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TOPICAL REVIEW

Layered polyelectrolyte complexes: physics of formation and molecular properties

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Abstract

Multilayers of charged polymers can be formed by the alternating adsorption of polyanions and polycations. By this so-called layer-by-layer self-assembly method, planar surfaces or colloidal templates can be coated. This method is reviewed here with respect to the basic physical principles governing multilayer formation. Particular emphasis is put on the adsorption process of a single polyelectrolyte layer to a multilayer surface as the process controlling the charge complexation and the local molecular structure. Then, the implications for the properties of the multilayer assembly are discussed. In particular, molecular properties such as the internal stoichiometry, the local interactions, and the conformation on a molecular scale are reviewed.

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Table of symbols and abbreviations

a	monomer length
ATR	attenuated total reflection
B	length of chains in blob conformation
c_{pol}, c_{pa}	concentration of polymer, or particles, respectively
c_{salt}	salt concentration
c_{ion}	ion concentration
δ	thickness of adsorbed layer
D_{pol}	polymer diffusion coefficient
DQF	double quantum filter
2D	two-dimensional
e	elementary charge
ε	dielectric constant
f	fraction of charged monomers on a chain
F	number of carbon atoms per charge on the monomer
FTIR	Fourier transform infrared
g	number of monomers per blob
ΔG_{sa}	Gibbs free energy of layer formation
IR	infrared
k_{ads}	rate of polymer adsorption onto a particle
κ	inverse Debye screening length
k_{B}	Boltzmann constant
l_{B}	Bjerrum length
l_0	persistence length of an uncharged chain
l_τ	persistence length of a charged chain
λ_{D}	Debye screening length
M_{w}	molecular weight
MAS	magic angle spinning
n	number of single polyion layers in a multilayer assembly

N	number of bilayers in a multilayer assembly
NMR	nuclear magnetic resonance
PAA	poly(acrylic acid)
PAMA	poly((dimethylamino)ethyl methacrylate)
PAH	poly(allylamine hydrochloride)
PDADMAC	poly(diallyl dimethyl-ammonium chloride)
PEMs	polyelectrolyte multilayers
PGA	poly(L-glutamic acid)
PLL	poly(L-lysine)
PMA	poly(methacrylic acid)
PSS	poly(styrene sulfonate)
PVP	poly(vinyl pyridine)
ρ_C	number of ion pairs per carbon
R_{pa}	particle radius
R_H	hydrodynamic radius of a polymer chain
R_g	radius of gyration of a polymer chain
R_0	end-to-end distance of a chain
R_2	transverse spin relaxation rate
R_{2sp}	specific transverse spin relaxation rate
σ	surface charge density
SHG	second harmonic generation
τ	charge density per unit length along a chain
ξ_{el}	blob diameter
ζ	zeta-potential

1. Introduction to developments in polyelectrolyte multilayer research

The field of nanostructured material formation is progressing rapidly, and a number of novel possibilities arise from employing self-assembly processes of polymers: by involving electrostatic interactions, multilayered materials with unique properties can be built. Hong and Decher first proved the concept, i.e. the alternating exposure of a charged substrate to solutions of positive or negative polyelectrolytes [1]. Provided that each adsorption step leads to charge inversion of the surface, the subsequent deposition finally results in a layered complex, stabilized by strong electrostatic forces, so-called self-assembled polyelectrolyte multilayers (PEMs). Since the electrostatic interactions are a very general principle, the process is very versatile with respect to the incorporation of different charged compounds or nanoobjects. As building blocks, for example, inorganic nanoparticles such as gold colloids [2], functional polymers such as temperature-sensitive compounds [3, 4], orientable chromophores [5, 6], charged biopolymers such as DNA [7, 8], and mesogenic units inducing local order [9] have been employed. Further work involves the deposition of proteins into multilayers [10–12]. An overview of the recent achievements of the preparation has already been given in other reviews [13–16].

The electrostatic build-up mechanism can even be combined with other processes, such as Langmuir–Blodgett transfer [17] or specific binding [18]. All of these developments open wide possibilities for tailored layer design, with very specific properties and functionalities. As applications of planar PEMs, for example, sensor materials, functional coatings, and selective membranes are discussed and explored.

