in surface area available for adsorption leads to an increase in the adsorbed amount in successive adsorption cycles, and therefore to nonlinear growth in (PDADMAC+PSS)_{*n*}. In the case of (PAH+PSS)_{*n*}, the lower charge density of these polymers leads to a less important effect of assembly conditions in the growth regime. The above arguments are in good agreement with the different roughness of (PDADMAC+PSS)_{*n*} and (PAH+PSS)_{*n*} multilayers reported in the literature¹⁴ and suggest that it is possible to understand the growth of PEMs without making use of the interdiffusion process, although interdiffusion is not

excluded.^{10,12,33} The above explanation for the origin of the two types of growth regimes is compatible with the model recently proposed by Haynie et al.,¹³ who showed that the existence of inhomogeneous adsorbed layers (fuzzy layers) is enough to lead to nonlinear growth of multilayers.

3.2. Adsorption Kinetics. In addition to the effect of assembly conditions discussed above, analysis of the adsorption kinetics should allow one to discuss the processes involved in adsorption of the layers. More specifically, it would be important to establish a possible correlation between growth mechanism and kinetic processes as an alternative to the usual criterion of plotting the thickness, h , versus the number of layers, N . In our previous works we have demonstrated that the adsorption kinetics of polyelectrolyte layers may be analyzed by a bimodal model^{34,35} that is a simplified version of the one previously proposed by Raposo et al.:¹⁶

$$\Gamma = \Gamma_{\infty} - A_1 e^{-t/\tau_1} - A_2 e^{-t/\tau_2} \quad (1)$$

where A_1 and A_2 are amplitudes and τ_1 and τ_2 are characteristic times for the two kinetic processes, Γ is the adsorbed mass a time t , and Γ_{∞} is the adsorbed mass at equilibrium ($t = \infty$). For all the multilayers studied in this work, eq 1 described the experimental data within experimental precision (see Figure 3),

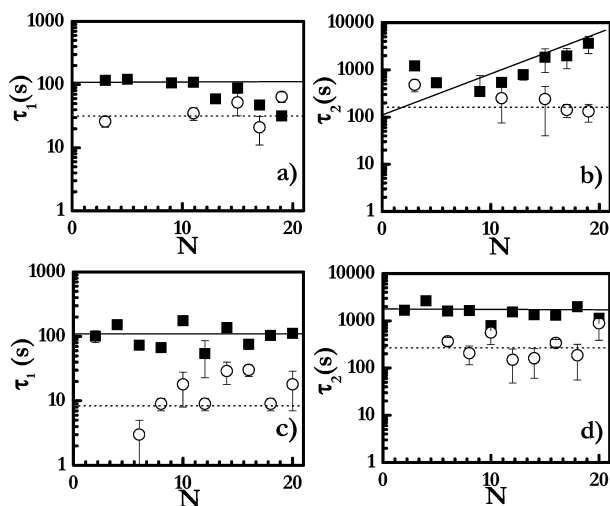


Figure 3. Kinetic times obtained via D-QCM from analysis of adsorption processes by use of the model proposed by Raposo et al.¹⁶ of multilayers of (PDADMAC+PSS)_n and (PAH+PSS)_n assembled from solution with $I = 500$ mM. (a) τ_1 vs N for polycation layers in different multilayers; (b) τ_2 vs N for polycation layers in different multilayers; (c) τ_1 vs N for PSS layers in different multilayers; (d) τ_2 vs N for PSS layers in different multilayers. (■) (PDADMAC+PSS)_n; (○) (PAH+PSS)_n. The lines are guides for the eye.

independent of the polyelectrolyte type and layer number.^{14,27} The characteristic time τ_1 can be ascribed to the transport of chains to the surface and their adsorption. This process is not a true diffusive ones (the amount of adsorbed material does not show a $t^{1/2}$ dependence) due to the important effect of the electrostatic in the adsorption process. This makes it necessary, in accordance with the mean-field calculations by Cohen-Stuart,¹⁹ to consider in this first adsorption step both diffusion in the bulk and adsorption through an electrostatic barrier.³⁶ The characteristic time τ_2 represents a second slower process that may be related to reorganization of the polymer chains adsorbed onto the last layer and diffusion of the chains through the multilayer. Details about the applicability of this model to

analysis of the adsorption kinetics of polyelectrolyte layers may be found in the literature.^{14,37,38}

The results below discussed must be considered as the first experimental study that analyzes the dynamic of adsorption of polyelectrolyte layers and the modification induced by different experimental parameters in the kinetic processes that take place during assembly of polyelectrolyte multilayers (Figure 4).

