Review Article

Deposition Mechanisms in Layer-by-Layer or Step-by-Step Deposition Methods: From Elastic and Impermeable Films to Soft Membranes with Ion Exchange Properties

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The modification of solid-liquid interfaces with polyelectrolyte multilayer films appears as a versatile tool to confer new functionalities to surfaces in environmentally friendly conditions. Indeed such films are deposited by alternate dipping of the substrates in aqueous solutions containing the interacting species or spraying these solutions on the surface of the substrate. Spin coating is more and more used to produce similar films. The aim of this short review article is to provide an unifying picture about the deposition mechanisms of polyelectrolyte multilayer films. Often those films are described as growing either in a linear or in a supralinear growth regime with the number of deposited "layer pairs". The growth regime of PEM films can be controlled by operational parameters like the temperature or the ionic strength of the used solutions. The control over the growth regime of the films as a function of the number of deposition steps allows to control their functional properties: either hard and impermeable films in the case of linear growth or soft and permeable films in the case of supralinear growth. Such different properties can be obtained with a given combination of interacting species by changing the operational parameters during the film deposition.

1. Introduction

The functionalization of surfaces is of interest since the appearance of technology in the antiquity. More and more surface coatings, as painting, were developed not only to change the aesthetic appearance of a material but also to protect it against the environment (for instance against oxidants) and more and more to provide it with an additional functionality, for instance drug release. This last point is of particular importance in the functionalization of biomaterials.

The need for a better control of surface chemistry and the understanding that the fundamental chemical unit is either an atom or a stable assembly thereof, that is, a molecule, incited researchers to deposit single molecular layers at surfaces. Hence, during almost the half first of the 20th century; the investigation of polymer and colloid deposition was restricted to the deposition of monolayers.

The Langmuir or Langmuir-Blodgett deposition method [1], consisting in the transfer of amphiphilic molecules from the water-air interface, to a solid-air interface allows for the transfer of multiple layers. But to reach that goal, it requires very clean substrates and a dust-free atmosphere. In addition the multilayers of amphiphiles are not robust from a mechanical point of view and the deposition process is very slow. Some strategies have been developed to crosslink such assemblies using unsaturated molecules and UV light to induce intermolecular bonds.

The first layer-by-layer deposition experiments from colloids (assemblies having an hydrodynamic radius between $1\,nm$ and about $1\,\mu m$) were performed using oppositely charged silica particles [2]. The buildup of such assemblies could be followed by means of an optical microscope. The possibility to obtain multilayered architectures of smaller assemblies was then totally neglected during almost 35 years.

The need to obtain alternative deposition strategies to overcome the shortcomings of multilayered films obtained by the Langmuir or the Langmuir-Blodgett deposition methods led the researchers at the Institute for Physical Chemistry in Mainz to obtain layered architectures from polymers and bolaamphiphiles [3]. Very rapidly this concept was adapted for the alternated adsorption of oppositely charged polymers [4]. Such polymers are called polyelectrolytes. One has to distinguish between strong and weak polyelectrolytes. The former one carry a surface charge density (average charge per unit length of the polymer) that is independent from the pH of the aqueous solution whereas the ionization of the latter one is pH dependent. Since the first papers describing such architectures obtained trough sequential deposition steps have been published by Decher et al. in 1991, a fantastic enthusiasm for such coatings has appeared in the scientific community. This deposition method will lead to coatings produced in a "Layer-by-layer" (LBL) manner. Nowadays, at the beginning of 2012, more than 1000 scientific papers are published a year, tens of patents have been deposited and some commercial products based on the LBL technology have been pushed on the market. To cite only a few: coatings for contact lenses (Ciba Vision), coatings for chromatography columns (Agilent Technologies).

The success of this coating technology relies on its simplicity and versatility as it can be easily automated (Figure 1) and, since that the LBL coatings can be deposited not only on planar substrates but also on colloids, nanoparticles [5] and in the pores [6] of all these materials.

It is the aim of this small review to describe the fundamental mechanisms allowing for the deposition of such films and to provide a unifying view of this field in which each combination of polyelectrolytes is often treated by itself without comparison with other systems. The main message of this paper is to show that films produced from the alternated deposition of mutually interacting species can have properties similar to those of rigid and impermeable materials or to those of highly permeable gels. In addition, such multilayered films display a dynamic response to external stimulus like a change in ionic strength or in the environmental temperature. Finally, some major application fields of LBL films will be described. It is not our aim to be exhaustive, but to provide a comprehensive overview of the "LBL" deposition research. Interested readers may find some specialized and exhaustive review articles [7, 8].

2. Kinds of Molecules That Can Be Deposited, Deposition Methods and Growth Regimes of Films Produced in an LBL Manner

If LBL films are produced from oppositely charged polyelectrolytes, one speaks about polyelectrolyte multilayer films (PEMs). It was rapidly demonstrated that the LBL deposition methods do not only work with oppositely charged polyelectrolytes, to yield PEM films, but also with all kind of multitopic molecules presenting mutually interacting binding sites. Among such molecules, one can site the following.

(i) Polymers carrying hydrogen donor and acceptor moieties [9–11].

   The fundamental mechanisms allowing for the deposition of films prepared by the alternated adsorption of hydrogen bond donors and acceptors have been reviewed recently [12].

(ii) Stereoregular polymers carrying sites of opposite chirality [13].

(iii) Host-guest interactions [14].

(iv) Charge transfer interactions [15].

(v) Specific biorecognition interactions like those between streptavidin and polymers carrying avidin moieties [16].

(vi) π-π interactions between molecules carrying aromatic cycles and carbon nanotubes [17].

(vii) Covalent interactions using, for instance, polymers carrying azides which react through 1,3 cycloadditions with polymers carrying alkynes, one of the possible "click chemistry" based reactions [18].

The LBL deposition method can not only be applied to polymers but also on combinations of polymers and particles or just with mutually interacting nanoparticles [19].

The huge versatility of the LBL deposition methods appears even more when one considers the different possibilities to deposit such films at solid liquid interfaces. During almost 10 years, almost all the films produced in an LBL manner have been deposited using alternated dipping of the substrate to be coated in solutions containing the interacting species (for instance polyelectrolytes carrying surface charge densities of opposite sign, or hydrogen bond donors and acceptors). Two adsorption steps have to be separated by rinse steps with the solvent (most often water or an aqueous electrolyte solution) in order not only to remove weakly adsorbed polyelectrolytes but also to avoid cross-contamination of the solutions containing the molecules to be deposited. Indeed, if the polyelectrolytes interact on a surface, they also interact in their solution: it is a well-known phenomenon (even if a lot of research remains to be performed in this field) that the mixture of oppositely charged polyelectrolytes leads to phase separation, particularly in conditions where the ratio of the number of positive and negative charges is close to one [20]. Later on, this phase separation phenomenon and its relationship with the fundamental understanding of the interactions at the origin of the deposition of PEM films will be explained.

Several successful trials have been made to avoid the intermediate rinsing steps in order to increase the deposition speed of PEM films. Among such methods one can note the "dewetting" method [21].

The alternated dip coating method is easy to implement and can be robotized in an straightforward manner. It is however time consuming since each adsorption and rinsing step usually lasts over several minutes. Indeed molecules to be deposited have to diffuse at the interface, to adsorb, and to find their equilibrium conformation, a process that may be extremely slow.
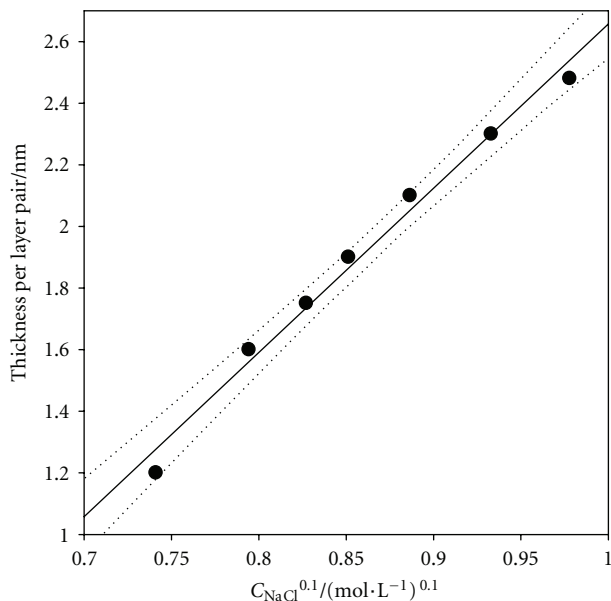
FIGURE 1: Evolution of the thickness increment per layer pair for PEI-(PSS-PAH)$_n$ films deposited on glass substrates from a Tris (Tris(hydroxymethyl)aminomethane) buffer at pH = 7.4 in the presence of NaCl at different concentrations. The data have been plotted as the film thickness increment versus the NaCl concentration at a power α, with $\alpha = 0.10$. The film thickness has been measured by means of scanning angle reflectometry. Plotted with the data from [29].