This principle of layer formation has not only been applied to achieve adsorption onto planar substrates but has even been applied to colloidal particles [19], a development which had a major impact on the field. The use of colloidal surfaces is particularly attractive, since on the one hand, the formation of coated particles with the subsequent removal of the particle core has led to new hollow shell materials, which are themselves promising structures for future applications [20]. On the other hand, coated colloids can make typical volume techniques applicable to two-dimensional layer systems and thus broaden the range of accessible experimental parameters. For example, NMR and calorimetric methods became available to multilayer studies of thin films by employing colloidal templates [21–25].

Similar to planar polyelectrolyte multilayers, a large variability of possible building blocks was introduced into multilayers on colloids, for example employing biopolymers [26], inorganic nanoparticles [27], or multivalent ions [28]. The development of very stable, hollow polymeric shell structures after core removal by chemical decomposition led to the design of new types of nanostructures with a large application potential [20]. Hollow, thin-walled microcapsules have attracted particular interest in encapsulation applications, for example in drug delivery [29], or as microreactors, since the capsule interior can provide chemical conditions different from free solution as for example exploited in polymer synthesis in the interior [30]. In most applications, the permeability of the capsule wall is a crucial parameter, and applications are exploiting the semi-permeable nature of the wall, which can even be tuned by external conditions. While small molecular species can penetrate the shell, they are impermeable for larger molecular weight compounds [20]. Furthermore, applications in nonlinear optics such as photonic crystals, or in catalysis, are currently being explored. A review including these recent developments has recently appeared [16].

All potential applications require a basic understanding of the structure and its control in the process of layer formation, in order to tailor specific properties. There is thus a demand for further fundamental studies and for a basic physical understanding. Specific properties of PEMs, which are of fundamental physical interest, include the fact that PEMs form two-dimensionally stratified layers, which grow step by step into the third dimension. This leads to a behaviour being dominated by internal interfaces, and differing from the corresponding volume material properties. The amorphous nature of PEMs is another typical feature: while the properties of ordered organic monomolecular layers such as liquid crystals or amphiphiles can easily be dominated by the amount and nature of a few defects, in disordered systems the overall amorphous nature not only determines their properties, but also makes the materials less sensitive to details of the preparation process.

A number of external parameters, which can be varied during the deposition process, are known to influence the resulting layer structure. These are the salt content of the deposition solutions, the polyion concentration, the charge density of the polyions (either varied by charge dilution in copolymers or as a result of the pH in weak polyion solutions), the polyion rigidity and the molecular weight.

In the early days of PEM studies, they have mainly been characterized by structural parameters such as the multilayer thickness, for example to investigate the dependence of layer thickness on preparation conditions. Other structural problems were the degree of interpenetration of successive layers, the roughness and the surface coverage. In particular, x-ray and neutron reflectivity were very successful in investigating aspects of layer growth and internal entanglements [31–33]. These mesoscopic structural aspects of PEMs are nowadays rather well understood, and current studies enlighten the picture on a local molecular scale. Of particular interest today are permeabilities of planar layers or hollow capsules with respect to small ions, solvents or macromolecules, as they are crucial for most applications. Fundamental

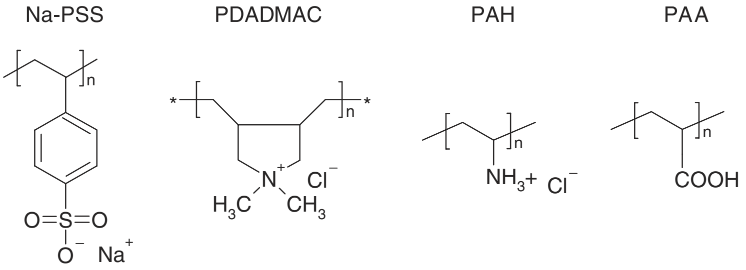

Figure 1. Polyelectrolytes employed for the self-assembly of multilayers.

work has further addressed questions of the role of secondary interactions, and the stability of weak polyelectrolyte assemblies. A problem of major importance is the internal composition, i.e. the polyanion/polycation stoichiometry and the presence or absence of counterions in the layers, as well as the response to variations of the external environment, such as salt concentration, pH, or temperature. In the case of weak polyelectrolytes, the dissociation equilibrium in multilayers is of particular interest. Furthermore, the swelling in water or other solvents provides crucial knowledge about internal local properties.