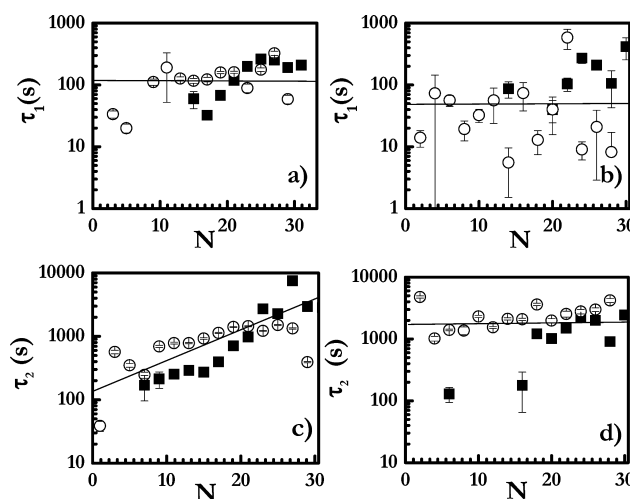


Figure 4. Times obtained via D-QCM and ellipsometry from analysis of adsorption processes by use of the model proposed by Raposo et al.¹⁶ of multilayers of (PDADMAC+PSS)_n assembled from solution with $I = 100$ mM. (a) τ_1 vs N for PDADMAC; (b) τ_1 vs N for PSS; (c) τ_2 vs N for PDADMAC; (d) τ_2 vs N for PSS. (■) Ellipsometric results; (○) D-QCM results. The lines are guide for the eyes.

3.2.1. Dependence of τ on N . Figure 3 shows the adsorption times obtained via D-QCM for different layers of a (PAH+PSS)_n multilayer with linear growth and a (PDADMAC+PSS)_n multilayer with nonlinear growth. In all the cases, τ_2 is almost 1 order of magnitude larger than τ_1 , similar results can be found in ref 14 for the same PEMs in assembly conditions where both multilayers grow linearly. The characteristic times for both processes show different dependences on the number of layers for the two systems studied. It is worth noticing that both D-QCM and ellipsometry lead to similar results (see Figure 4).

τ_1 is almost independent of N in both multilayers within the estimated uncertainty, as expected from the pseudodiffusive origin of this process,¹⁹ and depends only on the structure of the adsorbed polymer and the assembly conditions.³⁷ However, the behavior of τ_2 is different for the two PEMs studied. For the polycation chains, τ_2 is independent of N in the (PAH+PSS)_n multilayer, whereas for (PDADMAC+PSS)_n it depends on N . The situation is different for the PSS layers, in which τ_2 does not depend on N for any of the multilayers. This can be explained considering that, for (PAH+PSS)_n, the reorganization process occurs only in the layer that is being adsorbed, with small propagation in the three-dimensional structure of the multilayer. However, in (PDADMAC+PSS)_n the reorganization process of PDADMAC layers takes place with an additional contribution due to the interdiffusion of the chains through the whole structure of the multilayers. Therefore, an increase of τ_2 for at least one of the polyelectrolytes, PDADMAC, is expected as the multilayer grows, due to the larger volume through which they can diffuse. Therefore τ_2 has to be considered as an effective characteristic time for the PDADMAC layers because

it describes the kinetics of two different processes: (a) reorganization of the adsorbing chains in the plane of the multilayers, as in (PAH+PSS)_n, and (b) chain diffusion within the multilayer. This picture is in accordance with the recent evidence obtained by Xu et al.³⁹ by use of fluorescence recovering after photobleaching (FRAP). They observed that the reorganization of polyelectrolyte during the formation process of polyelectrolyte multilayers occurs following two directions of propagation with respect to the surface, parallel and perpendicular; the possibility exists that for certain pairs of polyelectrolytes or specific assembly conditions the perpendicular propagation of the reorganization process can be considered negligible.

Even though the assembly conditions do not change the N dependence of the two characteristic times, this does not mean that the values of τ_1 and τ_2 are not modified for changes in assembly conditions, as discussed below (see Figures 6–8).

3.2.2. Ionic Strength Dependence of τ_1 . Figure 5 shows the effect of I upon τ_1 , which depends on the polyelectrolyte and is

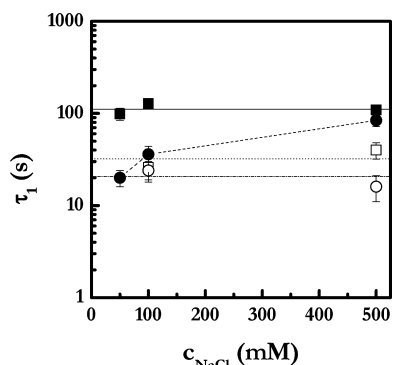


Figure 5. τ_1 vs I obtained via D-QCM from analysis of adsorption processes by use of the model proposed by Raposo et al.¹⁶ of multilayers of (PDADMAC+PSS)_n and (PAH+PSS)_n assembled from solution with different I . For (PDADMAC+PSS)_n multilayers: (■) PDADMAC; (●) PSS. For (PAH+PSS)_n multilayers: (□) PAH; (○) PSS. The lines are guides for the eye.

different for the two multilayers. For (PDADMAC+PSS)_n, τ_1 is independent of I for the PDADMAC layers, whereas it increases for the PSS layers. This is because τ_1 is related to a process that depends in part on interaction of the polymeric chains with the previous adsorbed layer, which in turn is related to the chain conformations and their effective charge density (especially that of the PSS chains)²⁷ that depends on I . However, PSS remains in coil conformation over the I range studied,²⁷ and as a consequence the PSS layers have a similar structure independent of I . This means that the affinity of PDADMAC chains for the PSS layers, and therefore its adsorption kinetics, is not affected by I . However, the conformational change induce on the PDADMAC chains lead to a slowing down of the PSS adsorption due to higher steric hindrance created by more coiled PDADMAC adsorbed chains. By similar arguments, it is possible to explain the I dependence of τ_1 observed for (PAH+PSS)_n by considering the less fuzzy structure of these PEMs than those with PDADMAC as polycation.