To speed up the deposition process, alternated spray deposition [22, 23] and spin-coating [24] have been found as good alternatives allowing for the deposition of a "layer" in a typical time of a few seconds. Simultaneous spray deposition from two spray cans containing the interacting molecules allows also to produce some coatings whose thickness increases linearly with the deposition time [25]. Even if such films may have many similar properties to films produced in a regular LBL manner, one cannot anymore speak about "LBL deposition".

Some investigations have shown that the nature of the deposition method may have a pronounced influence of the properties of the obtained coatings [26, 27]. It appears that spin coated films are thinner, more transparent and of higher elasticity than their counterparts produced via alternated dipping [26]. This may be explained by the influence of shear forces applied during the spin coating on the conformation of the adsorbing polymer chains (see Scheme 1).

The LBL deposition method allows to deposit PEM films on almost all kinds of surfaces irrespective of its chemical composition and surface charge: indeed only the thickness of the first few deposited layers is dependent on the used substrate. As soon as the surface coverage of the substrate reaches a critical level, the further deposition of polyelectrolytes is not influenced anymore by the surface chemistry of the substrate.

The advantage of the LBL deposition method is that the film growth rate can be well controlled at the nanometer scale. In most cases the film growth rate is a linear function of the number of the layer pairs deposited, one layer pair consisting in the successive adsorption of the two interacting partners (the same concept holds for LBL films build from polymers interacting through hydrogen bonds or the other possible modes of interactions previously described). These films will be denoted by (A-B)$_n$ in the following where A and B are the interacting species and n is the number of deposition cycles, commonly called the number of "layer pairs." The thickness increase corresponding to the deposition of one "layer pair" is of the order of a few nanometers and corresponds roughly to the sum of the characteristic size of the polycation and the polyanion. These sizes can be changed by modifying the conformation of the polyelectrolytes in solution. This is possible by playing on the charge density of the polyelectrolytes, that is, by changing the pH of the solution in the case of weak polyelectrolytes or by modifying the intramolecular interactions in a polyelectrolyte chain by screening the electrostatic interactions. This is easily achieved by playing with the salt concentration. In the low salt concentration regime, the film thickness increment per "layer pair", d, increases with the salt concentration (Figure 1) according to a power law of the type:

$$d \sim d_0 \left(\frac{C}{C_0} \right)^{\alpha}, \tag{1}$$

where d_0 is a characteristic film thickness, C the salt concentration used during the experiment, and $C_0 = 1$ mol/L.

For all the investigated polyelectrolyte pairs, the exponent α lies between 0.1 and 0.5 [28]. In the particular case of the films prepared from poly(allylamine hydrochloride) (PAH) and from poly(sodium-4-styrene sulfonate) (PSS) at pH = 7.4 and in the presence of NaCl, the exponent α is equal to 0.10 ± 0.04 [29].

Very soon in the history of LBL deposition, it was found that the average surface potential (measured as the zeta potential) of PEM films is alternated after each deposition step [29–31]. This finding is expected if the degree of interpenetration of the chains is not too high (we will deal with this point later on), meaning that each new adsorbed polyelectrolyte neutralizes almost all the charges of the previously adsorbed one just providing a small amount of excess charge through polymer loops or trains dangling in solution. This excess of surface charge constitutes then the driving force for further adsorption of an oppositely charged polyelectrolyte. It occurs in almost all the PEM films investigated up to now (Figure 2).

Upon the deposition of the last polyelectrolyte the surface composition change is also reflected by a change in its wettability for water. This is reflected by a regular change of the static water contact angle between two limiting values (Figure 3) [32, 33]. This has first been exemplified with films made from the alternated adsorption of PAH and poly(sodium acrylate) (PAA) [33].

The regular reversal of the surface potential seems however not to be an absolute requirement for the deposition
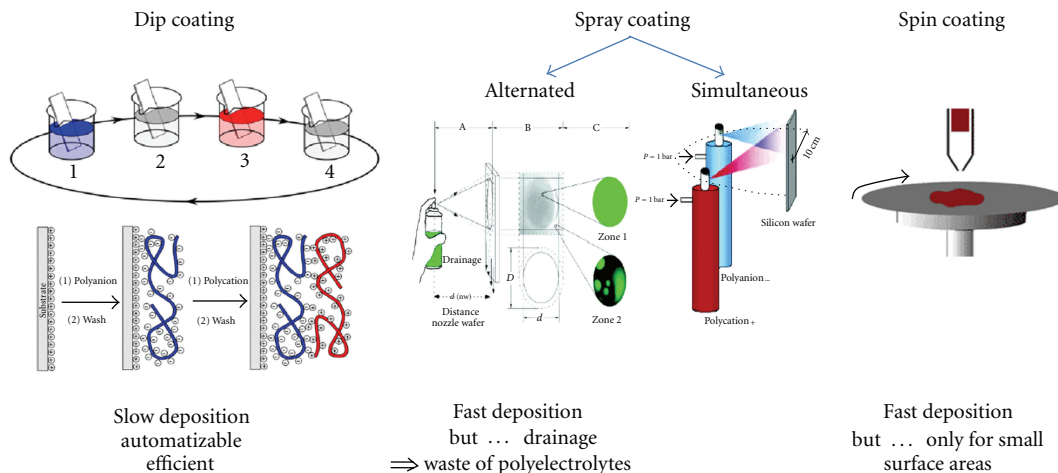
SCHEME 1: Illustration of the 3 most common deposition technologies leading to LBL or LBL-like coatings. The lower line outlines the major advantages and drawbacks of each of them.
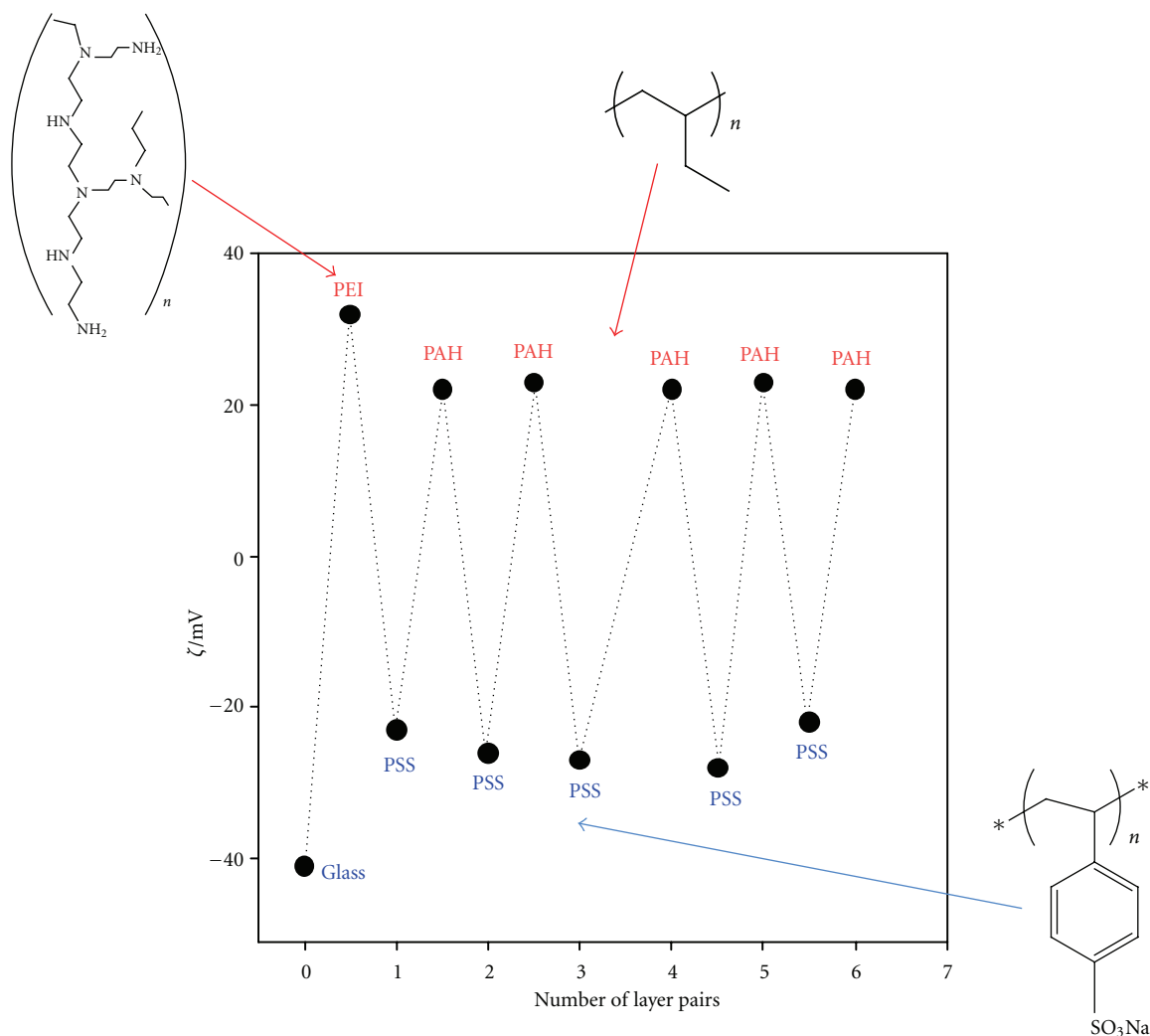