In parallel with experimental achievements, in the last couple of years, theoretical concepts of layer formation have been developed. Theories and models describing PEMs today range from phenomenological descriptions of layer structure and segment distribution to mean field and scaling approaches describing the adsorption process [34, 35].

A large number of properties and formation principles of PEMs can be described and explained by rather simple concepts, as they are described in this review. Nevertheless, PEMs remain tremendously complex materials and are far from being completely understood for several reasons. The electrostatic interaction is of a long range character and can extend beyond the layer thickness. In addition to attractive, also repulsive forces need to be considered. Furthermore, it is difficult to separate the influence of forces from that of entropic contributions. It is currently discussed that the kinetics of the layer formation process is relevant for the final properties, since the strong electrostatic forces slow down equilibration processes and can potentially cause very slow dynamics, such that the PEMs would even have to be considered nonequilibrium materials. Finally, another problem is the fact that the first layers near the template surface are known to differ from layers at a long distance.

In this paper, the basic principles of layer formation and internal properties of multilayer assemblies are reviewed, starting from simple concepts describing the initial adsorption process, and then advancing towards the development of more complex models and ideas of PEMs, as outlined in the two previous paragraphs. The focus is on fundamental physical properties and the evolution of more realistic models from first simple model ideas. This is in contrast to previous reviews, which have concentrated rather on the possibilities of self-assembly on a more phenomenological level, for example describing multilayer preparation achieved with respect to a large variety of materials [14–16], and for example focusing on how different molecular architectures affect the possibility of layer formation [15]. In the current paper, the experimental findings are discussed mainly for the most commonly employed polyelectrolytes shown in figure 1. For polyion pairs of PSS, PAH, PAA and PDADMAC, not only has the largest number of investigations been performed, but also the most quantitative and fundamental studies exist. Particular focus is here put on the formation process of PEMs, that is the charge complexation following the adsorption of each single layer.

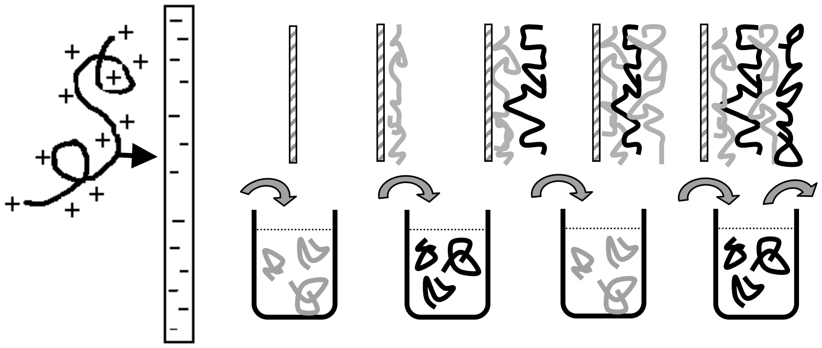

Figure 2. The procedure of self-assembly of multilayers on planar substrates.

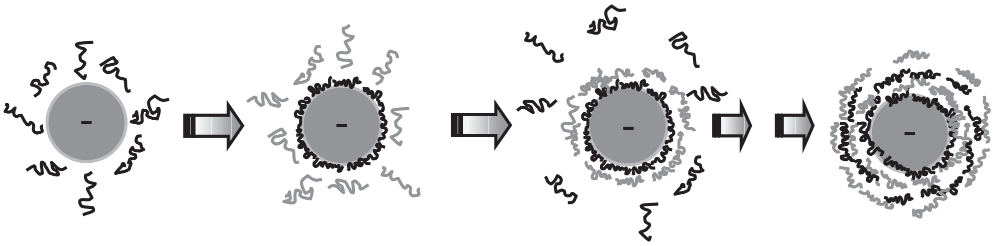

Figure 3. The principle of self-assembly of multilayers on colloidal particles.

