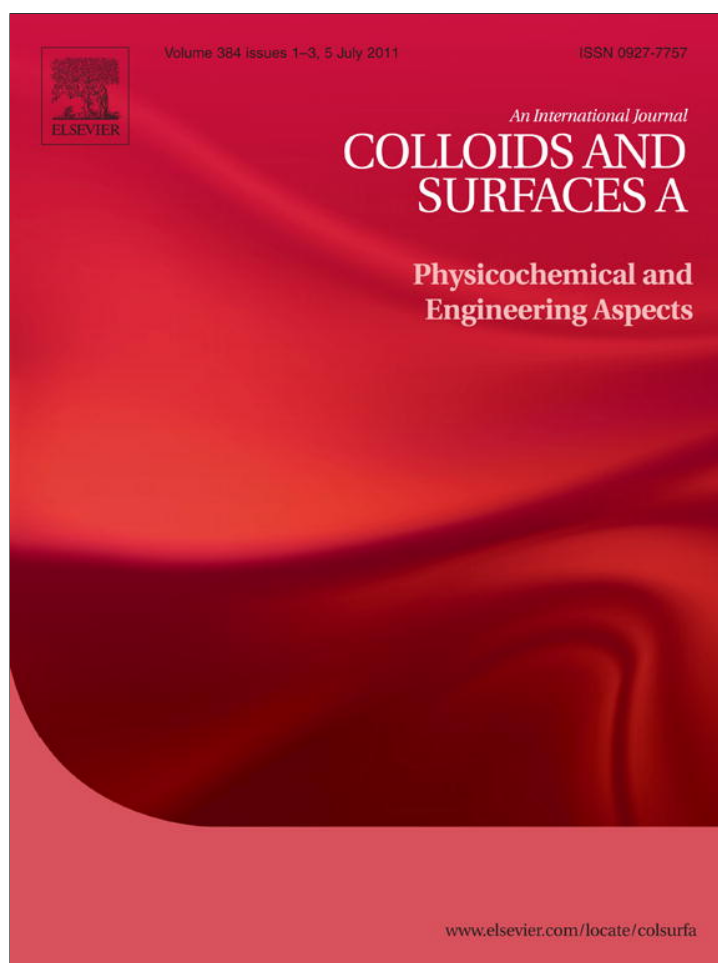


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

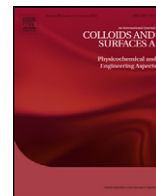
In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Evidence of the influence of adsorption kinetics on the internal reorganization of polyelectrolyte multilayers

Eduardo Guzmán*, Hernán Ritacco¹, Francisco Ortega, Ramón G. Rubio

Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040 Madrid, Spain

ARTICLE INFO

Article history:

Received 12 January 2011

Received in revised form 4 April 2011

Accepted 5 April 2011

Available online 12 April 2011

Keywords:

Polyelectrolyte multilayers

Adsorption kinetics

Internal structure

Stratification

Reorganization

ABSTRACT

X-ray reflectivity and adsorption kinetics of two different polyelectrolyte multilayers have been studied for polyelectrolyte multilayers (PEMs) composed of poly(diallyldimethyl ammonium chloride) (PDADMAC) and poly(sodium 4-styrenesulfonate) (PSS) polyelectrolyte pair and of poly(allylamine hydrochloride) (PAH) and PSS. The two characteristic times that describe the adsorption kinetics were found to be related to the X-ray reflectivity results, and their dependence on the number of adsorbed layers depends on the growth mechanisms (linear or superlinear) of the films. Therefore, it has been concluded that there is a correlation between the adsorption kinetics and the internal structure of the films. The time allowed for the adsorption of each polyelectrolyte controls the extension of the inter-diffusion within the multilayer, and therefore whether the film is formed by stratified layers or it has a uniform structure except for the first and last layers. While the roughness of the (PDADMAC + PSS)_n films strongly depends on the adsorption time, it is almost independent of it for the (PAH + PSS)_n multilayer. This behavior correlates with that of the longest characteristic time of the adsorption kinetics.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Nanostructured materials are nowadays a fundamental field of research with impact on many applications. Since the pioneering work of Decher et al. [1–3], polymer multilayers built using the layer-by-layer (LbL) technique [4] are one of the most versatile and promising systems among this type of materials. It is a cost-effective technique that consists in adding sequentially polyelectrolytes of opposite charges, where each layer is attached to the previous one by electrostatic interactions. A further advantage over classical techniques, such as the Langmuir–Blodgett technique [5], is the possibility of coating substrates of different nature and shape, such as colloidal particles [6,7], fluid interfaces [8,9], and liposomes [10], not being limited to flat solid substrates as the other more classical methods.

The knowledge of the variables that affect the building process of the polyelectrolyte multilayers is essential for the fabrication of biocompatible coatings with controlled structures and physicochemical properties. Among these variables are: the charge density of the polymer [11,12], polymer concentration [13], ionic strength

[14–16], solvent quality for the polyelectrolytes [15], pH [17], and temperature [18].

In the last years, many of the characteristics of the growing process, and the properties of these systems have been presented in the literature [1,3,19]. However some important facts related to the building process have received less attention. One important unsolved problem is the relation between the type of growing regime of the films (linear or superlinear), the kinetics of the adsorption of the layers, and the structure of the multilayers. Multilayers are non-equilibrium systems and their characteristics depend on the history of the system; for instance changes in the assembling protocol lead to the formation of films with different structural characteristics [20–22]. It has been shown experimentally that the existence of two different types of growth, linear and superlinear, is related to the internal reorganization of the whole structure of the multilayer [23–25]. However, there is no systematic study on how the adsorption may affect the different types of growth [16,26–28]. A related topic is to explore the possibility of freezing the multilayer structure by the arrest of the adsorption kinetics at intermediate states, as suggested by the molecular dynamics simulation results obtained by Panchagnula et al. [29].

Previous experimental studies for different multilayers have shown that the adsorption kinetics is a bimodal process [8,12,16,26,30] that can be modelled in terms of an Avrami's like model [30]. In a previous paper we studied (PDADMAC + PSS)_n multilayers using Neutron Reflectivity (NR) and X-Ray Photoelectron Spectroscopy (XPS), and we found that, if the adsorption of the

* Corresponding author. Current address: Istituto per L'Energetica e le Interfasi, CNR-IENI, Via de Marini 6, 16149 Genova, Italy.

E-mail address: eguzman@ge.ieni.cnr.it (E. Guzmán).

¹ Current address: Departamento de Física, Universidad Nacional del Sur, Alem 1253, CP8000 Bahía Blanca, Argentina.