FIGURE 2: Zeta potential of a PEM film made from PAH and from PSS from a Tris(hydroxymethyl)aminomethane buffer at pH 7.4 containing $5\,mg\cdot mL^{-1}$ of each polyelectrolyte. The glass substrate was first covered with a layer of poly(ethylene imine) (PEI) aimed to produce a stable anchoring layer. Results plotted from the data of reference [29]. The structure of the repeat unit of each employed polyelectrolyte is indicated.
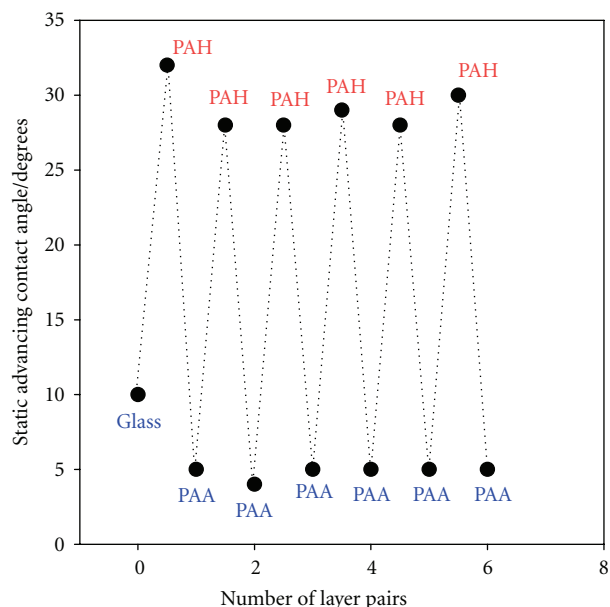
FIGURE 3: Static contact angles of water droplets (1 μL in volume) measured on PEM films made from PAH and PAA as the polyelectrolytes (dipping solutions at pH 2.5 containing 10^{-2} M of polyelectrolytes based on the repeat unit's molecular mass). Results plotted from the data of [33].

FIGURE 4: An example of exponential growth followed by a transition to linear growth for PEI-(PGA-PAH)$_n$ films deposited on silicon by means of alternated spray deposition (5s per deposition and buffer rinse step). The inset shows the thickness increase of the film for the first 22 layer pairs. The following function has been fitted to the data: $d = 2 + 9.52 \times \exp(0.13 \times n)$, where d (nm) and n are the film thickness and the number of "layer pairs," respectively. The slope of the linear growth regime following the first exponential growth is of 17.5 nm per "layer pair". These data have been plotted from the data of reference [41].

of a film from oppositely charged polyelectrolytes [34]. This recent finding made on deposits made from PAH as a polycation and from sodium polyphosphate (PSP) as a polyanion raises many questions about the driving force leading to PEM films.

In addition to the linear growth regime of the PEM films, two other film growth regimes have been observed: the supralinear [35–37] and the unstable adsorption-desorption regime [38]. The supralinear growth of PEM films offers the advantage to yield very thick films (more than 1 μm after less than 10 alternated deposition cycles when the films remain hydrated) compared to the characteristic size of the polyelectrolytes (a few nanometers) in a small number of deposition steps.

Linearly growing films display some fuzzy structuration with small interpenetration of the alternating chains as has been demonstrated by means of small angle neutron scattering [39, 40]. In these experiments, perdeuterated PSS chains, giving some scattering contrast with respect to hydrogenated chains, were deposited at regular levels during the film deposition. Even if some small intermixing occurs, the chains stay roughly at the position where they were initially deposited.

In strong contrast with linearly growing films, in the case of supralinear growth (Figure 4), which is indeed most often an exponential growth (up to a critical film thickness where the growth turns again in a linear regime but with an increment per layer pair that can be of a few hundreds of nm), the films are characterized *by a high chain mobility* not only in the direction perpendicular to the film, but also in the
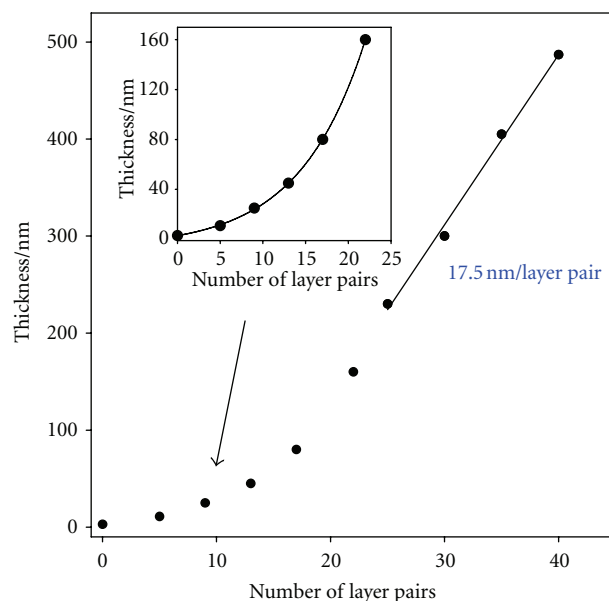
plane of the film. Figure 4 displays the change in thickness of films made by the alternated spraying of poly(-L-glutamic acid) (PGA) and PAH as a function of the number of layer pairs.

This chain mobility has been observed by means of confocal laser scanning microscopy (CLSM) combined with fluorescence recovery after photobleaching (FRAP) [37, 42, 43]. It was proven that the diffusion of at least one of the constituent chains in and out of the film can be at the origin of the exponential growth [37]. Indeed, let us make the assumption that the film is constituted by a fraction of fixed chains establishing relatively strong interactions with the oppositely charged polyelectrolyte. This assumption is reasonable, otherwise the films would never be stable. Imagine now that the film preparation ends with the adsorption of the diffusing polyelectrolyte. A further assumption is that the only species able to diffuse is the polycation (as was observed experimentally for films made from poly(-L-lysine), PLL, whereas Hyaluronic acid, HA, is not diffusing through the whole thickness of the film [37]. The adsorption of PLL from the solution stops when the intermolecular electrostatic repulsions between the similar charged chains overcome the attractive interactions with the oppositely charged chains. The nonadsorbed chains in solution are then removed upon rinsing with the electrolyte solution (water plus a small molecular mass electrolyte). The chemical

potential of these chains in solution drops to $-\infty$ as their concentration drops to zero. The weakly bound polycations should then desorb from the film in the solution in order to reach again equilibrium. This diffusion is nevertheless slowed down by the presence of an electrostatic barrier at the film solution interface (Scheme 2). When the film is then put in contact with the polyanion solution, which is assumed not to diffuse in the film, the polyanionic chains adsorb on the surface of the film. This leads to a neutralization of the positive charges at the origin of the initial diffusion (see Figure 2). Hence the film/solution interface acquires a negative charge and the electrostatic barrier impeding the diffusion of the fraction of free polycationic chains from the film to the solution disappears. Hence the polycationic chains start to diffuse in the solution where they build up complexes with the available polyanions. Provided the formed complexes adhere to the film, the growth of the film continues up to the level where all the available polycationic reservoir has been used. If the structure of the film is homogeneous, and if the contact time with the polyanion containing solution is sufficient, the amount of polycationic chains diffusing out of the film should be proportional to the film thickness. Hence the increase in film thickness, due to polycation-polyanion complexation at the film/solution interface, should be proportional to the film thickness. This leads naturally to a film thickness increasing exponentially with the number of deposition steps.

Of course when the film thickness becomes important and when the contact time between the film and the solution is not increased accordingly, there is not enough time for the polycations close to the film/substrate interface to diffuse towards the film/solution interface where inter-polyelectrolyte complexation and film growth occur. Hence at a certain level of film growth, only a constant part of the film should be affected by diffusion of free chains out of the film, leading again to a linear growth as shown in Figure 4. Note that the slope of the linear regime corresponds to the value of the derivative of the film thickness versus the number of deposited "layer pairs" at the end of the exponential regime. The notion of "layer pair" is relative here, since the exponentially growing films are totally intermixed in opposition to their linearly growing counterparts in which some stratification and memory of the deposition process remains, as already noted previously. We hence prefer to speak about films produced in a "step-by-step" (SBS) manner to avoid the confusion the term "LBL films" could bring in the reader's mind.