3.2.3. Concentration Dependence of τ_1 . Structural arguments similar to those used above allow one to explain the effect of the polycation concentration on τ_1 (Figure 6). For PSS, τ_1 is concentration-independent in both multilayers,

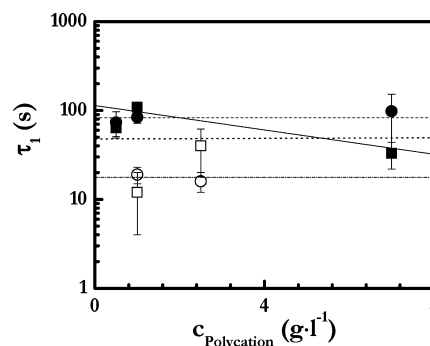


Figure 6. τ_1 vs $c_{\text{polycation}}$ obtained via D-QCM from analysis of adsorption processes by use of the model proposed by Raposo et al.¹⁶ of multilayers of (PDADMAC+PSS)_n and (PAH+PSS)_n assembled from solution with different concentrations of polycation and fixed $I = 500$ mM. For (PDADMAC+PSS)_n multilayers: (■) PDADMAC; (●) PSS. For (PAH+PSS)_n multilayers: (□) PAH; (○) PSS. The lines are guides for the eye.

whereas for the adsorption of PDADMAC and PAH there is a noticeable change with c , and the sign of $d\tau_1/dc$ is opposite for the two multilayers (Figure 7). As explained in the preceding

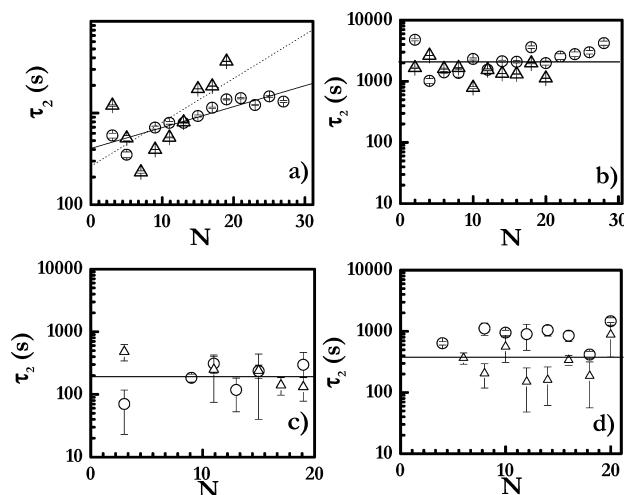


Figure 7. τ_2 vs N obtained via D-QCM from analysis of adsorption processes by use of the model proposed by Raposo et al.¹⁶ of multilayers of (PDADMAC+PSS)_n and (PAH+PSS)_n assembled from solutions with different I . (a) PDADMAC and (b) PSS in multilayers (PDADMAC+PSS)_n; (c) PAH and (d) PSS in multilayers (PAH+PSS)_n. (○) $I = 100$ mM; (△) $I = 500$ mM. The lines are guides for the eye.

section, the results can be explained by taking into account the fact that use of PDADMAC leads to the formation of more fuzzy multilayers than when PAH is the polycation.

3.2.4. Characteristic Time of the Reorganization Process. It is also important to understand the dependence of τ_2 on assembly conditions (Figures 7 and 9) because this allows us to obtain information about how the reorganization occurs in the two multilayers. For (PDADMAC+PSS)_n, τ_2 increases with N for the adsorption of PDADMAC, being independent of N for PSS independent of I or polycation concentration. This can be explained by the existence of interdiffusion during the adsorption of both polyelectrolytes in (PDADMAC+PSS)_n multilayers, independent of the type of growth that occurs in the multilayer as recently proposed by Haynie et al.¹³ The

existence of interdiffusion on linear growth of $(\text{PDADMAC}+\text{PSS})_n$ multilayers may be understood by taking into account that for low I the screening of the polyelectrolyte charges is small, and thus the Coulombic repulsion, both intrachain and interchain, leads to an electrostatic barrier for further adsorption of material. The adsorbed polymer reorganizes in the whole structure of the multilayer, leading to a smaller roughness than in the case of high I , thus resulting in a linear-growth multilayer. For low I the interdiffusion may be limited due to the low degree of extrinsic compensation that exists on the multilayer.^{24,27} As a consequence, the Donnan potential no longer is the most important driving force because the high charge density of the chains increases the repulsive interaction between the chains of polyelectrolyte.¹⁰ Note that the classical models have not considered the possibility of interdiffusion in linear multilayers.^{11,12,33} On the contrary, the Donnan potential¹⁰ dominates at high values of I due to the strong extrinsic compensation,²⁷ and therefore a larger number of molecules can diffuse, increasing the roughness and leading to superlinear growth.²⁷ However, PAH is a weak electrolyte and therefore it is reasonable to expect that in the I range studied the Donnan potential is not high enough to induce interdiffusion in $(\text{PAH}+\text{PSS})_n$.²³ This leads to the existence of only bidimensional reorganization of the polymer chains without a negligible propagation along the tridimensional structure of the multilayer. The results obtained for $(\text{PAH}+\text{PSS})_n$ clearly point out the absence of interdiffusion in this linear system, which calls for control of the interdiffusion due to the specific interactions that take place in the assembled polyelectrolyte pair. The different abilities for interdiffusion observed in both multilayers can only be attributed to the nature of the pair of polyelectrolytes and must be considered as the reason for the lack of stratification observed in our previous work for $(\text{PDADMAC}+\text{PSS})_n$,²⁷ in contrast to the formation of highly stratified multilayers in the $(\text{PAH}+\text{PSS})_n$ system observed by Schmitt et al.⁴⁰ and Lösche et al.⁴¹