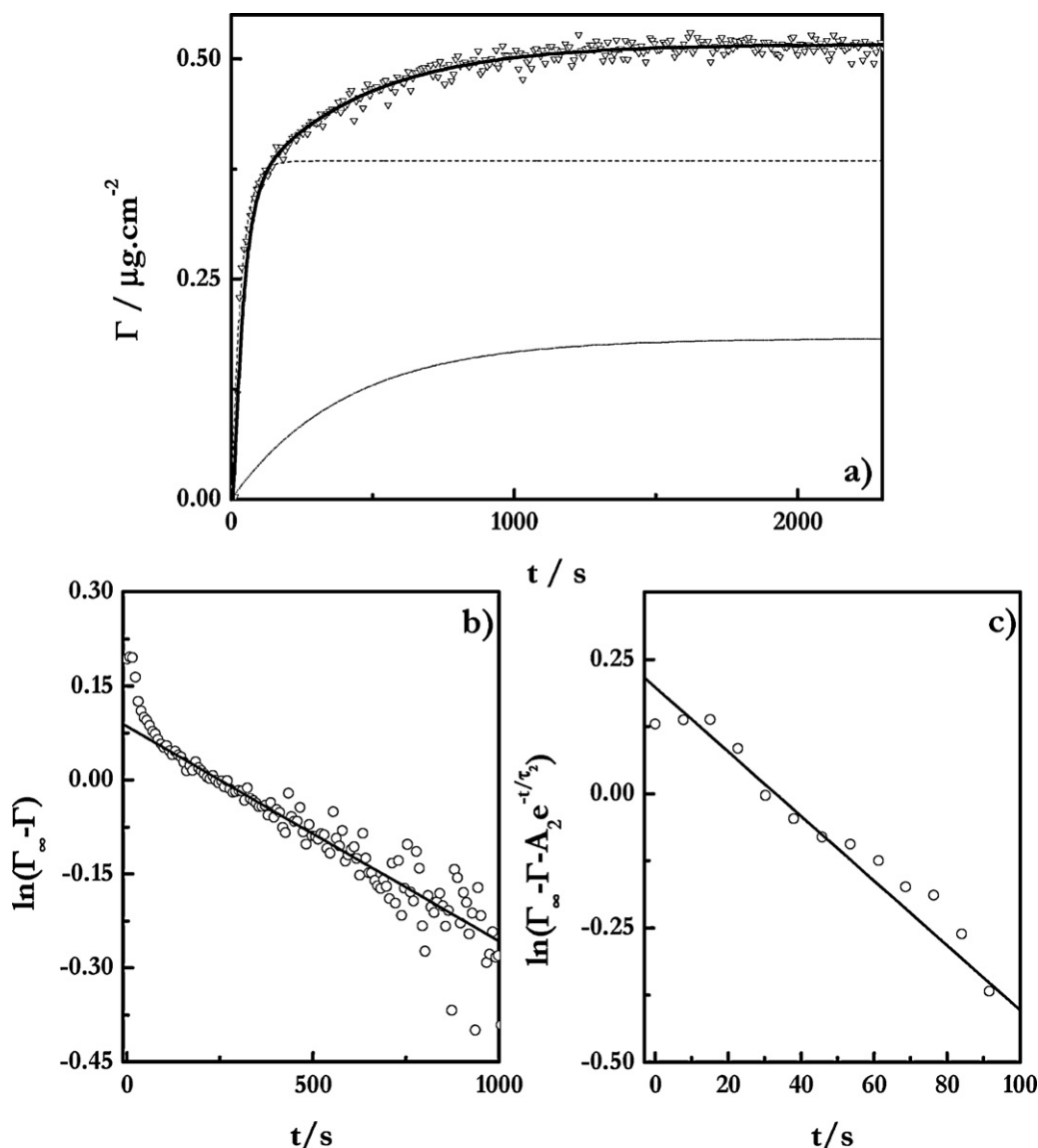


Fig. 1. Example of the analysis of the adsorption kinetics for a layer of PDADMAC adsorbed from a dipping solution with an ionic strength of 100 mM (5th layer). (a) Adsorption dynamics for the layer of polymer. The solid line shows the best fit to Eq. (1). The two exponential components are shown: - - - fast step and ··· slow step. (b) Plot of logarithm of $(\Gamma_{\infty} - \Gamma)$ vs. time, where Γ_{∞} represents the surface concentration at the steady-state of the adsorption process, after long adsorption times where the fastest exponential becomes negligible, it can be fitted to a straight line (solid line). (c) Short time behavior of the adsorption kinetics, a plot of $\ln(\Gamma_{\infty} - \Gamma - A_2 e^{-t/\tau_2})$ vs. time gives a straight line (solid line).

layers is allowed to proceed until arriving to the steady-state of the kinetic process, the multilayer does not show a sharp layered structure [16]. These results are contrary to those of Schmitt et al. [27], and of Lösche et al. [28] for multilayers of $(\text{PAH} + \text{PSS})_n$. A main difference between our studies [16] and previous studies in the literature [27,28,31] is the adsorption protocol: in our case the steady-state of the adsorption process was reached for each layer (usually more than 1 h of adsorption) [16], whereas a fixed and shorter time of 15–20 min for each layer was used in the multilayers built by other groups [27,28]. In relation to the effect of the adsorption time on the structure of polyelectrolyte multilayers Kharlampieva et al. [32] have recently shown that the multilayers are highly stratified when they were assembled using techniques that need low contact time between the solution and the surface (e.g. spraying or spin-coating: 30–180 s). However the multilayers lack their stratified structure when a dipping method that allows longer contact times between the solution and the surface (15–20 min) was used; these results are similar to those obtained by Félix et al. [33].

In this work we explore the possibility of finding a correlation between the internal reorganization of the films during the building process and the multilayer structure with the adsorption kinetics, and in particular with the longest characteristic adsorption time. This would allow one to control the growth mechanism and, as a consequence, the multilayer structure by changing the adsorption time. For this purpose, we compare the building process of multilayers of $(\text{PAH} + \text{PSS})_n$ and $(\text{PDADMAC} + \text{PSS})_n$ adsorbed under similar conditions. It is noticeable that although the polycations used are of different chemical nature (the PAH is a weak polyelectrolyte, whereas PDADMAC is a strong one), this does not seem to be the cause of the different growth mechanisms of the multilayers [26].