More details about the mechanism of exponential film growth can be found in [44].

Even if the mechanism described above seems reasonable and is partially confirmed by means of CLSM experiments for films made with fluorescently labelled polyelectrolytes, some other explanations have been proposed in the literature [45]. In addition, the model based on the diffusion of chains through the whole film thickness relies on the fact that the films are homogeneous in the direction perpendicular to their average plane. There is plenty of experimental evidence that both the linearly as well as the exponentially growing films [46] have at least a 3-zone structure: the films have different properties at the film/substrate and film/solution interfaces than in their central zone. It is hence possible that the transition from the exponential to the linear growth regime (cf. Figure 4) may be associated to some internal rearrangement of the film leading to a progressive modification of the internal film structure with time. Some increase in the film elasticity (as probed by means of colloidal probe Atomic Force Microscopy) has indeed been found as a function of the storage time for $(PLL-HA)_n$ films [47].

The polydispersity of the employed polyelectrolytes also plays an important role in the occurrence of exponential growth [48]: the higher the polydispersity of the polyelectrolyte the higher the tendency for exponential growth.

The major difference in structure between the linearly and exponentially growing films is depicted in Scheme 3.

The adsorption-desorption regime, in which each adsorbed polyelectrolyte is desorbed upon contact with the solution containing the oppositely charged polyelectrolyte, can be viewed as a situation where the polycation-polyanion complexes do not adhere to the substrate.

The difference in growth regime allows also a change in the properties of the obtained films.

The fundamental interactions allowing the deposition of films produced in an SBS manner will be described. Focus will be given on PEM films made from oppositely charged polyelectrolytes because it is for this kind of films that most of the mechanistic investigations have been performed. This will allow to understand the fundamental differences between the three known growth regimes of PEM films.

3. Interactions and Driving Forces Allowing for the Deposition of Films in a Step-by-Step Manner

It is natural to think that the driving forces leading to PEM films is the electrostatic interaction between oppositely charged chains. However, electrostatic interactions between oppositely charged polyelectrolytes in solution as well as between a solubilised polyelectrolyte and an oppositely charged polyelectrolyte already adsorbed are of very peculiar nature [51]. Indeed there is not only an enthalpic contribution due to the interactions between point charges on the oppositely polyelectrolyte chains, but also an entropic contribution due to chain dehydration, conformational changes, and release of counter ions. This last contribution comes from the fact that the charges on the polyelectrolyte chain are surrounded by counter ions from the aqueous solution. These small ions have to be removed from the close vicinity of the polymer chain during the complexation or adsorption process which induces an increase in their degrees of freedom and hence in the entropy of the system. Usually the balance between enthalpic and entropic contributions changes with the salt concentration of the solution [52, 53]. At low salt concentration, enthalpic contributions dominate, whereas entropic contributions become predominant for an
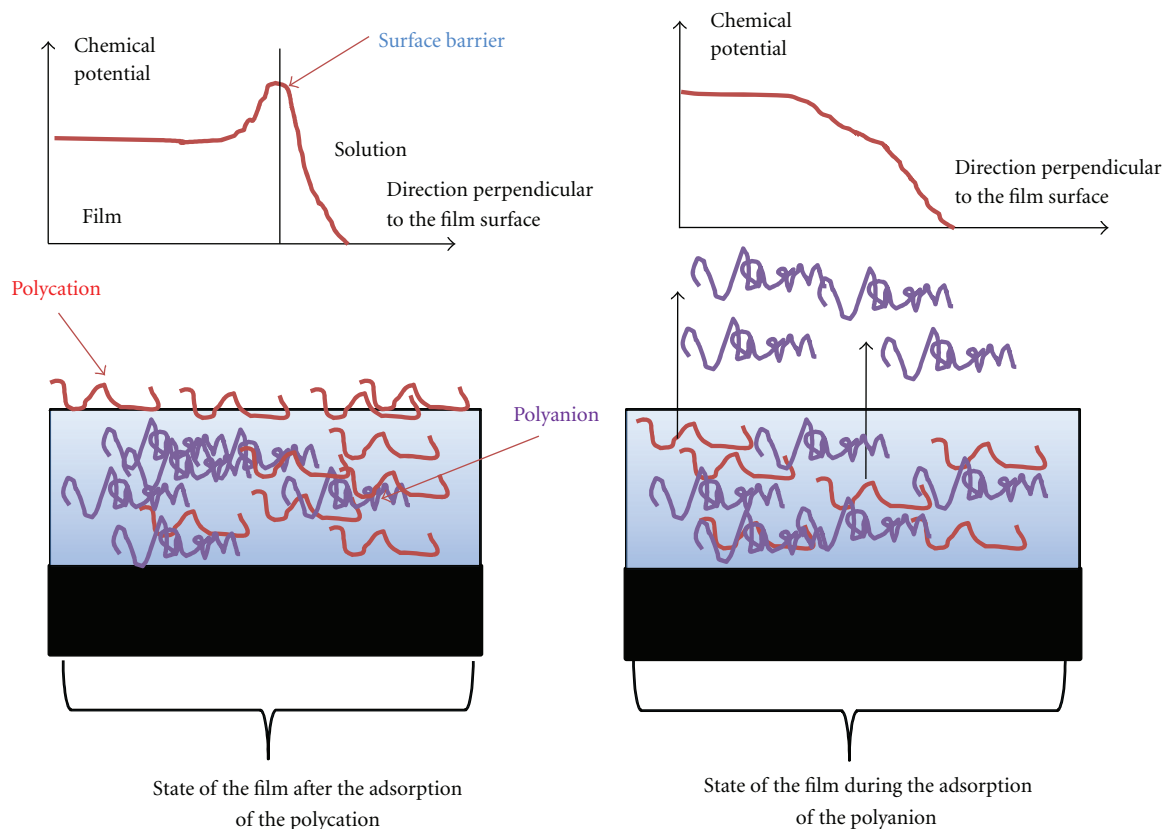
SCHEME 2: Representation of the energetic state of an exponentially growing PEM film in the direction perpendicular to the film plane for two different states of the film deposition sequence: after the deposition of the polycation (left column) and during the adsorption of the polyanion (right column). This scheme is inspired by the theory developed in [44].
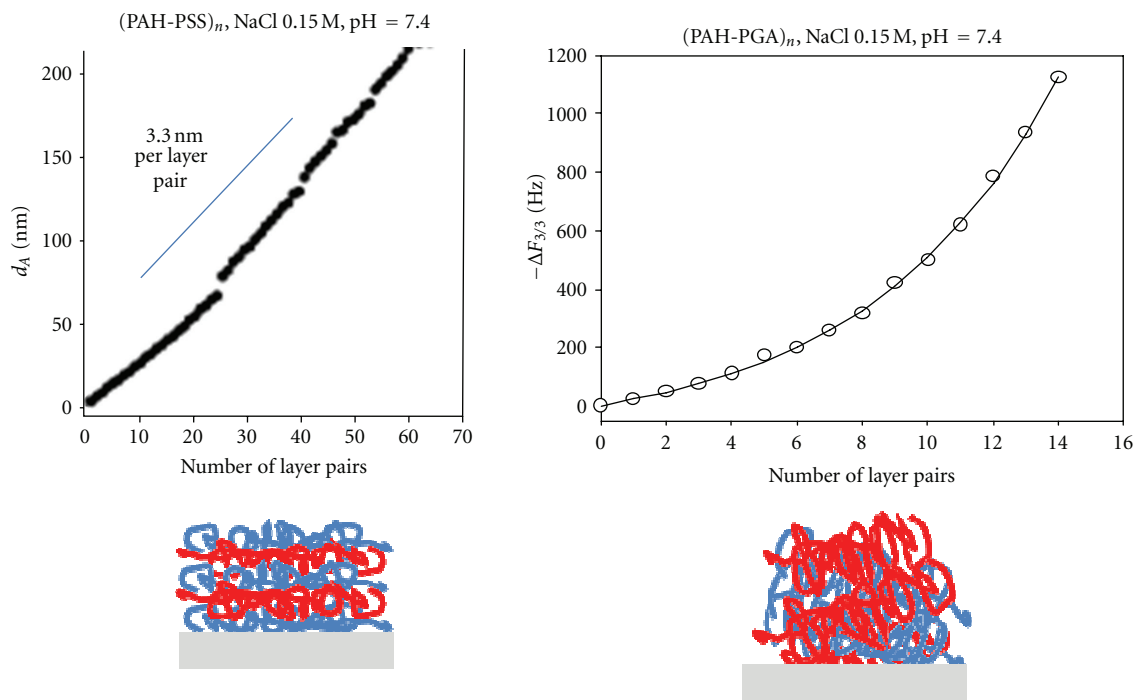
intermediate salt concentration. At higher salt concentrations, the screening of the electrostatic forces is so high that the formation of polyelectrolyte complexes and PEM films is totally hindered. The salt concentration at which the transition from an enthalpy-driven complexation to an entropy-driven one is dependent on the nature of the polyelectrolytes. Of course temperature plays a huge role in such processes where enthalpy-entropy compensation plays a role. It has been found that SBS films deposited from PAH and PSS (as in Figure 1) which display a linear growth at ambient temperature and in the presence of 1.0 M NaCl turn to exponential growth when the temperature is raised above $80°C$ [54]. Similarly at ambient temperature, the growth of the PEI-(PSS-PAH)$_n$ films turns to exponential when the concentration of the supporting electrolyte, NaCl, is increased [55]. These findings show that the nature of the film growth regime does not only depend on the nature of the used polyelectrolytes, but also on the interactions between them. Those can be modulated by external parameters like the temperature, the salt concentration as well as the addition of a cosolvent. This discussion shows that the nature of the growth regime of PEM films can be adjusted by playing on external parameters for a given combination of polyelectrolytes.