A more detailed analysis of the dependence of τ_2 on assembly conditions makes it possible to obtain a better understanding of the assembly of PEMs. In the $(\text{PDADMAC}+\text{PSS})_n$ system, τ_2 for PDADMAC increases with I (Figure 7), whereas for PSS τ_2 is independent of I . This also may be understood by considering the modifications of conformation and effective charge density of the polyelectrolyte chains induced by I , which allows control of the interaction between multilayers and new chains that adsorb. According to Ladam et al.,⁴² for the adsorption of a pair of polyelectrolytes it is possible to assume the existence of an overcompensation threshold independent of the assembly conditions. This can be probably considered the most important factor that determines the dependence of reorganization time on assembly conditions, and it means that the adsorption of polyelectrolytes always occurs until arriving to a certain charge density of the adsorbed layer. Considering that the charge density of the PSS chains is almost independent of I , the charge density of PDADMAC determines this overcompensation threshold. The increase of I reduces the charge density of the PDADMAC chains, which leads to the necessity of reorganization of a higher number of polycation chains to compensate the Donnan potential, and this slows down the reorganization process. When PSS is the polymer that adsorbs, the chains always find a surface with similar charge density, and as we commented above the charge density of PSS chains remains almost the same in all the range of I analyzed. Therefore, one may expect a similar reorganization for PSS

under all conditions; similar arguments allow us to explain the dependence on polycation concentration (Figure 8). In effect, τ_2 does not change for the adsorption of PSS and decreases with increasing polyelectrolyte concentration for adsorption in PDADMAC layers. This is explained because a higher number of chains are available, thus leading to a faster reorganization process of PDADMAC within the multilayer.

For $(\text{PAH}+\text{PSS})_n$ multilayers, the scenario is significantly different than that described for $(\text{PDADMAC}+\text{PSS})_n$. Figure 7 shows that, for $(\text{PAH}+\text{PSS})_n$, τ_2 is almost independent of I for adsorption of both polyelectrolytes, which reflects a limited effect of I on the effective charge density of PAH and PSS and therefore on their conformations. The effect of polycation concentration on τ_2 (Figure 8) is similar to that observed in

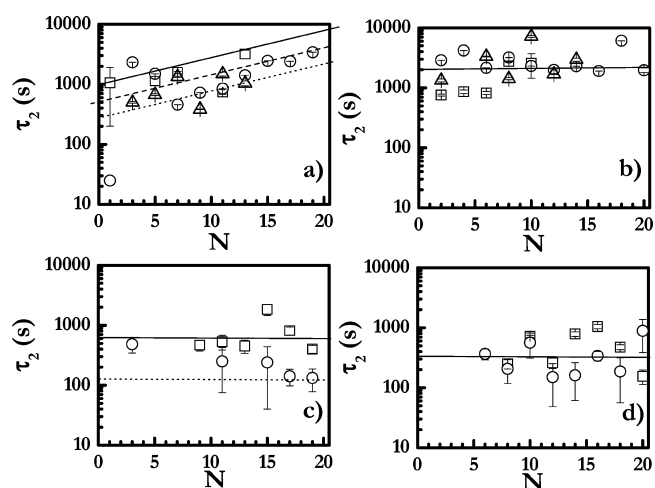


Figure 8. τ_2 vs N obtained via D-QCM from analysis of adsorption processes by use of the model proposed by Raposo et al.¹⁶ of multilayers of $(\text{PDADMAC}+\text{PSS})_n$ and $(\text{PAH}+\text{PSS})_n$ assembled from solution with different concentration of polycation. (a) PDADMAC and (b) PSS in multilayers $(\text{PDADMAC}+\text{PSS})_n$: $c_{\text{polycation}} = (\square) 0.5$, $(\circ) 1$, and $(\triangle) 7$ mg/mL. (c) PAH and (d) PSS in multilayers $(\text{PAH}+\text{PSS})_n$: $c_{\text{polycation}} = (\square) 1$ and $(\circ) 2.5$ mg/mL. The lines are guides for the eye.

$(\text{PDADMAC}+\text{PSS})_n$ films. However, the existence of interdiffusion must be completely ruled out for the multilayers formed by PAH and PSS, at least under the experimental conditions studied.