2. Experimental

2.1. Chemicals

The polyanion used was sodium salt of poly(4-styrene sulfonate) (PSS). The PSS molecular weight was 70 kDa. The polycations

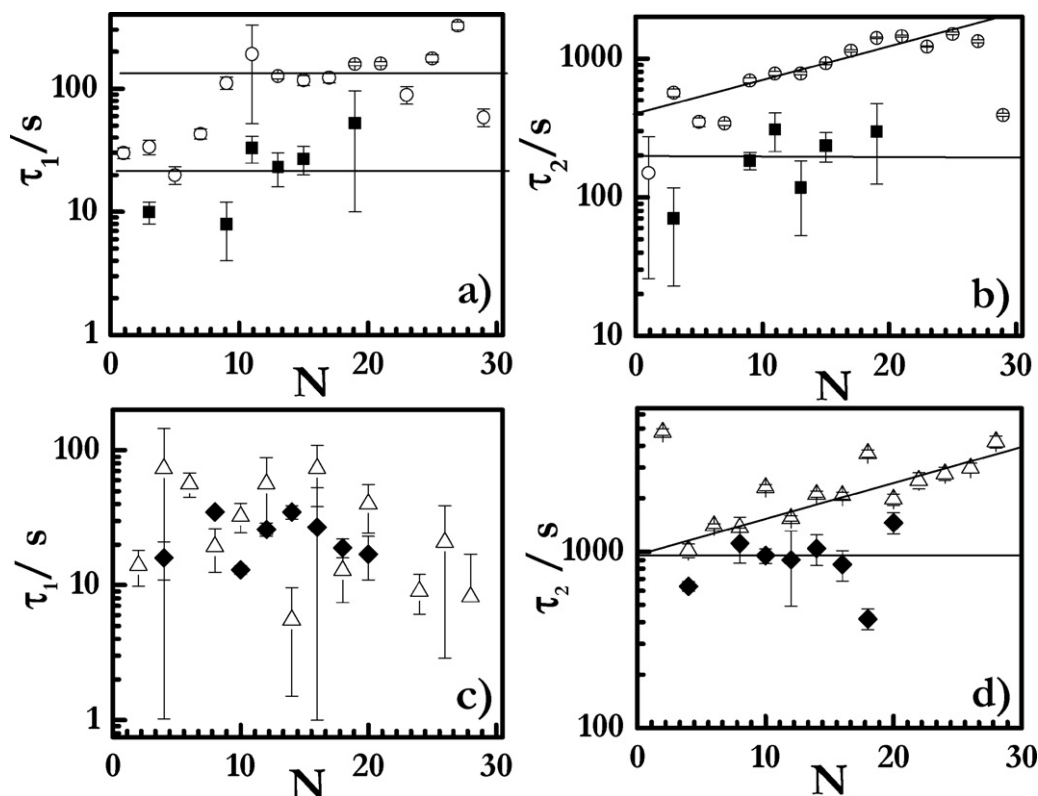


Fig. 2. Kinetic times obtained from the analysis of the adsorption processes using Eq. (1) for multilayer of (PDADMAC+PSS)_n and (PAH+PSS)_n assembled from solutions with $c_{\text{NaCl}} = 100$ mM. (a) τ_1 vs. N for the polycation layers in different multilayers. (○) PDADMAC; (■) PAH. (b) τ_2 vs. N for the polycation layers in different multilayers. (○) PDADMAC; (■) PAH. (c) τ_1 vs. N for the PSS layers in different multilayers. (Δ) In multilayer (PDADMAC+PSS)_n. (◆) In multilayer (PAH+PSS)_n. (d) τ_2 vs. N for the PSS layers in different multilayers. (Δ) In multilayer (PDADMAC+PSS)_n. (◆) In multilayer (PAH+PSS)_n.

used were poly(diallyldimethylammonium) chloride (PDADMAC) with a molecular weight of this polymer being in the range of 200–350 kDa, and poly(allylamine) (PAH) with a molecular weight of 17 kDa. All the polymers were purchased from Sigma–Aldrich (Germany) 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. Techniques

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% $\text{H}_2\text{SO}_4(\text{conc})/30\% \text{H}_2\text{O}_2(\text{aq})$) over a period of 30 min and then thoroughly rinsed with pure water. The characteristic frequency in vacuum was $f_0 = 5$ MHz. In order to charge the gold electrode of the quartz crystal, a self-assembled monolayer of the sodium salt of 3-mercapto propanosulfonic acid was self-assembled onto the gold electrode [8,12,16]. D-QCM provided the impedance spectra of the crystal for the fundamental mode and for odd overtones of the fundamental resonance up to the 11th (central frequency $f_{11} = 55$ MHz). We have used the model of Johannsmann et al. [34] in order to relate the changes of the quartz sensor impedance spectra with the acoustical thickness, h_{ac} , and the shear modulus of the adsorbed film [8,12,16]. The dead-time of the D-QCM measurements is approximately 7 s.

For the ellipsometric experiments, we have used an imaging null-ellipsometer from Nanofilm (Model EP3, Germany), and all the experiments have been carried out on a solid–liquid cell at a fixed angle of 60° . Silicon wafers (Siltronix, France) were used as the substrates [16]. The ellipsometric angles Δ and Ψ describe the

changes in the state of polarization when the light is reflected at a surface [35]. The uncertainty of Δ and Ψ were $\pm 0.1^\circ$ and $\pm 0.05^\circ$, respectively. In order to obtain the ellipsometric thickness, h_{op} , a four layer model has been used, as in a previous work [16,36]. The dead-time of the ellipsometry measurements is around 18 s.

The X-ray experiment was made in a conventional diffractometer X'Pert Pro MRD from Panalytical (Netherlands) using silicon as substrate. The reflectivity was measured in the momentum transfer range of $0.035 < q_z < 0.12 \text{ \AA}^{-1}$. The analysis of the data was made using the software Package Parrat 32 from HMI (Berlin, Germany).

Measurements of the contact angle, θ , of a water drop on the surface of the multilayer were made using a commercial device from GBX (Model Digidrop, France). The precision of the measurements was obtained statistically from the results of the measurements in different zones of the sample. The mean error of the θ values was $\pm 2^\circ$.

2.3. Layer-by-layer assembly

The multilayers were built from polyelectrolyte solutions of concentration $c \approx 1 \text{ mg mL}^{-1}$ with different ionic strengths obtained using NaCl. The adsorption of the layers was studied till the steady-state was reached in the case of the kinetic studies, whereas for the studies of the effect of the adsorption time in the multilayer structure, different adsorption times of the layers were considered. Between the adsorption of successive layers, the 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 the 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 leads to an abrupt shift of the signal both in the