Recent research shows that there is a strong relationship between interpolyelectrolyte interactions in solution, leading or not to phase separation, and the possibility or not to obtain PEM films using a step-by-step deposition strategy [50, 56]. If one considers the intensity of the scattered light from a polycation-polyanion mixture in conditions where the amount of anionic sites matches the amount of cationic ones, that is, in conditions optimal for phase separation, as a function of the salt concentration, it appears that the obtained curve is almost homothetic to the PEM thickness evolution with the same polyelectrolytes. Indeed two different curve shapes have been observed: either a monotonous increase or the occurrence of a maximum (Figure 5).

In the case where the intensity of scattered light and the film thickness increase with the salt concentration in a monotonous manner, the film growth is pretty slow and mostly linear with the number of deposition steps. On the other hand, in the case where the intensity of scattered light and the thickness versus salt concentration display a maximum, the growth regime turns from linear at low salt concentration to exponential in the region of the maximum. At very low salt concentration the growth behavior of the film looks often zig-zag like, typical of an adsorption-desorption process [50].

Hence the outcome of PEM film deposition as well as a qualitative prediction of the growth regime can be predicted

$(PAH-PSS)_n$, NaCl 0.15 M, pH = 7.4

3.3 nm per layer pair

d_A (nm) vs Number of layer pairs

$(PAH-PGA)_n$, NaCl 0.15 M, pH = 7.4

$-\Delta F_{3/3}$ (Hz) vs Number of layer pairs

Scheme 3: Representation of the two most significant deposition regimes of PEM films (the adsorption-desorption regime [38] is not represented here because it leads to almost no film deposition). Note that the only difference between the two growth curves is the nature of the polyanion: the strong polyelectrolyte PSS (left column) being replaced by the weak PGA (right column). A representation of the chain packing in each kind of film is represented below the growth curves, the polycations and polyanions being represented in red and blue, respectively. The deposition of the $(PAH-PSS)_n$ and $(PAH-PGA)_n$ films has been investigated by means of optical waveguide lightmode spectroscopy and quartz crystal microbalance, respectively [49].

on the basis of interpolyelectrolyte *phase diagrams*. This is very helpful to help to speed up the design of SBS films in advance, that is, before their deposition.

4. Selected Properties of Films Produced in a SBS Manner

The linearly and exponentially growing films display rather clear cut different properties which make them interesting for a broad range of possible applications.

Usually the linearly growing films display "internal charge compensation," this means that, with exception to the film/substrate and film/solution interface, the amount of charges provided by the polycation exactly matches the amount of charges provided by the polyanion, meaning that the bulk of the film does not need to incorporate counter ions to ensure its electrical neutrality [57]. These films are nevertheless hydrated [58, 59] and display some porosity at the nanometer scale. This porosity has been quantified by means of NMR cryoporometry in the case of $(PAH-PSS)_n$ films [60]. In quite good agreement with the cryoporometry experiments, the same films display some permeability for ions having an ionic radius of the order of one nanometer [61]. $(PSS-PAH)_n$ [62] and $(PDADMAC-PSS)_n$ films (where PDADMAC stands for poly(diallyldimethyl aminomethane)) become however impermeable to multivalent ions like hexacyanoferrate when the number of "layer pairs" is typically higher than 5.

Usually the linearly growing films behave like elastic solids, with an elastic modulus progressively decreasing when the salt concentration of the solution in contact with the film increases [63, 64]. At the same time, the ion doping [65] of the film increases and the stratification of the layers progressively disappears [66], making such films close to those obtained during an exponential growth regime.

In opposition to linearly growing films, exponentially growing ones are highly hydrated (up to 80–90% of water in volume fraction) [67]. They are extrinsically charge-compensated which allows them to behave as ion exchange membranes [68, 69]. From a mechanical point of view they are close to liquids as has been shown by piezo-rheometry [70].

A global view of the film properties depending on the growth regime is represented in Scheme 4.

The properties of PEM films can hence be changed which allows a great versatility in their applications as will be shown in the next paragraph.

5. Selected Applications of Films Produced in a SBS Manner

In the field of materials science, PEM films have been used to develop electronic devices like diodes (films incorporation
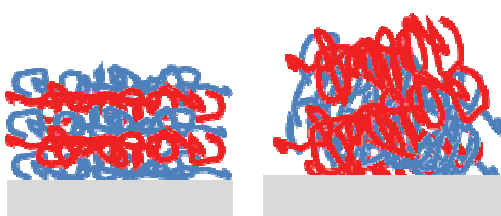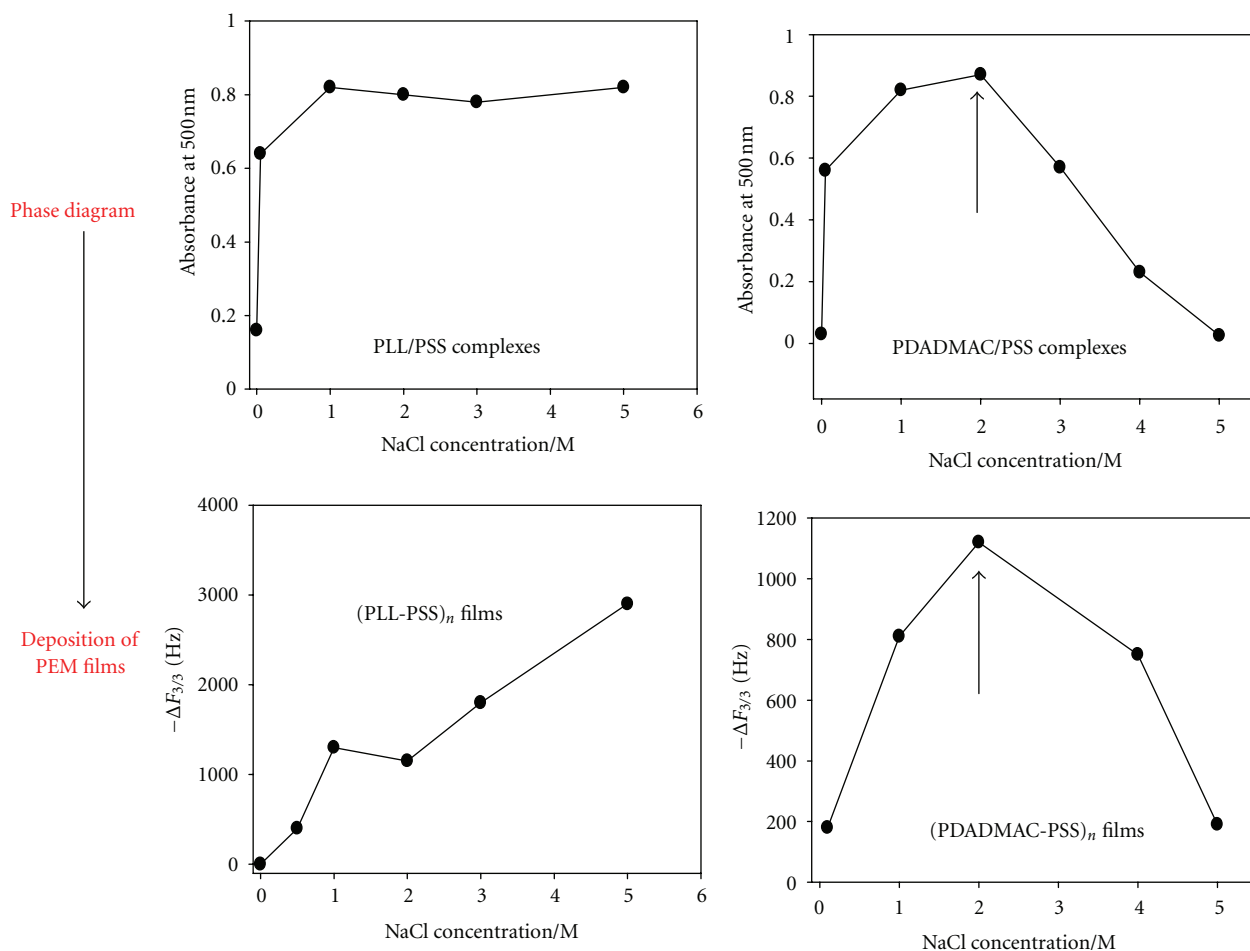
FIGURE 5: Relationship between polyelectrolyte complexation in solution (upper row: the interaction between polyelectrolytes in a 1 : 1 stochiometry, on the basis of monomer units, is quantified by means of light scattering) and PEM film deposition (lower row: the film deposition is quantified by means of quartz crystal microbalance with dissipation monitoring from polyelectrolyte solutions at the same concentration as that used for the phase diagrams). Two different combinations of oppositely charged polyelectrolytes are represented: poly(L-lysine hydrobromide)/poly(sodium 4-styrene sulfonate) (PLL/PSS) and poly(diallyldimethyl ammonium chloride)/poly(sodium 4-styrene sulfonate) (PDADMAC/PSS) adapted from [50].