In addition to the study of dependence of reorganization time τ_2 on N , analysis of the dependence of this reorganization time on the thickness of the multilayer gives further information about the reorganization of polyelectrolyte chains within the multilayer structure. From Figures 9 and 10, it is possible to observe the linear dependence of adsorption on thickness for the adsorption of PDADMAC layers, whereas the adsorption of PAH and PSS layers does not show any dependence on multilayer thickness. These different dependences on thickness must be considered as a further confirmation of the different mechanisms of adsorption involved in the deposition process of the different polymers. The quasi-linear dependence of adsorption on h_{ac} observed for PDADMAC points out that the increase in thickness does not modify substantially the interdiffusion process, which depends only on the available thickness where reorganization of polymer chains occurs. In addition, it is noteworthy that the different assembly conditions induce different velocities to the

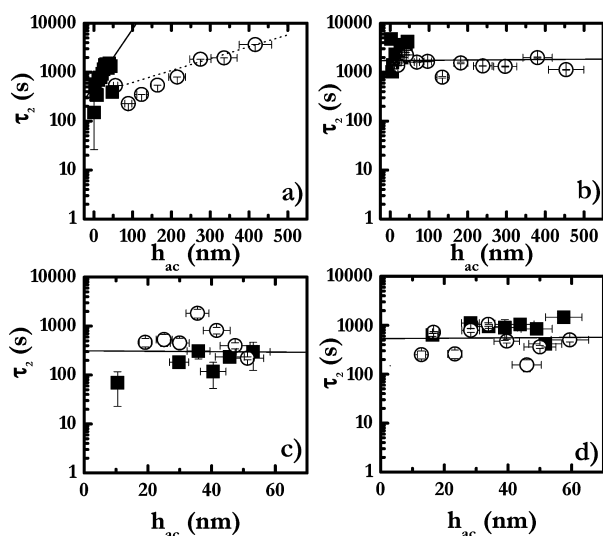


Figure 9. τ_2 vs h_{ac} obtained via D-QCM for multilayers of (PDADMAC+PSS) $_n$ and (PAH+PSS) $_n$ assembled from solutions with different I . (a) PDADMAC and (b) PSS in multilayers (PDADMAC+PSS) $_n$; (c) PAH and (d) PSS in multilayers (PAH+PSS) $_n$. (■) $I = 100$ mM; (○) $I = 500$ mM. The lines are guides for the eye.

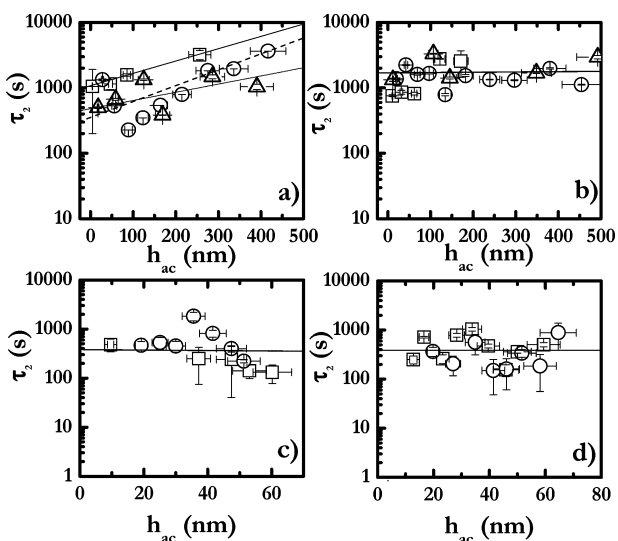


Figure 10. τ_2 vs h_{ac} obtained via D-QCM for multilayers of (PDADMAC+PSS) $_n$ and (PAH+PSS) $_n$ assembled from solution with different concentration of polyelectrolyte. (a) PDADMAC and (b) PSS in multilayers (PDADMAC+PSS) $_n$: $c_{\text{polyelectrolyte}} = (\square) 0.5$, (○) 1, and (△) 7 mg/mL. (c) PAH and (d) PSS in multilayers (PAH+PSS) $_n$: $c_{\text{polyelectrolyte}} = (\square) 1$ and (○) 2.5 mg/mL. The lines are guides for the eye.

interdiffusion process that can be related to the existence of the Donnan potential as driving force; when the ionic strength or the polyelectrolyte concentration is low, the Donnan potential is not so much important during the layer adsorption that provoke the hindering of the interdiffusion process, whereas interdiffusion is favored when the ionic strength conditions are high, which provokes an important contribution to the Donnan equilibrium and to the adsorption process.

3.2.5. Dependence of Amplitudes A_1 and A_2 of Kinetic Processes on Growth. Analysis of the amplitudes of kinetic processes (Figures 11 and 12) confirm the different scenarios proposed above for the adsorption dynamic and growth of

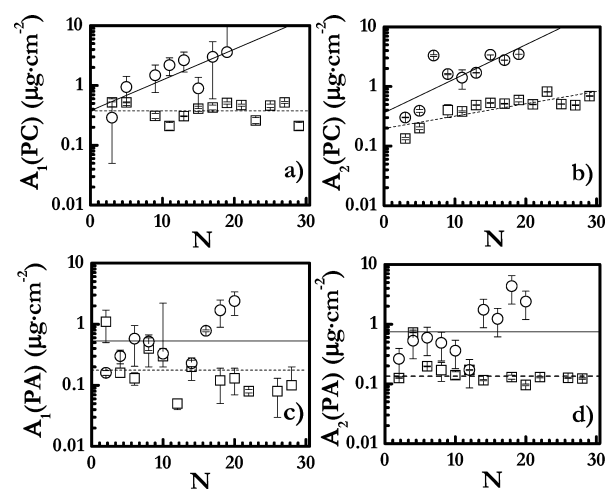


Figure 11. Dependence of amplitude, obtained via D-QCM, of the two kinetic processes on N for a multilayer of (PDADMAC+PSS) $_n$ assembled from solutions with polyelectrolyte concentration of 1 mg/mL and two different I : (□) 100 and (○) 500 mM. (a) A_1 and (b) A_2 for adsorption of PDADMAC layers; (c) A_1 and (d) A_2 for adsorption of PSS layers. The lines are guides for the eye.