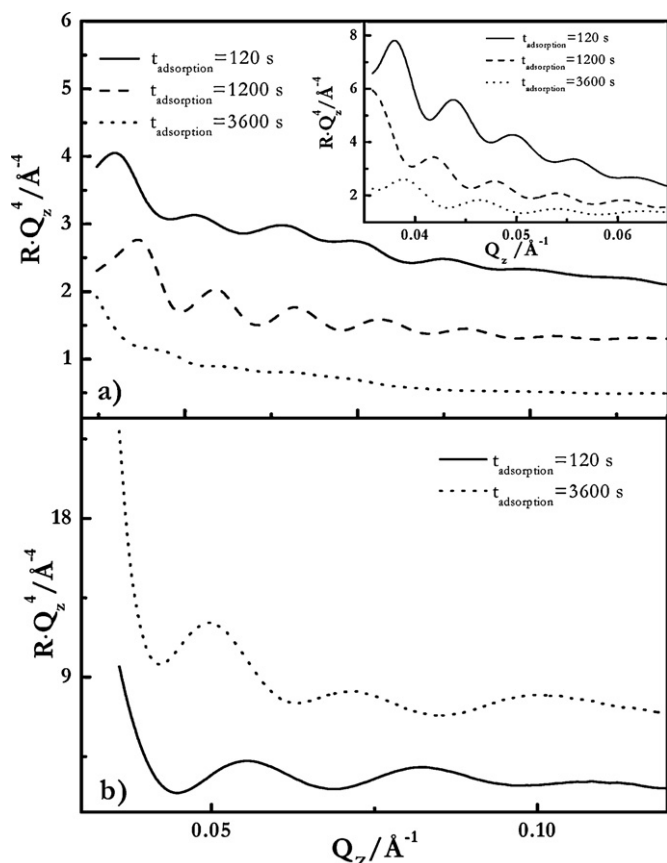


Fig. 3. Reflectivity profiles for multilayers with $N=24$ build from solution of ionic strength $c_{\text{NaCl}}=100$ mM, where the layers were adsorbed using different times. (a) (PDADMAC+PSS) $_n$. The inserted figure show the results for $c_{\text{NaCl}}=500$ mM. (b) (PAH+PSS) $_n$.

D-QCM and in the ellipsometry techniques; these sharp changes were not taken into account in the analysis of the adsorption process [8].

3. Results and discussion

The growth process of (PDADMAC+PSS) $_n$ and (PAH+PSS) $_n$ multilayers has been extensively studied (see Fig. S.1) [16,37–41]. Independently of the ionic strength conditions, the growth of (PAH+PSS) $_n$ has been found to be linear [38,42]. However, for (PDADMAC+PSS) $_n$ multilayers the growth mechanism depends on the ionic strength [37,43,44]. In spite of this change in growth mechanism, it has been previously shown that in these multilayers, the interdiffusion takes place independently of the ionic strength conditions thus leading to uniform composition through the multilayer [16], although the differences in the growth mechanism have been related frequently attributed to the existence or not of interdiffusion of the chains through the whole structure of the multilayers [25,32,33]. This implies that, for non-linear growth regime, the polymer chains still maintain some mobility [45] that is controlled by the process of association and dissociation of ionic pairs [29]. Chain reorganization within the multilayers strongly affect the kinetics of adsorption as already discussed theoretically by Cohen-Stuart [46]. In a recent paper Lane et al. [47] studied the adsorption kinetics in multilayers of PSS and poly[1-[4-[3-carboxy-4-hydroxyphenylazo]benzenesulfonamido]-1,2-ethanediyl] sodium salt using dual-beam polarization interferometry and D-QCM. They explained their adsorption kinetic results in terms of three different processes; such a description is qualitatively similar to the descrip-

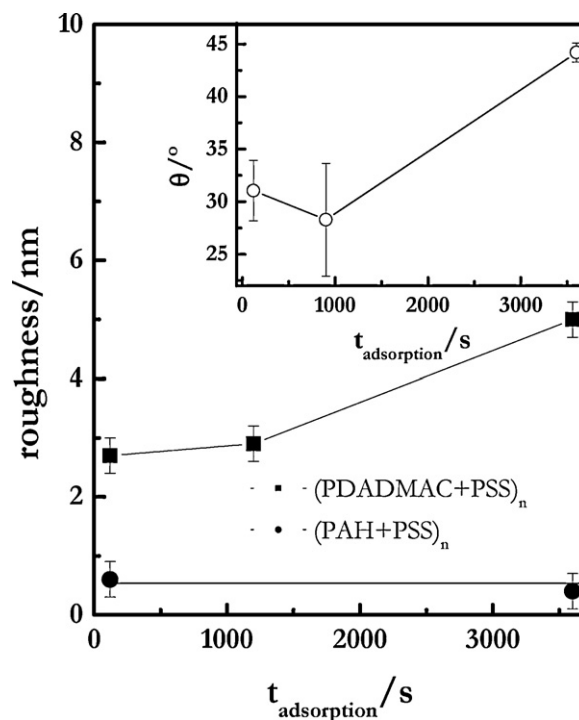


Fig. 4. Roughness of multilayers (PDADMAC+PSS) $_n$ and (PAH+PSS) $_n$ with $N=24$ where the layers were adsorbed using different times, obtained for the analysis of the reflectivity data. The inserted figure corresponds to the water contact angle, θ , on the surface of the multilayer (PDADMAC+PSS) $_n$ with $N=24$. The lines are only guided for the eyes.

tion of neutral polymer adsorption kinetics given by Linse and Källrot using Brownian dynamics simulations [48]. However, Lane et al. [47] found that the shortest characteristic adsorption time was well below the dead time of their experimental techniques. We have shown in previous works that, within the accessible time window of our experimental techniques, the adsorption kinetics may be analyzed using a bimodal model [8,12,16,49,50] derived from the one previously proposed by Raposo et al. [30]:

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

where A_1 and A_2 are the amplitudes and τ_1 and τ_2 are the characteristic times for the two kinetic processes, Γ is the adsorbed mass a time t , and Γ_{∞} is the adsorbed mass at the steady-state of the adsorption process ($t=\infty$). For all the multilayers studied in this work Eq. (1) described the experimental data within the experimental precision, independently of the polyelectrolyte type and of the layer number, an example of the kinetic analysis is shown in Fig. 1, further details about the analysis of the kinetic processes are given in our previous publications [8,16]. The characteristic time τ_1 represents a first fast adsorption step that is related to the transport of chains to the surface and fast mass deposition (it is not a true diffusive process because the amount of adsorbed material does not show a $t^{1/2}$ dependence). This is in qualitative agreement with the mean-field calculations of Cohen-Stuart for the adsorption of polyelectrolyte onto solid surfaces [46]. The characteristic time τ_2 represents a second slower process that may be related to the internal reorganization of the polymer chains adsorbed onto the last layer and/or the diffusion of the chains through the multilayer. Fig. 2 shows the characteristic adsorption times for both processes in the two multilayers studied; in all the cases τ_2 is almost one order of magnitude larger than τ_1 . The characteristic times for both kinetic processes show different dependences on the number of layers for the two different systems studied.