clays during the layering process) [71], as anticorrosion coatings [72], as antireflective [73] (with self cleaning applications) and superhydrophobic coatings [74]. Recently, PEM films incorporating clays or other nanoparticles have been described as excellent fire retardants on the surface of polymer films [75]. More and more PEM films are used as membranes separating the anode and the cathode in fuel cells [76].

PEM films can also be used as sensing matrixes atop an electrochemical [77] or optical transducers. Enzymes can be encapsulated in such films and remain active for longer time durations than in solution [78]. Many bioapplications of PEM films are reported and have been reviewed [79, 80]. Of particular interest is the finding that a change in the mechanical properties allows to fine tune not only the cellular adhesion [81], but also the level of nuclear expression of the adherent cells [82].

6. Conclusions and Perspectives

Films produced in a step-by-step manner can be deposited on a plethora of different substrates in an robotized manner using either alternated dipcoating, spray deposition or spin coating. The fact that different kinds of polymers, interacting either through electrostatic interactions, hydrogen bonding, or other kinds of weak or covalent interactions, offers a very versatile surface functionalization method. One fascinating aspect of films made from polyelectrolytes, PEM films, is the very easy deposition method which strongly contrasts with the complexity of the underlying mechanisms. There remain many fundamental investigations to be performed to better understand the relationship between the structure of the monomer units, the molecular mass and its distribution, as well as the external parameters (nature of the substrate, nature of the used electrolyte [38, 83]) on the deposition

	Linear growth	Exponential growth
Water content	Low (20–30% in volume fraction)	High (60–80% in volume fraction)
Presence of ions from the electrolyte	Very small (intrinsic charge compensation)	Usually high (extrinsic charge compensation)
Permeabiltity	For water, small ions (depending on their size and valency) and small molecules	For water, large ions (depending on the sign of their charge and valency), large molecules and even for colloids
Mechanical properties	Elastic solids	Liquids or weak gels

SCHEME 4: Influence of the growth regime and of the structure of PEM films on their properties.

kinetics and the dynamic responsiveness of the films to external stimulus. Exchange processes between polyelectrolytes in the films and in the solution may also occur [84–86] with the consequence of a pronounced change in film composition and morphology.

Even more important, for future large scale applications, is to reach homogeneity of PEM films on large scale substrates (typically in the square meter range).

References

[1] A. R. Bishop and R. G. Nuzzo, "Self-assembled monolayers: recent developments and applications," *Current Opinion in Colloid & Interface Science*, vol. 1, no. 1, pp. 127–136, 1996.

[2] R. K. Iler, "Multilayers of colloidal particles," *Journal of Colloid & Interface Science*, vol. 21, no. 6, pp. 569–594, 1966.

[3] G. Decher, J. D. Hong, and 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*, vol. 210-211, no. 2, pp. 831–835, 1992.

[4] G. Decher and J. D. Hong, "Buildup of ultrathin multilayer films by a self-assembly process: II. Consecutive adsorption of anionic and cationic bipolar amphiphiles and polyelectrolytes on charged surfaces," *Berichte der Bunsengesellschaft für Physicalischen Chemie*, vol. 95, no. 11, pp. 1430–1434, 1991.

[5] G. Schneider and G. Decher, "From functional core/shell nanoparticles prepared via layer-by-layer deposition to empty nanospheres," *Nano Letters*, vol. 4, no. 10, pp. 1833–1839, 2004.

[6] D. V. Volodkin, N. I. Larionova, and G. B. Sukhorukov, "Protein encapsulation via porous CaCO₃ microparticles templating," *Biomacromolecules*, vol. 5, no. 5, pp. 1962–1972, 2004.

[7] K. Ariga, J. P. Hill, and Q. Ji, "Layer-by-layer assembly as a versatile bottom-up nanofabrication technique for exploratory research and realistic application," *Physical Chemistry Chemical Physics*, vol. 9, no. 19, pp. 2319–2340, 2007.

[8] P. Lavalle, J. C. Voegel, D. Vautier, B. Senger, P. Schaaf, and V. Ball, "Dynamic aspects of films prepared by a sequential deposition of species: perspectives for smart and responsive materials," *Advanced Materials*, vol. 23, no. 10, pp. 1191–1221, 2011.

[9] W. B. Stockton and M. F. Rubner, "Molecular-level processing of conjugated polymers. 4. Layer-by-layer manipulation of polyaniline via hydrogen-bonding interactions," *Macromolecules*, vol. 30, no. 9, pp. 2717–2725, 1997.

[10] A. Laschewsky, E. Wischerhoff, S. Denzinger, H. Ringsdorf, A. Delcorte, and P. Bertrand, "Molecular recognition by hydrogen bonding in polyelectrolyte multilayers," *Chemistry A*, vol. 3, no. 1, pp. 34–38, 1997.

[11] S. A. Sukhishvili and S. Granick, "Layered, erasable, ultrathin polymer films," *Journal of the American Chemical Society*, vol. 122, no. 39, pp. 9550–9551, 2000.

[12] E. Kharlampieva, V. Koziovskaya, and S. A. Sukhishvili, "Layer-by-layer hydrogen-bonded polymer films: from fundamentals to applications," *Advanced Materials*, vol. 21, no. 30, pp. 3053–3065, 2009.

[13] T. Serizawa, K. I. Hamada, T. Kitayama, N. Fujimoto, K. Hatada, and M. Akashi, "Stepwise stereocomplex assembly of stereoregular poly(methyl methacrylate)s on a substrate," *Journal of the American Chemical Society*, vol. 122, no. 9, pp. 1891–1899, 2000.

[14] A. van der Heyden, M. Wilczewski, P. Labbé, and R. Auzély, "Multilayer films based on host-guest interactions between biocompatible polymers," *Chemical Communications*, no. 30, pp. 3220–3222, 2006.

[15] Y. Shimazaki, R. Nakamura, S. Ito, and M. Yamamoto, "Molecular weight dependence of alternate adsorption through

charge-transfer interaction," *Langmuir*, vol. 17, no. 3, pp. 953–956, 2001.

[16] T. Cassier, K. Lowack, and G. Decher, "Layer-by-layer assembled protein/polymer hybrid films: nanoconstruction via specific recognition," *Supramolecular Science*, vol. 5, no. 3-4, pp. 309–315, 1998.

[17] J. Zhu, B. S. Shim, M. Di Prima, and N. A. Kotov, "Transparent conductors from carbon nanotubes LBL-assembled with polymer dopant with π-π electron transfer," *Journal of the American Chemical Society*, vol. 133, no. 19, pp. 7450–7460, 2011.

[18] G. K. Such, J. F. Quinn, A. Quinn, E. Tjipto, and F. Caruso, "Assembly of ultrathin polymer multilayer films by click chemistry," *Journal of the American Chemical Society*, vol. 128, no. 29, pp. 9318–9319, 2006.

[19] D. Lee, M. F. Rubner, and R. E. Cohen, "All-nanoparticle thin-film coatings," *Nano Letters*, vol. 6, no. 10, pp. 2305–2312, 2006.

[20] H. Bungenberg de Jong, "Crystallisation-coacervation-flocculation," in *Colloid Science II*, H. R. Kruyt, Ed., Elsevier, 1952.