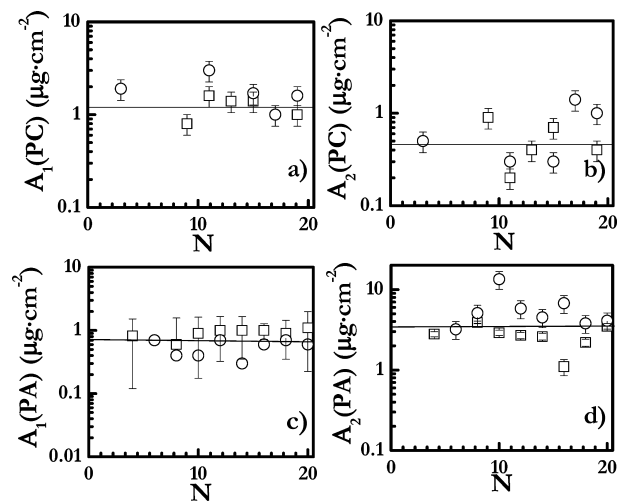


Figure 12. Dependence of amplitude, obtained via D-QCM, of the two kinetic processes on N for a multilayer of (PAH+PSS) $_n$ assembled from solutions with polyelectrolyte concentration of 1 mg/mL and two different I : (□) 100 and (○) 500 mM. (a) A_1 and (b) A_2 for adsorption of PAH layers; (c) A_1 and (d) A_2 for adsorption of PSS layers. The lines are guides for the eye.

polyelectrolyte multilayers. For adsorption of PSS layers, the amplitudes are constant in both multilayers as a result of unaltered adsorption of PSS under the considered conditions. Similar behavior is observed for the PAH layers. However, for the PDADMAC layers the situation is different. A_1 is independent of N for linear growth films, whereas it strongly increases with N for (PDADMAC+PSS) $_n$ multilayers that grow exponentially. This can be explained as a consequence of the adsorption of higher amount of material in successive cycles due to the increased area available for adsorption. A_2 increases with N independent of the assembly conditions due to the higher importance of the reorganization process as the thickness of the films increases. Additionally, for exponential growth multilayers A_2 is higher than for those that grow linearly, which is explained by arguments similar to those used

to explain the dependence on N . It is noticeable that nonregular behavior is found for amplitudes of the adsorption steps of PSS in $(\text{PAH}+\text{PSS})_n$ with $A_2 > A_1$ under the different assembly conditions considered. This imbalance might be ascribed to the coupling between the two steps involved in the adsorption that does not allow separation of the contributions due to different processes.

Analysis of the dependence on N of relative amplitudes of the kinetic processes, $R_j = A_j/(A_1 + A_2)$, where A_1 and A_2 are amplitudes of the kinetic processes and $j = 1, 2$, confirm the different scenarios proposed above for the adsorption dynamic and growth of the polyelectrolyte multilayers (Figures 13 and

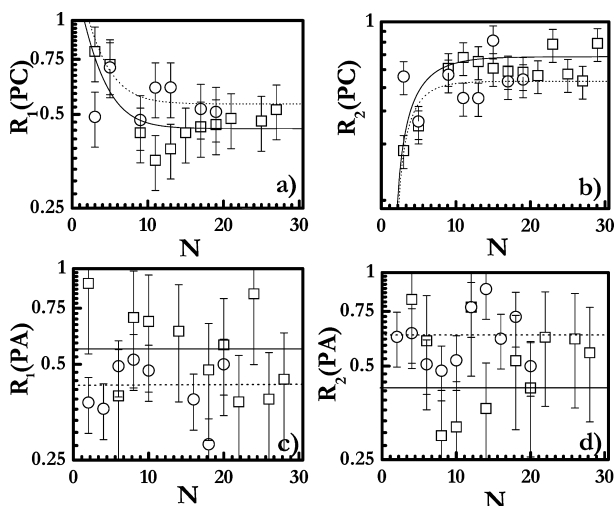


Figure 13. Dependence of relative amplitudes, obtained via D-QCM, of the two kinetic processes on N for a multilayer of $(\text{PDADMAC}+\text{PSS})_n$ assembled from solutions with polyelectrolyte concentration of 1 mg/mL and two different I : (\square) 100 and (\circ) 500 mM. (a) R_1 and (b) R_2 for adsorption of PDADMAC layers; (c) R_1 and (d) R_2 for adsorption of PSS layers. The lines are guides for the eye.