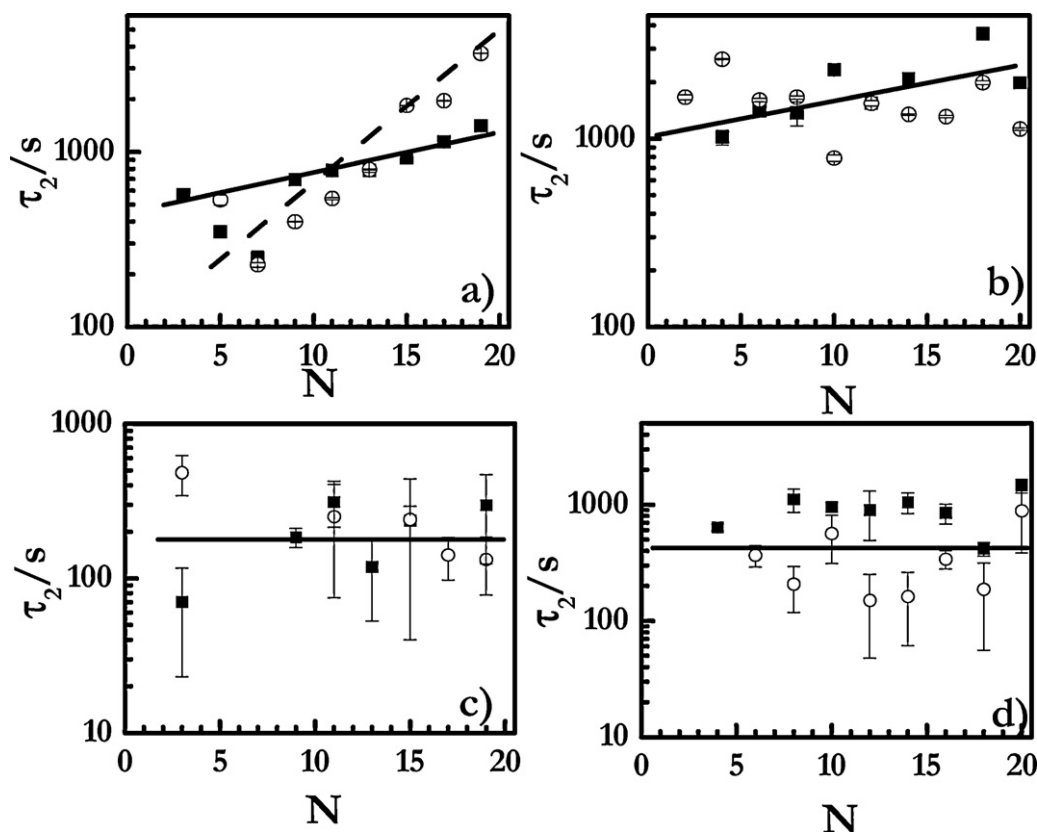


Fig. 5. Kinetic times obtained from the analysis of the reorganizational adsorption processes using Eq. (1) for multilayer of (PDADMAC+PSS)_n and (PAH+PSS)_n assembled from solutions with different ionic strengths. (a) τ_2 vs. N for the PDADMAC layers in (PDADMAC+PSS)_n multilayers. (■) $c_{\text{NaCl}} = 100$ mM; (○) $c_{\text{NaCl}} = 500$ mM. (b) τ_2 vs. N for the PSS layers in (PDADMAC+PSS)_n multilayers. (■) $c_{\text{NaCl}} = 100$ mM; (○) $c_{\text{NaCl}} = 500$ mM. (c) τ_2 vs. N for the PAH layers in (PAH+PSS)_n multilayers. (■) $c_{\text{NaCl}} = 100$ mM; (○) $c_{\text{NaCl}} = 500$ mM. (d) τ_2 vs. N for the PSS layers in (PAH+PSS)_n multilayers. (■) $c_{\text{NaCl}} = 100$ mM; (○) $c_{\text{NaCl}} = 500$ mM.

The characteristic time τ_1 , which is well above the dead-time of our experimental techniques, is independent of N (in the first layers the results are slightly different because of the influence of the interactions with the substrate) in the two multilayers studied. This may be due to the pseudo-diffusive origin of this process, thus τ_1 only depends on the structure of the adsorbed polymer, and on the assembling conditions (ionic strength of the solutions). This is further confirmed by the fact that in multilayers of (PDADMAC+PSS)_n and (PAH+PSS)_n, the layers of PSS show similar values of τ_1 , despite that the counter polyelectrolyte is different.

In the case of multilayers of (PAH+PSS)_n, τ_2 does not depend on N , whereas for (PDADMAC+PSS)_n multilayers, τ_2 increases with N both for PDADMAC and for PSS layers. In the case of typical linear growth systems, as (PAH+PSS)_n, the reorganization process may be interpreted as a process that takes place only in the layer that is adsorbing, with a small propagation in the three-dimensional structure of the multilayer. However for (PDADMAC+PSS)_n, the reorganization process takes place by interdiffusion of the chains through the whole structure of the multilayers [25,32,33]. Therefore an increase of τ_2 is expected as the thickness of multilayer increases due to the larger volume through which they can diffuse. According to all the above, τ_2 would in fact be an effective characteristic time for (PDADMAC+PSS)_n because two processes would take place: one would be the reorganization of the adsorbing chains in the plane of the multilayers as in (PAH+PSS)_n, and the other one would be associated to chain diffusion within the multilayer. This is in agreement with the three stage model proposed for Lane et al. [47] for the adsorption process of multilayers formed by PSS and poly[1-[4[(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl sodium salt], even though, as already said, the characteristic times of the

last two processes cannot be determined independently by the experimental techniques used in the present work.

Additionally, for (PDADMAC+PSS)_n it was possible to obtain some insight about the strength of the electrostatic interaction between the surface net charge of the film and the different polyelectrolytes during the adsorption. In the case of the PSS layers τ_2 is higher than the corresponding time for the adsorption of PDADMAC layers. The adsorption of PDADMAC layers takes place on a low charge density surface, whereas the PDADMAC chains present a high charge density, thus leading to a faster reorganization than in the case of the adsorption of PSS where the opposite scenario is present (polymer with low charge density and highly charged surface).

If, as stated above, the relaxation times are somehow related to the two different growing mechanisms, it seems reasonable to assume that the final structure of the multilayers may depend on the time allowed for the polyelectrolytes to adsorb. This was already suggested by Lavalle et al. [24] in the study of multilayers formed by poly(L-glutamic acid) and poly(L-lysine), even though they did not make any experimental test of this suggestion. If the total adsorption time used for the assembling of the layers is much smaller than τ_2 , the effect of interdiffusion upon the structure of the multilayer might not be observed [29]. Furthermore, this would lead to rather different film roughness in the two multilayers, as it is indeed observed in Fig. 3. Fig. 4 shows that for (PDADMAC+PSS)_n roughness increases with the adsorption time, while for (PAH+PSS)_n it is constant. The increase in roughness is due to two contributions: the increase of film thickness and the reorganization of the chains within the multilayers. It is well known that interdiffusion of chains within the multilayers leads to higher thickness and roughness, and to superlinear