[21] B. S. Shim, P. Podsiadlo, D. G. Lilly et al., "Nanostructured thin films made by dewetting method of layer-by-layer assembly," *Nano Letters*, vol. 7, no. 11, pp. 3266–3273, 2007.

[22] J. B. Schlenoff, S. T. Dubas, and T. Farhat, "Sprayed polyelectrolyte multilayers," *Langmuir*, vol. 16, no. 26, pp. 9968–9969, 2000.

[23] A. Izquierdo, S. S. Ono, J.-C. Voegel, P. Schaaf, and G. Decher, "Dipping versus spraying: exploring the deposition conditions for speeding up layer-by-layer assembly," *Langmuir*, vol. 21, no. 16, pp. 7558–7567, 2005.

[24] P. A. Chiarelli, M. S. Johal, D. J. Holmes, J. L. Casson, J. M. Robinson, and H. L. Wang, "Polyelectrolyte spin-assembly," *Langmuir*, vol. 18, no. 1, pp. 168–173, 2002.

[25] C. H. Porcel, A. Izquierdo, V. Ball, G. Decher, J.-C. Voegel, and P. Schaaf, "Ultrathin coatings and (poly(glutamic acid)/polyallylamine) films deposited by continuous and simultaneous spraying," *Langmuir*, vol. 21, no. 2, pp. 800–802, 2005.

[26] J. Seo, J. L. Lutkenhaus, J. Kim, P. T. Hammond, and K. Char, "Effect of the layer-by-layer (LbL) deposition method on the surface morphology and wetting behavior of hydrophobically modified PEO and PAA LbL films," *Langmuir*, vol. 24, no. 15, pp. 7995–8000, 2008.

[27] O. Félix, Z. Zheng, F. Cousin, and G. Decher, "Are sprayed LbL-films stratified? A first assessment of the nanostructure of spray-assembled multilayers by neutron reflectometry," *Comptes Rendus Chimie*, vol. 12, no. 1-2, pp. 225–234, 2009.

[28] J. Ruths, F. Essler, G. Decher, and 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*, vol. 16, no. 23, pp. 8871–8878, 2000.

[29] G. Ladam, P. Schaad, J.-C. Voegel, P. Schaaf, G. Decher, and F. J. G. Cuisinier, "In situ determination of the structural properties of initially deposited polyelectrolyte multilayers," *Langmuir*, vol. 16, no. 3, pp. 1249–1255, 2000.

[30] N. G. Hoogeveen, M. A. C. Stuart, and G. J. Fleer, "Formation and stability of multilayers of polyelectrolytes," *Langmuir*, vol. 12, no. 15, pp. 3675–3681, 1996.

[31] F. Caruso, E. Donath, and H. Möhwald, "Influence of polyelectrolyte multilayer coatings on Förster resonance energy transfer between 6-carboxyfluorescein and rhodamine B-labeled particles in aqueous solution," *Journal of Physical Chemistry B*, vol. 102, no. 11, pp. 2011–2016, 1998.

[32] W. Chen and T. J. McCarthy, "Layer-by-layer deposition: a tool for polymer surface modification," *Macromolecules*, vol. 30, no. 1, pp. 78–86, 1997.

[33] D. Yoo, S. S. Shiratori, and M. F. Rubner, "Controlling bilayer composition and surface wettability of sequentially adsorbed multilayers of weak polyelectrolytes," *Macromolecules*, vol. 31, no. 13, pp. 4309–4318, 1998.

[34] N. Cini, T. Tulun, G. Decher, and V. Ball, "Step-by-step assembly of self-patterning polyelectrolyte films violating (almost) all rules of layer-by-layer deposition," *Journal of the American Chemical Society*, vol. 132, no. 24, pp. 8264–8265, 2010.

[35] D. L. Elbert, C. B. Herbert, and J. A. Hubbell, "Thin polymer layers formed by polyelectrolyte multilayer techniques on biological surfaces," *Langmuir*, vol. 15, no. 16, pp. 5355–5362, 1999.

[36] C. Picart, Ph. Lavalle, P. Hubert et al., "Buildup mechanism for poly(L-lysine)/hyaluronic acid films onto a solid surface," *Langmuir*, vol. 17, no. 23, pp. 7414–7424, 2001.

[37] C. Picart, J. Mutterer, L. Richert et al., "Molecular basis for the explanation of the exponential growth of polyelectrolyte multilayers," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 99, no. 20, pp. 12531–12535, 2002.

[38] D. Kovacevic, S. van der Burgh, A. de Keizer, and M. A. C. Stuart, "Specific ionic effects on weak polyelectrolyte multilayer formation," *Journal of Physical Chemistry B*, vol. 107, no. 32, pp. 7998–8002, 2003.

[39] J. Schmitt, T. Grünewald, G. Decher, P. S. Pershan, K. Kjaer, and M. Lösche, "Internal structure of layer-by-layer adsorbed polyelectrolyte films: a neutron and X-ray reflectivity study," *Macromolecules*, vol. 26, no. 25, pp. 7058–7063, 1993.

[40] G. Decher, "Fuzzy nanoassemblies: toward layered polymeric multicomposites," *Science*, vol. 277, no. 5330, pp. 1232–1237, 1997.

[41] M. Michel, A. Izquierdo, G. Decher, J.-C. Voegel, P. Schaaf, and V. Ball, "Layer by layer self-assembled polyelectrolyte multilayers with embedded phospholipid vesicles obtained by spraying: integrity of the vesicles," *Langmuir*, vol. 21, no. 17, pp. 7854–7859, 2005.

[42] C. Picart, J. Mutterer, Y. Arntz, J.-C. Voegel, P. Schaaf, and B. Senger, "Application of fluorescence recovery after photobleaching to diffusion of a polyelectrolyte in a multilayer film," *Microscopy Research and Technique*, vol. 66, no. 1, pp. 43–57, 2005.

[43] L. Jourdainne, S. Lecuyer, Y. Arntz et al., "Dynamics of poly(L-lysine) in hyaluronic acid/poly(L-lysine) multilayer films studied by fluorescence recovery after pattern photobleaching," *Langmuir*, vol. 24, no. 15, pp. 7842–7847, 2008.

[44] Ph. Lavalle, C. Picart, J. Mutterer et al., "Modeling the buildup of polyelectrolyte multilayer films having exponential growth," *Journal of Physical Chemistry B*, vol. 108, no. 2, pp. 635–648, 2004.

[45] N. Hoda and R. G. Larson, "Modeling the buildup of exponentially growing polyelectrolyte multilayer films," *Journal of Physical Chemistry B*, vol. 113, no. 13, pp. 4232–4241, 2009.

[46] C. Betscha and V. Ball, "Large distribution in the Donnan potential of hexacyanoferrate anions permeating in and partially dissolving (PAH-HA)$_n$ polyelectrolyte multilayer films," *Soft Matter*, vol. 7, no. 5, pp. 1819–1829, 2011.

[47] L. Richert, A. J. Engler, D. E. Discher, and C. Picart, "Elasticity of native and cross-linked polyelectrolyte multilayer films," *Biomacromolecules*, vol. 5, no. 5, pp. 1908–1916, 2004.

[48] B. Sun, C. M. Jewell, N. J. Fredin, and D. M. Lynn, "Assembly of multilayered films using well-defined, end-labeled poly(acrylic acid): influence of molecular weight on exponential growth in a synthetic weak polyelectrolyte system," *Langmuir*, vol. 23, no. 16, pp. 8452–8459, 2007.

[49] F. Boulmedais, V. Ball, P. Schwinté, B. Frisch, P. Schaaf, and J.-C. Voegel, "Buildup of exponentially growing multilayer polypeptide films with internal secondary structure," *Langmuir*, vol. 19, no. 2, pp. 440–445, 2003.

[50] H. Mjahed, J.-C. Voegel, A. Chassepot et al., "Turbidity diagrams of polyanion/polycation complexes in solution as a potential tool to predict the occurrence of polyelectrolyte multilayer deposition," *Journal of Colloid & Interface Science*, vol. 346, no. 1, pp. 163–171, 2010.

[51] A. S. Michaels, "Polyelectrolyte complexes," *Industrial and Engineering Chemistry*, vol. 57, no. 10, pp. 32–40, 1965.

[52] N. Laugel, C. Betscha, M. Winterhalter, J.-C. Voegel, P. Schaaf, and V. Ball, "Relationship between the growth regime of polyelectrolyte multilayers and the polyanion/polycation complexation enthalpy," *Journal of Physical Chemistry B*, vol. 110, no. 39, pp. 19443–19449, 2006.

[53] J. van der Gucht, E. Spruijt, M. Lemmers, and M. A. C. Stuart, "Polyelectrolyte complexes: bulk phases and colloidal systems," *Journal of Colloid & Interface Science*, vol. 361, no. 2, pp. 407–422, 2011.