2. The layer-by-layer self-assembly procedure

2.1. Preparation of planar multilayers

Multilayer systems can be prepared using the method of layer-by-layer self-assembly. As substrates, cleaned hydrophilic surfaces such as glass, silica or mica, which exhibit a non-zero surface charge, have been employed. The adsorption of a first layer is accomplished by immersion of the charged substrate into a solution of a polyion of opposite charge. After a typical adsorption time of 20 min, the substrate is washed in water to remove excess polymer. Under the conditions described in section 3, the adsorption of a polyion layer leads to surface charge overcompensation. Therefore the sign of net charge is inversed and adsorption of an oppositely charged polyion becomes possible. In most cases drying is performed after layer deposition. The principle is demonstrated in figure 2. A controlled and reproducible layer build-up can be achieved for a large range of materials and conditions. To describe multilayers, here n denotes the total number of monolayers and N the number of bilayers of type $(A/B)_N$.

Planar multilayer assemblies are typically characterized by small angle x-ray reflectivity, quartz crystal microbalance data, or optical absorption. The majority of experiments characterizing multilayers, especially the early structural investigations, have been performed in air, where layers, kept at ambient conditions, contain about 10–20 wt% water of hydration [33]. Recently, studies of the internal properties also involved the state of multilayers in contact with aqueous solution, where *in situ* studies provide a detailed understanding of the layer formation process.

2.2. *Coating colloids: diffusion control and supersaturation*

The coating of colloids (see figure 3) is achieved by the alternating addition of polycations and polyanions to particle dispersions with intermediate washing and centrifugation steps to remove excess polyions [19, 20]. Alternatively, a protocol using ultrafiltration has been developed [36]. This enabled the multilayer coating of curved surfaces in the size range of 20 nm to several micrometres.

In the fabrication of multilayers adsorbed to colloids, additional aspects have to be considered: competing with the formation of a defined monolayer around the particle is the process of coagulation of partly covered particles. The corresponding timescales of adsorption and coagulation therefore are crucial for successful multilayer formation on single colloids, as is seen from the following: the rate of polymer chain adsorption onto a particle is given by [37]

$$k_{\mathrm{ads}} = 4\pi R_{\mathrm{pa}} D_{\mathrm{pol}} c_{\mathrm{pol}}, \tag{2.1}$$

using the assumption of an irreversible and diffusion controlled adsorption. R_{pa} is the radius of the particle, D_{pol} the polymer diffusion coefficient and c_{pol} the polymer concentration. The competing process, the rate of collisions between particles, can be described by

$$k_{\mathrm{coll}} = 4\pi R_{\mathrm{pa}} 2 D_{\mathrm{pa}} c_{\mathrm{pa}} \tag{2.2}$$

with D_{pa} and c_{pa} as the diffusion coefficient and concentration of particles, respectively. The factor 2 takes into account the fact that both objects are diffusing.

Each collision between particles can lead to irreversible coagulation, because partially covered particle surfaces can show a strong attractive electrostatic interaction. The parameter regime employed for coating therefore involves ‘supersaturation’, i.e. a polymer concentration in solution, which is large compared to the saturation concentration required to achieve complete surface coverage. To avoid coagulation, the polyion adsorption rate has to be large compared to the particle collision rate, i.e. $k_{\mathrm{ads}} \gg k_{\mathrm{coll}}$, which results in the condition

$$\frac{R_{\mathrm{H}}}{R_{\mathrm{pa}}} \ll \frac{c_{\mathrm{pol}}}{c_{\mathrm{pa}}}. \tag{2.3}$$

The requirement of a fast chain adsorption is thus fulfilled if the polymer concentration is large compared to the particle concentration. This condition becomes more and more critical when coating of small particles is required. An additional limit is given by the radius of the particles: for particles with a radius of the order of the radius of gyration of the polymer, R_{g}, bridging coagulation is competing with layer formation. Then, a drastic reduction of the particle concentration is required for controlled layer formation. In this case, a reduction of the molecular weight can prevent bridging, such that the coating of particles as small as several tens of nanometres can be achieved.