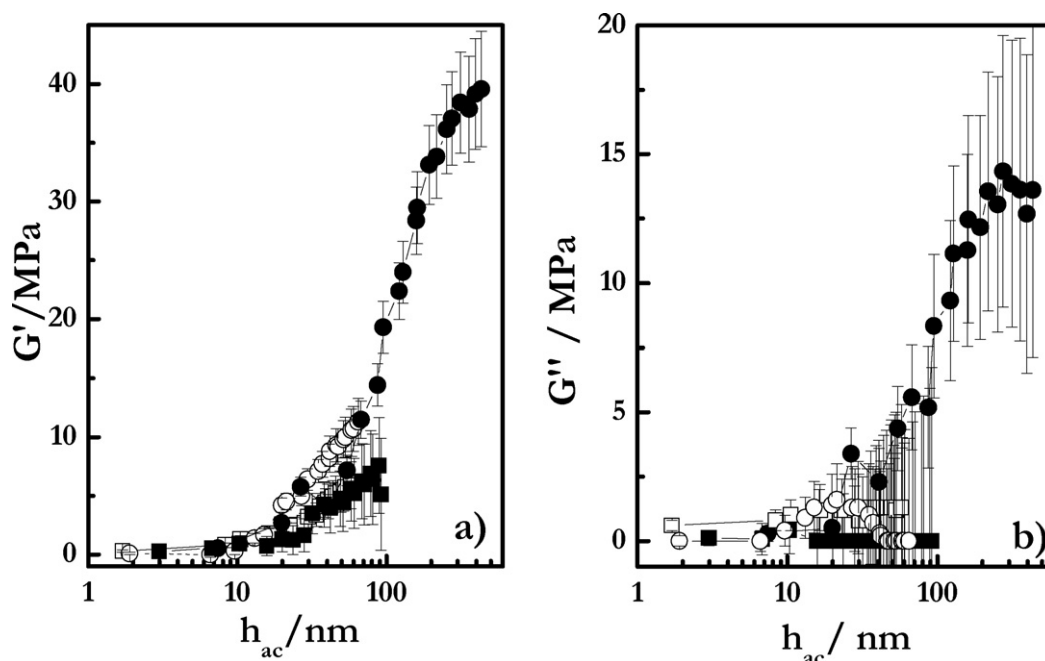


Fig. 6. Mechanical properties of the multilayers. (a) G' vs. h_{ac} . (b) G'' vs. h_{ac} . Where h_{ac} corresponds to the thicknesses obtained using D-QCM. In both graphs: $c_{NaCl} = 100$ mM is represented by squares and $c_{NaCl} = 500$ mM is represented by circles. Open symbols correspond to $(PAH + PSS)_n$ and solid symbols correspond to $(PDADMAC + PSS)_n$. The lines are only guided for the eyes.

growth; therefore, it is possible to conclude that longer adsorption times are associated to a transition from linear to superlinear growth for $(PDADMAC + PSS)_n$. As it can be observed, the behavior of $(PAH + PSS)_n$ is completely different, with values that are independent of the adsorption time which would be in agreement with the layered structure described by Lavalle et al. [38]. The importance of the adsorption time found in this work is in agreement with the recent structural studies of Kharlampieva et al. [32].

It is worth to discuss why the growing regime of $(PDADMAC + PSS)_n$ changes from linear to non-linear as the ionic strength is increased. For low NaCl concentration the screening of the polyelectrolyte charges is smaller, thus the Coulombic repulsion might constitute an electrostatic barrier for the further adsorption of material. The adsorbed polymer reorganizes in the whole structure of the multilayer leading to a smaller roughness that in the case of high ionic strengths. This fact may be due to the existence of a limited interdiffusion for low ionic strengths as consequence of the low degree of extrinsic compensation that exists on the multilayer [16], thus the Donnan potential is not very important [51]. However, when the ionic strength increases, the Donnan potential [51] plays a relevant role due to the strong extrinsic compensation [16]. As a consequence a larger number of molecules can diffuse through the multilayer thus increasing the roughness and leads to superlinear growth [23]. However, in multilayers of $(PAH + PSS)_n$, no effect is observed in the structural pattern as the adsorption time is increased. This is a typical behavior of multilayers that grow linearly where the existence of internal reorganization is negligible in accordance with the existence of intrinsic compensation on the multilayer [52], and therefore the global structure of the layers is not modified.

Fig. 5 shows that the ionic strength affects the characteristic time of the reorganization process. In the case of multilayers $(PDADMAC + PSS)_n$, increasing the ionic strength increases the time necessary to reach to the steady-state for the adsorption of PDADMAC layers, whereas in the case of PSS layers the reorganizational time is independent on the ionic strength. In the case of $(PAH + PSS)_n$ multilayers the layers of both polymers are unaffected by the changes in the ionic strength. These different times for the reor-

ganization process are in agreement with the results commented above.

For low adsorption times, $t_{adsorption} \sim 120$ s, it may be assumed that the reorganization process does not take place in agreement with the adsorption kinetics results for multilayers of $(PDADMAC + PSS)_n$ (see Fig. 3, τ_1 is $\sim 118 \pm 20$ s for PDADMAC layers, $\sim 72 \pm 40$ s for PSS layers and $\sim 27 \pm 7$ s for PAH layers). In this case only the adsorption of material from the solution would take place onto the preformed layer. However, increasing the adsorption time allows the reorganization process to become important.

The interdiffusion on the multilayers must be also related to their internal structure, and this is strongly related to the mechanical properties of the multilayers [53,54]. The D-QCM technique allows one to obtain the complex shear modulus according to Johannsmann formalism [16,27,28,34]. Fig. 6 shows the results for G' and G'' of the different multilayers as function of the thickness obtained using D-QCM (acoustical thickness, h_{ac}). In the case of $(PAH + PSS)_n$ multilayers the mechanical behavior may be considered typical of rigid films (with $G'' \approx 0$) in all the assembling conditions. However in the case of $(PDADMAC + PSS)_n$, the viscous part of the mechanical behavior becomes more relevant as the ionic strength increases leading to a mechanical viscoelastic behavior typical of a rubber-like material [8,16] [it must be taken into account that the D-QCM measurements are carried out at high frequencies (5–55 MHz)!]. The existence of a softer behavior in multilayers of $(PDADMAC + PSS)_n$ makes the interdiffusion within the whole structure of the films easier. The elastic behavior of $(PAH + PSS)_n$ multilayers is in agreement with an impeded interdiffusion process within the films. Similar mechanical behavior of several linear and non-linear growing multilayers was previously reported by Picart et al. [55] and by Hubsch et al. [56].

4. Conclusions

The experimental results presented in this work allow us to conclude that structure of polyelectrolyte multilayers may depend on the adsorption time, $(PDADMAC + PSS)_n$ being a good example.

The results also point out that the elastic ($G'' \approx 0$), or viscoelastic ($G' \sim G''$) character of the multilayer, and the ionic strength may control the interdiffusion process within the multilayer. This phenomenon is important for having multilayers with a well-defined layered or an almost homogeneous structure.