[54] M. Salomäki, I. A. Vinokurov, and J. Kankare, "Effect of temperature on the buildup of polyelectrolyte multilayers," *Langmuir*, vol. 21, no. 24, pp. 11232–11240, 2005.

[55] C. Picart, C. Gergely, Y. Arntz et al., "Measurement of film thickness up to several hundreds of nanometers using optical waveguide lightmode spectroscopy," *Biosensors and Bioelectronics*, vol. 20, no. 3, pp. 553–561, 2004.

[56] V. Izumrudov, E. Kharlampieva, and S. A. Sukhishvili, "Salt-induced multilayer growth: correlation with phase separation in solution," *Macromolecules*, vol. 37, no. 22, pp. 8400–8406, 2004.

[57] J. B. Schlenoff, H. Ly, and M. Li, "Charge and mass balance in polyelectrolyte multilayers," *Journal of the American Chemical Society*, vol. 120, no. 30, pp. 7626–7634, 1998.

[58] M. Schönhoff, V. Ball, A. R. Bausch et al., "Hydration and internal properties of polyelectrolyte multilayers," *Colloids and Surfaces A*, vol. 303, no. 1-2, pp. 14–29, 2007.

[59] J. E. Wong, F. Rehfeldt, P. Hänni, M. Tanaka, and R. V. Klitzing, "Swelling behavior of polyelectrolyte multilayers in saturated water vapor," *Macromolecules*, vol. 37, no. 19, pp. 7285–7289, 2004.

[60] F. Vaca Chavez and M. Schönhoff, "Pore size distributions in polyelectrolyte multilayers determined by nuclear magnetic resonance cryoporometry," *Journal of Chemical Physics*, vol. 126, no. 10, Article ID 104705, 7 pages, 2007.

[61] X. Liu and M. L. Bruening, "Size-selective transport of uncharged solutes through multilayer polyelectrolyte membranes," *Chemistry of Materials*, vol. 16, no. 2, pp. 351–357, 2004.

[62] S. Han and B. Lindholm-Sethson, "Electrochemistry at ultrathin polyelectrolyte films self-assembled at planar gold electrodes," *Electrochimica Acta*, vol. 45, no. 6, pp. 845–853, 1999.

[63] J. Heuvingh, M. Zappa, and A. Fery, "Salt softening of polyelectrolyte multilayer capsules," *Langmuir*, vol. 21, no. 7, pp. 3165–3171, 2005.

[64] J. A. Jaber and J. B. Schlenoff, "Mechanical properties of reversibly cross-linked ultrathin polyelectrolyte complexes," *Journal of the American Chemical Society*, vol. 128, no. 9, pp. 2940–2947, 2006.

[65] T. R. Farhat and J. B. Schlenoff, "Doping-controlled ion diffusion in polyelectrolyte multilayers: mass transport in reluctant exchangers," *Journal of the American Chemical Society*, vol. 125, no. 15, pp. 4627–4636, 2003.

[66] H. W. Jomaa and J. B. Schlenoff, "Salt-induced polyelectrolyte interdiffusion in multilayered films: a neutron reflectivity study," *Macromolecules*, vol. 38, no. 20, pp. 8473–8480, 2005.

[67] T. J. Halthur and U. M. Elofsson, "Multilayers of charged polypeptides as studied by in situ ellipsometry and quartz crystal microbalance with dissipation," *Langmuir*, vol. 20, no. 5, pp. 1739–1745, 2004.

[68] E. Hübsch, G. Fleith, J. Fatisson et al., "Multivalent ion/polyelectrolyte exchange processes in exponentially growing multilayers," *Langmuir*, vol. 21, no. 8, pp. 3664–3669, 2005.

[69] B. Wang and J.-I. Anzai, "Redox reactions of ferricyanide ions in layer-by-layer deposited polysaccharide films: a significant effect of the type of polycation in the films," *Langmuir*, vol. 23, no. 13, pp. 7378–7384, 2007.

[70] D. Collin, Ph. Lavalle, J. Méndez-Garza, J.-C. Voegel, P. Schaaf, and Ph. Martinoty, "Mechanical properties of cross-linked hyaluronic acid/poly-(L-lysine) multilayer films," *Macromolecules*, vol. 37, no. 26, pp. 10195–10198, 2004.

[71] M. Eckle and G. Decher, "Tuning the performance of layer-by-layer assembled organic light emitting diodes by controlling the position of isolating clay barrier sheets," *Nano Letters*, vol. 1, no. 1, pp. 45–49, 2001.

[72] T. R. Farhat and J. B. Schlenoff, "Corrosion control using polyelectrolyte multilayers," *Electrochemical and Solid-State Letters*, vol. 5, no. 4, pp. B13–B15, 2002.

[73] H. Shimomura, Z. Gemici, R. E. Cohen, and M. F. Rubner, "Layer-by-layer-assembled high-performance broadband antireflection coatings," *ACS Applied Materials and Interfaces*, vol. 2, no. 3, pp. 813–820, 2010.

[74] L. Zhai, F. Ç. Cebeci, R. E. Cohen, and M. F. Rubner, "Stable superhydrophobic coatings from polyelectrolyte multilayers," *Nano Letters*, vol. 4, no. 7, pp. 1349–1353, 2004.

[75] Y.-C. Li, J. Schulz, S. Mannen et al., "Flame retardant behavior of polyelectrolyte-clay thin film assemblies on cotton fabric," *ACS Nano*, vol. 4, no. 6, pp. 3325–3337, 2010.

[76] M. Michel, A. Taylor, R. Sekol et al., "High-performance nanostructured membrane electrode assemblies for fuel cells made by layer-by-layer assembly of carbon nanocolloids," *Advanced Materials*, vol. 19, no. 22, pp. 3859–3864, 2007.

[77] B. Wang, X. Du, M. Wang, W. Gong, and J.-I. Anzai, "A facile preparation of H_2O_2 sensors using layer-by-layer deposited thin films composed of poly(ethyleneimine) and carboxymethyl cellulose as matrices for immobilizing hemin," *Electroanalysis*, vol. 20, no. 9, pp. 1028–1031, 2008.

[78] L. Derbal, H. Lesot, J.-C. Voegel, and V. Ball, "Incorporation of alkaline phosphatase into layer-by-layer polyelectrolyte films on the surface of affi-gel heparin beads: physicochemical characterization and evaluation of the enzyme stability," *Biomacromolecules*, vol. 4, no. 5, pp. 1255–1263, 2003.

[79] Z. Tang, Y. Wang, P. Podsiadlo, and N. A. Kotov, "Biomedical applications of layer-by-layer assembly: from biomimetics to tissue engineering," *Advanced Materials*, vol. 18, no. 24, pp. 3203–3224, 2006.

[80] T. Boudou, T. Crouzier, K. Ren, G. Blin, and C. Picart, "Multiple functionalities of polyelectrolyte multilayer films:

new biomedical applications," *Advanced Materials*, vol. 22, no. 4, pp. 441–467, 2010.

[81] L. Richert, F. Boulmedais, Ph. Lavalle et al., "Improvement of stability and cell adhesion properties of polyelectrolyte multilayer films by chemical cross-linking," *Biomacromolecules*, vol. 5, no. 2, pp. 284–294, 2004.

[82] L. Kocgozlu, Ph. Lavalle, G. Koenig et al., "Selective and uncoupled role of substrate elasticity in the regulation of replication and transcription in epithelial cells," *Journal of Cell Science*, vol. 123, no. 1, pp. 29–39, 2010.

[83] V. Ball, J.-C. Voegel, and P. Schaaf, "Effect of thiocyanate counterion condensation on poly(allylamine hydrochloride) chains on the buildup and permeability of polystyrenesulfonate/ polyallylamine polyelectrolyte multilayers," *Langmuir*, vol. 21, no. 9, pp. 4129–4137, 2005.

[84] H. W. Jomaa and J. B. Schlenoff, "Accelerated exchange in polyelectrolyte multilayers by "catalytic" polyvalent ion pairing," *Langmuir*, vol. 21, no. 18, pp. 8081–8084, 2005.

[85] V. Ball, E. Hübsch, R. Schweiss, J.-C. Voegel, P. Schaaf, and W. Knoll, "Interactions between multivalent ions and exponentially growing multilayers: dissolution and exchange processes," *Langmuir*, vol. 21, no. 18, pp. 8526–8531, 2005.

[86] V. Ball, A. Laachachi, V. Toniazzo, and D. Ruch, "Influence of the nature of the polycation on the adsorption kinetics and on exchange processes in polyelectrolyte multilayer films," *Journal of Colloid & Interface Science*, vol. 366, no. 1, pp. 96–104, 2012.