14). R_1 and R_2 are constant for the adsorption of PSS layers in both multilayers. This is a result of unaltered adsorption of PSS for the experimental conditions used and the absence of interdiffusion along the whole structure of the multilayer. Similar behavior is observed for the PAH layers. However, for the PDADMAC layers the situation is different: R_1 decreases with N , whereas R_2 increases. This can be related to the increased effect of diffusion of the PDADMAC chains across the whole structure of the multilayer.

It is important to notice that the importance of the process is different depending of the type of growth of the multilayer. Analysis of the amplitudes points out that the ratio between the amplitudes for the second process for nonlinear and linear growth is around 4:2.5, which indicates the importance contribution of mass adsorption during the reorganization process in nonlinear growth PEMs. This is in accordance with the distribution of the new polymeric chains along the whole structure of the multilayer and not in a limited region (limited tridimensional propagation or reorganization in the film–solution interface).

The kinetic results rule out the classical explanation of differences between the two types of growth mechanisms as a result of the existence or not of interdiffusion,^{12,33} suggesting a scenario in which the growth mechanism is controlled essentially by the nature and charge density of the chains. As

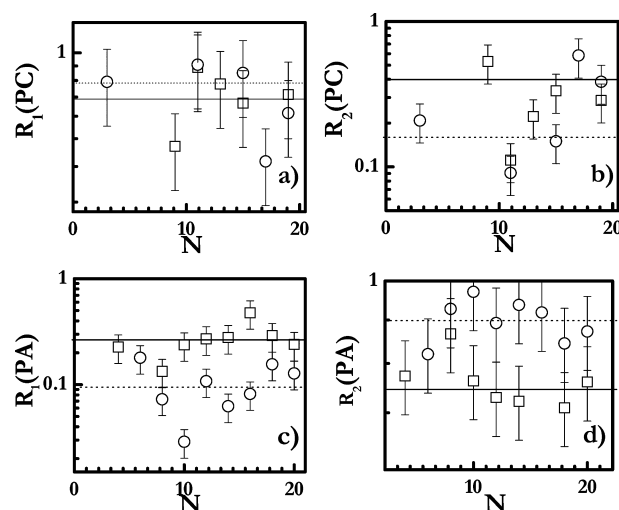


Figure 14. Dependence of relative amplitudes, obtained via D-QCM, of the two kinetic processes on N for a multilayer of $(\text{PAH}+\text{PSS})_n$ assembled from solutions with polyelectrolyte concentration of 1 mg/mL and two different I : (\square) 100 and (\circ) 500 mM. (a) R_1 and (b) R_2 for adsorption of PAH layers; (c) R_1 and (d) R_2 for adsorption of PSS layers. The lines are guides for the eye.

a summary, Figure 15 schematizes the two different adsorption steps in relation to the adsorption kinetics of a polyelectrolyte layer for multilayers in which the reorganization occurs with (Figure 15a) and without (Figure 15b) propagation along the whole structure of the multilayer. A cartoon indicating the different process involved in adsorption and the effect on structures of the PEMs is shown in Figure 15c.

3.3. Mechanical Properties. Mechanical properties of the PEMs are reported in Table 1 as the real and imaginary parts of the shear modulus, G' and G'' . In linear growth multilayers, we found that $G' > G''$, which implies the rigid character of these multilayers, whereas nonlinear growth multilayers show an increasing importance of G'' , which points out the softer character of these films. This is explained considering the structural scenario that exists in the different multilayers.

The results above presented point out that analysis of adsorption kinetics of the assembly of polyelectrolyte layers allow us to evaluate the dynamics processes that occur during assembly of the layers. This, together with knowledge of the influence of adsorption kinetics on the structure of PEMs, allows us to propose a scenario for the growth of polyelectrolyte multilayers where characteristics of the polyelectrolyte pair and changes in the properties due to assembly conditions play a key role in control of the growth trend of the PEMs, which is not related to the dynamic processes that occur during adsorption of the layers. This pointed out the extraordinary importance of the polyelectrolyte conformations in the assembly and properties of PEMs.

4. CONCLUSIONS

The electrostatic self-assembly of polyelectrolyte multilayers (PEMs) formed by PSS as polyanion and two different polycations, PDADMAC and PAH, has been studied by D-QCM and ellipsometry. The study has been focused on explaining the growth mechanism and adsorption kinetics of polyelectrolyte multilayers. The results point out the existence of two different growth trends in polyelectrolyte multilayers. These may be modified by assembly conditions (polymer type,