Acknowledgements

This work was supported in part by MICINN under grants FIS2009-14008-C02-01, by ESA under grants FASES and PASTA, and by E.U. under grant FP7-MULTIFLOW. E.G. was supported by a FPU fellowship from MICINN. H.R. was supported by a Ramón y Cajal contract from MICINN. The authors are grateful to the UIRC of the CAI of Spectroscopy for the use of its facilities, and to the CAI of X-ray diffraction for the reflectivity experiments.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.colsurfa.2011.04.005.

References

- [1] G. Decher, Fuzzy nanoassemblies: toward layered polymeric multicomposites, *Science* 277 (1997) 1232–1237.
- [2] G. Decher, J.-D. Hong, J. Schmitt, Buildup of ultrathin multilayer films by a self-assembly process: III. Consecutively alternating adsorption of anionic and cationic polyelectrolytes on charged surfaces, *Thin Solid Films* 210/211 (1992) 831–835.
- [3] G. Decher, J.B. Schlenoff, *Multilayer Thin Films-Sequential Assembly of Nanocomposite Materials*, Wiley-VCH Verlag, Berlin, 2003.
- [4] R.K. Iler, Multilayers of colloidal particles, *J. Colloid Interface Sci.* 21 (1966) 569–594.
- [5] K.B. Blodgett, Monomolecular films of fatty acids on glass, *J. Am. Chem. Soc.* 56 (1934) 495.
- [6] F. Caruso, H. Lichtenfeld, M. Giersig, H. Möhwald, Electrostatic self-assembly of silica nanoparticle–polyelectrolyte multilayers on polystyrene latex particles, *J. Am. Chem. Soc.* 120 (1998) 8523–8534.
- [7] G.B. Sukhorukov, E. Donath, S. Davis, H. Lichtenfeld, F. Caruso, V.I. Popov, H. Möhwald, Stepwise polyelectrolyte assembly on particle surfaces: a novel approach to colloid design, *Polym. Adv. Technol.* 9 (1998) 759–767.
- [8] E. Guzmán, H. Ritacco, F. Ortega, T. Svitova, C.J. Radke, R.G. Rubio, Adsorption kinetics and mechanical properties of ultrathin polyelectrolyte multilayers: liquid-supported versus solid-supported films, *J. Phys. Chem. B* 113 (2009) 7128–7137.
- [9] J. Ruths, F. Essler, G. Decher, H. Riegler, Polyelectrolytes I: polyanion/polycation multilayers at the air/monolayer/water interface as elements for quantitative polymer adsorption studies and preparation of hetero-superlattices on solid surfaces, *Langmuir* 16 (2000) 8871–8878.
- [10] A.A. Yaroslavov, A.A. Rakhnyanskaya, E.G. Yaroslavova, A.A. Efimova, F.M. Menger, Polyelectrolyte-coated liposomes: stabilization of the interfacial complexes, *Adv. Colloid Interface Sci.* 142 (2008) 43–52.
- [11] R. Steitz, W. Jaeger, R. von Klitzing, Influence of charge density and ionic strength on the multilayer formation of strong polyelectrolytes, *Langmuir* 17 (2001) 4471–4474.
- [12] E. Guzmán, V. San Miguel, C. Peinado, F. Ortega, R.G. Rubio, Polyelectrolyte multilayers containing triblock copolymers of different charge densities, *Langmuir* 26 (2010) 11494–11502.
- [13] T. Saarinen, M. Österberg, J. Laine, Adsorption of polyelectrolyte multilayers and complexes on silica and cellulose surfaces studied by QCM-D, *Colloids Surf. A* 330 (2008) 134–142.
- [14] J.B. Schlenoff, S.T. Dubas, Mechanism of polyelectrolyte multilayer growth. Charge overcompensation and distribution, *Macromolecules* 34 (2001) 592–598.
- [15] S.T. Dubas, J.B. Schlenoff, Factors controlling the growth of polyelectrolyte multilayers, *Macromolecules* 32 (1999) 8153.
- [16] E. Guzmán, H. Ritacco, J.E.F. Rubio, R.G. Rubio, F. Ortega, Salt-induced changes in the growth of polyelectrolyte layers of poly(diallyl-dimethylammonium chloride) and poly(4-styrene sulfonate of sodium), *Soft Matter* 5 (2009) 2130–2142.
- [17] X. Zhang, Y.P. Sun, M.L. Gag, X.X. Kong, J.C. Shen, Effects of pH on the supramolecular structure of polymeric molecular deposition films, *Macromol. Chem. Phys.* 197 (1996) 509–515.
- [18] M. Salomaki, I.A. Vinokurov, J. Kankare, Effect of temperature on the buildup of polyelectrolyte multilayers, *Langmuir* 21 (2005) 11232–11240.
- [19] J.A. Jaber, J.B. Schlenoff, Recent developments in the properties and applications of polyelectrolyte multilayers, *Curr. Opin. Colloid Interface Sci.* 11 (2006) 324–329.
- [20] D. Zimnitsky, V.V. Shevchenko, V.V. Tsukruk, Perforated freely suspended layer-by-layer nanoscale membranes, *Langmuir* 24 (2008) 5996–6006.
- [21] J.L. Lutkenhaus, K. McEnnis, P.T. Hammond, Nano- and microporous layer-by-layer assemblies containing linear poly(ethyleneimine) and poly(acrylic acid), *Macromolecules* 41 (2008) 6047–6054.
- [22] K. Büscher, K. Graf, H. Ahrens, C.A. Helm, Influence of adsorption conditions on the structure of polyelectrolyte multilayers, *Langmuir* 18 (2002) 3585–3591.
- [23] N. Hoda, R.G. Larson, Modeling the buildup of exponentially growing polyelectrolyte multilayer films, *J. Phys. Chem. B* 113 (2009) 4232–4241.
- [24] P. Lavalle, C. Picart, J. Mutterer, C. Gergely, H. Reiss, J.C. Voegel, B. Senger, P. Schaaf, Modeling the buildup of polyelectrolyte multilayer films having exponential growth, *J. Phys. Chem. B* 108 (2004) 635–648.
- [25] C. Picart, J. Mutterer, L. Richert, Y. Luo, G.D. Prestwich, P. Schaaf, J.C. Voegel, P. Lavalle, Molecular basis for the explanation of the exponential growth of polyelectrolyte multilayers, *Proc. Natl. Acad. Sci. U.S.A.* 99 (2002) 12531–12535.
- [26] R. von Klitzing, Internal structure of polyelectrolyte multilayer assemblies, *Phys. Chem. Chem. Phys.* 8 (2006) 5012–5033.
- [27] J. Schmitt, T. Grünwald, K. Kjaer, P. Pershan, G. Decher, M. Lösche, The internal structure of layer-by-layer adsorbed polyelectrolyte films: a neutron and X-ray reflectivity study, *Macromolecules* 26 (1993) 7058–7063.
- [28] M. Lösche, J. Schmitt, G. Decher, W.G. Bouwman, K. Kjaer, Detailed structure of molecularly thin polyelectrolyte multilayer films on solid substrates as revealed by neutron reflectometry, *Macromolecules* 31 (1998) 8893–8906.
- [29] V. Panchagnula, J. Jeon, A.V. Dobrynin, Molecular dynamics simulations of electrostatic layer-by-layer self-assembly, *Phys. Rev. Lett.* 93 (2004) 037801.
- [30] M. Raposo, R.S. Pontes, L.H.C. Mattoso, O.N. Oliveira, Kinetics of adsorption of poly(o-methoxyaniline) self-assembled films, *Macromolecules* 30 (1997) 6095–6101.
- [31] I. Estrela-Lopis, S. Leporatti, S. Moya, A. Brandt, E. Donath, H. Möhwald, SANS studies of polyelectrolyte multilayers on colloidal templates, *Langmuir* 18 (2002) 7861–7866.
- [32] E. Kharlampieva, V. Kozlovskaya, J. Chan, J.F. Ankner, V.V. Tsukruk, Spin-assisted layer-by-layer assembly: variation of stratification as studied with neutron reflectivity, *Langmuir* 25 (2009) 14017–14024.
- [33] O. Félix, Z. Zheng, F. Cousin, G. Decher, Are sprayed LbL-films stratified? A first assessment of the nanostructure of spray-assembled multilayers by neutron reflectometry, *Compt. Rend. Chim.* 12 (2009) 225–234.
- [34] D. Johannsmann, K. Mathauer, G. Wegner, W. Knoll, Viscoelastic properties of thin films probed with a quartz crystal resonator, *Phys. Rev. B* 46 (1992) 7808–7815.
- [35] R.M.A. Azzam, N.M. Bashara, *Ellipsometry and Polarized Light*, Elsevier, North-Holland, 1987.
- [36] H.G. Tompkins, *A User's Guide to Ellipsometry*, Academic Press Inc., Amsterdam, 1993.
- [37] R.A. McAloney, M. Sinyor, V. Dudnik, M.C. Goh, Atomic force microscopy studies of salt effects on polyelectrolyte multilayer film morphology, *Langmuir* 17 (2001) 6655–6663.
- [38] P. Lavalle, C. Gergely, F.J.G. Cuisinier, G. Decher, P. Schaaf, J.C. Voegel, C. Picart, Comparison of the structure of polyelectrolyte multilayer films exhibiting a linear and an exponential growth regime: an in situ atomic force microscopy study, *Macromolecules* 35 (2002) 4458–4465.
- [39] E. Blomberg, E. Poptoshev, F. Caruso, Surface interactions during polyelectrolyte multilayer build-up. 2. The effect of ionic strength on the structure of preformed multilayers, *Langmuir* 22 (2006) 4153–4157.
- [40] D.A. Gorin, A.M. Yashchenok, A.O. Manturov, T.A. Kolesnikova, H. Möhwald, Effect of layer-by-layer electrostatic assemblies on the surface potential and current voltage characteristic of metal-insulator-semiconductor structures, *Langmuir* 25 (2009) 12529–12534.
- [41] F. Caruso, H. Lichtenfeld, E. Donath, H. Mohwald, Investigation of electrostatic interactions in polyelectrolyte multilayer films: binding of anionic fluorescent probes to layers assembled onto colloids, *Macromolecules* 32 (1999) 2317–2328.
- [42] E. Poptoshev, B. Schoeler, F. Caruso, Influence of solvent quality on the growth of polyelectrolyte multilayers, *Langmuir* 20 (2004) 829–834.
- [43] M. Salomaki, T. Laiho, J. Kankare, Counteranion-controlled properties of polyelectrolyte multilayers, *Macromolecules* 37 (2004) 9585–9590.
- [44] M. Salomaki, P. Tervasmaki, S. Areva, J. Kankare, The Hofmeister anion effect and the growth of polyelectrolyte multilayers, *Langmuir* 20 (2004) 3679–3683.
- [45] P. Podsiadlo, M. Michel, K. Critchley, S. Srivastasa, M. Qin, J.W. Lee, E. Verploegen, A.J. Hart, Y. Qi, N.A. Kotov, Diffusional self-organization in exponential layer-by-layer films with micro- and nanoscale periodicity, *Angew. Chem. Int. Ed.* 48 (2009) 7073–7077.
- [46] M.A. Cohen-Stuart, Kinetics of polyelectrolyte adsorption, *J. Phys.: Condens. Matter* 9 (1997) 7767–7783.
- [47] T.J. Lane, W.R. Fletcher, M.V. Gormally, M.S. Johal, Dual-beam polarization interferometry resolves mechanistic aspects of polyelectrolyte adsorption, *Langmuir* 24 (2008) 10633–10636.
- [48] P. Linse, N. Källrot, Polymer adsorption from bulk solution onto planar surface: effect of polymer flexibility and surface attraction in good solvent, *Macromolecules* 43 (2010) 2054–2068.
- [49] E. Guzmán, F. Ortega, N. Baghdadi, G.S. Luengo, R.G. Rubio, Effect of the molecular structure on the adsorption of conditioning polyelectrolytes on solid substrates, *Colloids Surf. A*, in press.