Successful deposition of PEMs to colloids is typically monitored by electrophoresis [19, 38]. Figure 4 shows the ζ-potential depending on the number of layers deposited, n, for multilayers of PAH/PSS formed on polystyrene latex particles: starting from a negative potential of the bare particles due to the latex stabilization charges, the potential is positive after deposition of the polycation and negative after deposition of the polyanion. The total layer thickness, as determined by single-particle light scattering, increases linearly with n. These results demonstrate a regular growth of the multilayer system and indicate a reproducibility of each single deposition step.

A similarly regular ζ-potential and layer thickness have been observed after deposition of various polyion pairs. An interesting feature is the fact that for a large number of systems the ζ-potential oscillates between the same values, with saturation occurring around 30–40 mV

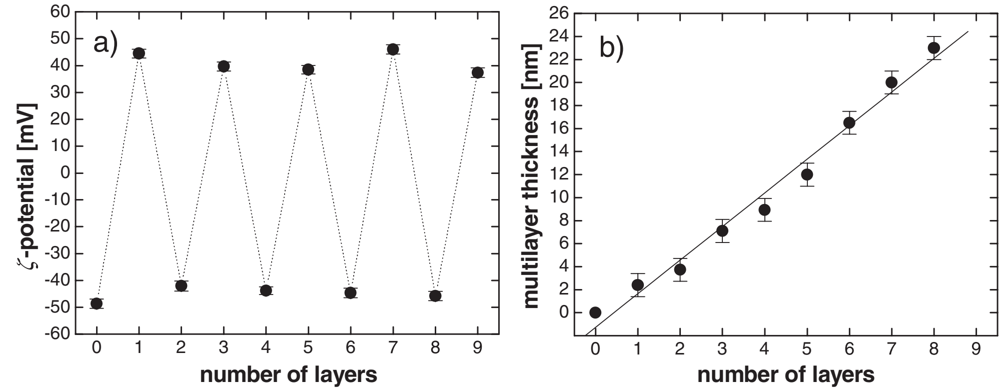

Figure 4. The dependence of the ζ-potential and total layer thickness on the number of layers deposited onto colloidal particles. Here $(\mathrm{PAH/PSS})_N$ has been adsorbed from 0.25 M salt on polystyrene latex of radius $R = 233$ nm, according to [23].

after polycation adsorption, and around −40 to −50 mV after polyanion adsorption [20, 38]. This implies that saturation occurs when a fixed potential is reached, independently of the material employed. It provides evidence for the electrostatic repulsion by the outer layer being the mechanism controlling the adsorbed amount, and limiting further adsorption, not the polyion stoichiometry with respect to the underlying layer. For polyions of a lower charge density, e.g. copolymers, lower values of the ζ-potential can be obtained [3]. This suggests that, at least for high charge density polyions, the amount deposited is limited by the repulsive potential of the already deposited chains.

In the following, no distinction between planar and colloidal templates is made, since the geometry of the surface does not affect layer formation as long as the particle radius R is large compared to the polymer radius of gyration, R_g. Important differences between planar and colloidal templates are, however, given by differences in the preparation protocol typically employed for either case: in most published studies, planar layers are dried after each deposition step, whereas apparently colloids are not. Generally, identical properties of layer assemblies can only be ensured if the preparation history, involving all concentrations and pH values of polyion solutions and washing solutions, are identical.

3. Polyion adsorption and charge overcompensation

The formation of multilayers is influenced by a range of parameters and conditions, which provide opportunities for controlling film properties. They are given here in the order of decreasing relevance [35]: salt concentration, dielectric constant of solvent deposited from, type of salt, deposition time, polyion concentration, molecular weight of polyions, degree of charge or ionization along the chain. This section describes the mechanisms involved in the formation of an adsorption layer, starting from a very simple approach based on the coil structure in solution. Then, more refined theories of polyelectrolyte adsorption are reviewed, and finally specific aspects for the adsorption to soft surfaces involving charge complexation are discussed.