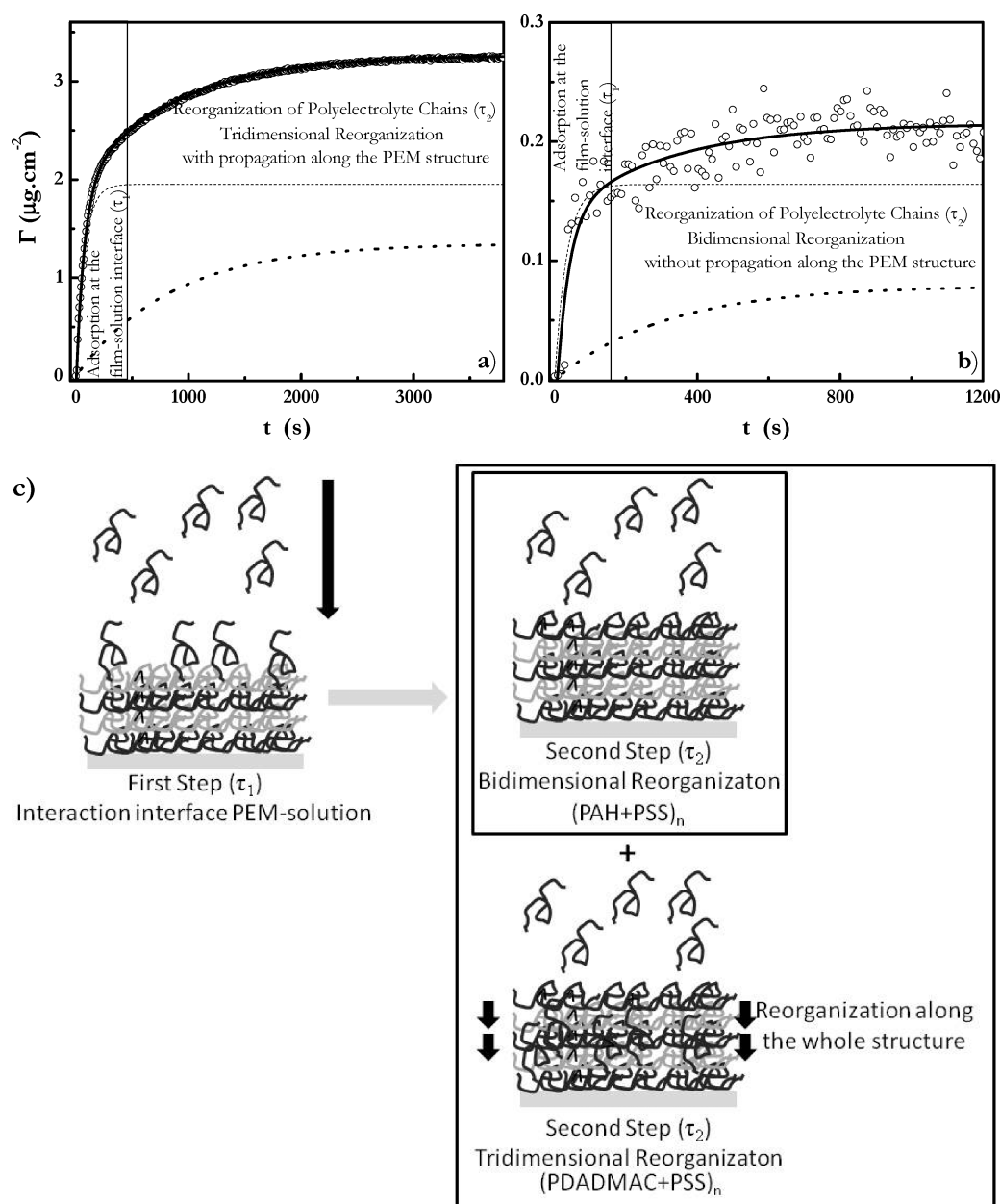


Figure 15. Adsorption dynamics for layers of different polycations in multilayers of (a) $(\text{PDADMAC}+\text{PSS})_n$ (nonlinear growth with interdiffusion) and (b) $(\text{PAH}+\text{PSS})_n$ (linear growth without interdiffusion) adsorbed from a dipping solution with $I = 500$ mM, representing models of nonlinear and linear growth multilayers. (—) Best fit to eq 1. Two exponential components are shown: (---) fast step and (···) slow step. The two adsorption regions that influence the internal structure of the polyelectrolyte multilayers are evident. (c) Scheme of different processes involved in adsorption for multilayers.

Table 1. Mechanical Properties as G' and G'' of $(\text{PDADMAC}+\text{PSS})_n$ and $(\text{PAH}+\text{PSS})_n$ Multilayers under Different Assembly Conditions. Results obtained using D-QCM.

$(\text{PDADMAC}+\text{PSS})_n$					$(\text{PAH}+\text{PSS})_n$				
N	I (mM)	C_{PDADMAC} ($\text{g}\cdot\text{L}^{-1}$)	G' (MPa)	G'' (MPa)	N	I (mM)	C_{PAH} ($\text{g}\cdot\text{L}^{-1}$)	G' (MPa)	G'' (MPa)
20	50	1	4 ± 1	1 ± 6	20	100	1	6 ± 2	1 ± 4
20	100	1	14 ± 6	0 ± 7	20	500	1	11 ± 2	0 ± 4
20	500	1	39 ± 5	14 ± 6	20	500	2.5	2 ± 2	5 ± 4
14	500	7	9 ± 3	7 ± 4					

ionic strength, and polymer concentration). Independent of the type of growth, the adsorption kinetics of the layers presents a bimodal character. Analysis of the kinetics for adsorption of different layers have pointed out that the possible existence of

interdiffusion along the multilayer structure during the adsorption process, but the results rule out the existence of correlation between interdiffusion and growth mechanism. The results allow a new scenario to be proposed where the growth

trend of PEMs is related only to structural features of the considered system, that is, the ability to modulate conformation and the charge density of the chains, by the change in the assembly conditions that determines the adsorption of PEMs.

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Notes

The authors declare no competing financial interest.

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