- [50] E. Guzmán, F. Ortega, M.G. Prolongo, M.A. Rubio, R.G. Rubio, On the way to functional coatings: polyelectrolyte multilayers, *J. Mater. Sci. Eng. U.S.A.* 4 (10) (2010) 1–13.
- [51] N. Laugel, F. Boulmedais, A.E.E. Haitami, P. Rabu, G. Rogez, J.-C. Voegel, P. Schaaf, V. Ball, Tunable synthesis of Prussian blue in exponentially growing polyelectrolyte multilayer films, *Langmuir* 25 (2009) 14030–14036.
- [52] J.B. Schlenoff, H. Ly, M. Li, Charge and mass balance in polyelectrolyte multilayers, *J. Am. Chem. Soc.* 120 (1998) 7626–7634.
- [53] A.A. Antipov, G.B. Sukhorukov, H. Möhwald, Influence of the ionic strength on the polyelectrolyte multilayers' permeability, *Langmuir* 19 (2003) 2444–2448.
- [54] A. Fery, B. Schöler, T. Cassagneau, F. Caruso, Nanoporous thin films formed by salt-induced structural changes in multilayers of poly(acrylic acid) and poly(allylamine), *Langmuir* 17 (2001) 3779–3783.
- [55] C. Picart, P. Laval, P. Hubert, F.J.G. Cuisinier, G. Decher, P. Schaaf, J.C. Voegel, Buildup mechanism for poly(L-lysine)/hyaluronic acid films onto a solid surface, *Langmuir* 17 (2001) 7414–7424.
- [56] E. Hubsch, V. Ball, B. Senger, G. Decher, J.C. Voegel, P. Schaaf, Controlling the growth regime of polyelectrolyte multilayer films: changing from exponential to linear growth by adjusting the composition of polyelectrolyte mixtures, *Langmuir* 20 (2004) 1980–1985.