3.1. The influence of salt and of the coil conformation in solution

Correlating the adsorption behaviour of a coil with its solution conformation, the simplest approach describing multilayer formation is the picture of a ‘hit-and-stick’ adsorption, i.e. the irreversible adsorption of chains with their solution conformation onto the surface and a subsequent collapse along the surface normal, neglecting lateral rearrangements at the surface. The amount deposited, or the layer thickness, is then determined by the area occupied by a chain, which is the cross sectional area of the chain in solution.

The motivation for such a model is given by the strong interaction of a large number of polyion charges with an oppositely charged surface, which can lead to kinetic entrapment of coils, preserving their structure in solution. The argument for neglecting any equilibration after adsorption is the fact that the simultaneous release of a large number of bonds is highly improbable, as the Coulomb interaction of two oppositely charged segments, at typical distances, is larger than k_BT.

Such a simple picture of the adsorption is for example supported by the fact that polyelectrolyte multilayers are not equilibrium structures. There is no evidence for thermodynamic equilibrium in multilayer structures, since they are never spontaneously formed, but depend on the alternating adsorption of polyions. Assuming thermodynamic equilibrium is not reached in PEMs, kinetic entrapment in a structure formed and controlled by the adsorption procedure has a dominant influence. In such a model, the influence of a number of parameters on the layer structure can be qualitatively understood, such as the thickness dependence on salt concentration, which can be related to the salt dependence of the conformation in solution.

While uncharged chains in a good solvent can be described using Gaussian statistics with accounting for excluded volume effects, the conformation of polyelectrolyte chains is additionally governed by the electrostatic repulsion of the charges on the chain. An important parameter in the description is the Bjerrum length l_B, which is defined as the distance where the electrostatic interaction equals the thermal energy,

$$\frac{e^2}{4\pi\varepsilon l_B} = k_B T, \tag{3.1}$$

which is $l_B = 7$ Å for water at room temperature. The electrostatic repulsion leads to an increased persistence length of the chain, l_τ.

Semi-rigid charged chains can still be described by excluded volume statistics, but with an increased persistence length l_τ, and thus an increased end-to-end distance R_0 of $R_0^2 = 2Nal_\tau$. In salt solutions, the electrostatic interaction is screened and decays with the Debye length $\lambda_D = \kappa^{-1}$, where $\kappa^2 = 8\pi c_{\mathrm{salt}} l_B$. Given l_0 as the persistence length of the uncharged chain, the self-repulsion of the polyion chain leads to an increase of the persistence length, which is dependent on the extent of salt screening, resulting in

$$l_\tau = l_0 + (\tau^2 l_B)/(4\kappa^2), \tag{3.2}$$

with $\tau = f/a$ given as the charge density per unit length, calculated from f as the fraction of charged monomers along the chain, and a as the monomer length. Here, Manning condensation, which occurs at higher charge densities on the chain, is neglected. The rigidity of the chain therefore increases with increasing charge density and decreasing ionic strength.

By adsorbing polyions from salt solutions of varying electrolyte concentration, the layer thickness can be controlled over a wide range [1]. Screening of the polyion charges in a strong electrolyte solution leads to a smaller radius of gyration. Thus, adsorption of smaller coils will take place, which occupy a lower surface area per chain, leading to a larger area density of segments and consequently to a larger layer thickness. This qualitatively explains the formation of thicker layers in the presence of salt. Taking thus R_g^{-2} as a measure of the amount deposited, and neglecting l_0 in equation (3.2), the surface coverage should roughly scale with the salt concentration as $c_{\mathrm{salt}}^{\alpha}$, with $\alpha = 1$. Indeed, several authors experimentally found a linear dependence on c_{salt} [33, 39]. However, in other cases different power laws of the adsorbed amount or layer thickness dependence on the salt concentration were obtained, as the thickness scales with $c_{\mathrm{salt}}^{\alpha}$ with $\alpha = 0.5$ [17, 40], or the adsorbed amount scaling with an exponent of $\alpha = 0.05$–0.15 [41].

The largely differing values might arise from deviations of the chain conformation from excluded volume statistics due to the limitations of the description by l_τ. In fact, in the case of very flexible chains, an improved description of the chain conformation in solution is given by the picture of the 'electrostatic blob': the charged chain is divided into subunits of Gaussian conformation, the so-called 'blobs' [42–44]. The blob size is given by the distance at which the electrostatic interactions between neighbouring blobs are equal to the thermal energy. Within one blob, then the electrostatic repulsion is not dominant and Gaussian conformation applies. This results in a blob diameter of [42]

$$\xi_{\mathrm{el}} = a(a/f^2 l_{\mathrm{B}})^{1/3}. \tag{3.3}$$

The length of the blob arrangement, B, then results in

$$B = (N/g)\xi, \tag{3.4}$$

where g is the number of monomers per blob. Again assuming an irreversible immobilization of chains with their solution conformation at the interface, the parameter, which should control the layer thickness, is the blob size ξ_{el}. Such a model can describe the adsorption dependence on the molecular weight M_{w}: in experimental studies the molecular weight does not have an influence on the layer thickness [45]. This finding agrees with the picture of electrostatic blobs, since the diameter of the blob—and thus the surface area occupied by it—is independent of M_{w}. For a random coil, in contrast, the radius of gyration scales with $M_{\mathrm{w}}^{1/2}$, or $M_{\mathrm{w}}^{0.6}$, accounting for excluded volume effects, and such a scaling should be evident in layer thickness data. In fact, while thin layers showed no dependence on molecular weight, since they consist of flatly adsorbed chains, thicker layers in a loopy conformation, i.e. when one chain is fully charged, had a thickness dependence on molecular weight scaling with $M_{\mathrm{w}}^{0.3}$ [46].

From such simple considerations of a 'hit-and-stick' model, thus a simplified picture of the adsorption and complexation can emerge. While a number of features of multilayer formation, such as the irreversibility of the adsorption, and the increase of layer thickness due to salt and the independence on molecular weight, can be explained by the simple arguments above, others are not well described. For example, the discussion of the rearrangement processes occurring on adsorption–complexation already shows that the salt influence should be far more complex. The models employed for the description of the chain in solution depend on the regime, for example, flexible versus rigid chains, high or low salt conditions, and no unified approach exists. The next section gives an overview of the theoretical descriptions of adsorption employed for specific regimes, starting with 'hard' surfaces, where models already exist. In the following section, the implications of adsorption to a 'soft' interface are discussed.

3.2. Theories of adsorption to hard charged surfaces

Polyelectrolyte monolayer adsorption to oppositely charged surfaces has been the subject of a large number of experimental studies (see, for example, [37–43] in [47]). The general understanding is that highly charged chains adsorb as thin layers with a flat chain conformation. Through pH variations, salt screening or charge dilution along the chain, more flexible chains are formed; these result in thicker layers of a more loopy type.

The amount of polyelectrolyte adsorbed depends on the charge density of the surface, σ. Thus, σ and the charge density along the chain are the dominating parameters in polyelectrolyte adsorption to hard surfaces. An important question is, whether or to what extent a compensation or overcompensation of the surface charge occurs, since charge reversal is a prerequisite for the subsequent deposition of multilayers. Several theoretical descriptions of polyelectrolyte adsorption have dealt with this question.

For weakly charged flexible chains, Joanny employed a self-consistent mean field approach to describe adsorption in the extreme cases of high and low ionic strength [48]: in the limit of low ionic strength, that is $\kappa\delta \ll 1$, with δ being the thickness of the adsorbed layer, a slight charge overcompensation is found. The excess charge is proportional to the inverse screening length κ [48, 49]. The overcompensation is merely due to an extension of a few chain segments into the z-direction, which is equal to or larger than the screening length. This implies that the charge overcompensation is provided by the loops and tails. These are covalently attached to the trains, while the trains directly interact with the charges on the surface.

At high ionic strength, not only the self-repulsion of the chain segments, but also the attractive interaction of segments to the surface, are strongly screened. Therefore, adsorption to a hard wall in the high salt case is not dominated by electrostatics, but driven by a short-range attractive potential. Since the electrostatic interactions are less relevant, a strong charge overcompensation can be achieved, which is provided by a large fraction of loops at the surface, since the chain becomes more flexible [48, 50]. However, at extremely low surface charge, no adsorption takes place. In summary, at low ionic strength, a slight charge overcompensation is found for flat adsorbing chains, while at high ionic strength a strong overcompensation can be provided by loops and tails [48].

In contrast to flexible ones, semi-flexible chains form flatly adsorbing layers, where no mean field description applies. For this case, using scaling arguments, a phase diagram describing the dependence of different charge reversal mechanisms on surface charge density and screening length has been presented [51, 52]. Here, lateral correlations between adsorbed polymer chains are relevant. Such rather two-dimensional, flat layers are for example obtained from PDADMAC.

3.3. Adsorption to soft charged surfaces: phenomenological multilayer growth

Multilayer growth has predominantly been followed monitoring layer thickness changes with each deposition cycle. Already in the very first demonstrations of multilayer build-up, the total layer thickness was the parameter employed to characterize layer formation. It is easily accessible from x-ray reflectivity measurements, where Kiessig fringes result from the interference of reflections at the film/air and at the substrate/film interfaces, respectively [1].

For most polyion pairs, a linear growth of the layer thickness with layer number is observed [1, 9, 31, 38, 53]. In a number of cases, the first few layers are an exception to this rule. Following the first deposition cycles, a substantially lower adsorbed amount or thickness can be observed, and only after several cycles is a constant thickness increase found [54]. As demonstrated in the previous section, for the first monolayer, the substrate surface charge is an important parameter determining the first layer properties. A nonlinear growth of the first few layers has been considered as a multiplication of surface functionality [55]. Finally, after several layers, a stationary regime is reached, and the film properties become independent of substrate surface charge. In addition, for flexible chains the stratification on a flat surface might lead to an adsorbed amount which is lower than that adsorbed onto a rough and soft surface, resulting in a lower layer thickness on a ‘hard’ surface. A roughness increase in combination with monolayer thickness increase has indeed been observed for the first layers. The increase of roughness and thickness continues over a few layers [33]. Finally, a regime of stationary growth is reached, where both parameters are constant.

In some rare cases, no linear regime of regular layer growth is reached, and the thickness increase can be pseudo-exponential as, for example, for poly(L-glutamic acid) (PGA)/ poly(L-lysine) (PLL) [56] or hyaluronic acid/PLL [57]. The fact that in these systems more material gets adsorbed with increasing layer number n, points to a layer structure which changes with n. Such observations have for example been correlated with an increasing surface roughness, providing an increasing total surface and thus with each adsorption step a larger number of charges available for complexation [17]. In more recent views, exponential growth was attributed to a complete rearrangement of the multilayers with each new layer addition, and polymer diffusion experiments provide evidence of a very large chain mobility [58].

For the majority of polyion combinations, however, multilayer growth is linear, and the forthcoming sections will focus on this case.

3.4. Adsorption to soft charged surfaces: complexation and stoichiometry

The adsorption of a polyion layer to a 'soft' polymeric surface differs significantly from the adsorption to a 'hard' surface of the same surface charge density, σ. This is not only due to the surface charge being distributed in the z-direction (z is the surface normal), but also to the flexibility of the underlying layer. An important process is the entanglement into the outer multilayers, which drives the complexation and determines the segment distribution width of each layer.

Some studies have followed the formation of a polyion layer on an oppositely charged polymeric support in detail. Donath *et al* [59] employed electrophoretic fingerprinting and found results consistent with one third of the charges of the outer layer undergoing ion pair formation with the underlying polyion layer. The remaining two thirds of the last layer charges are then compensated by counterions, which can be released on adsorption of a next layer. The degree of complexation has also been investigated by a combined study of nuclear spin relaxation and ζ-potential measurements, which follow the formation of a PAH layer with increasing PAH concentration [24]. While for adsorption to a hard surface, charge reversal is achieved at a polymer amount of 50% of that required for saturation, for adsorption to multilayers charge reversal is reached only at 100% of the first layer coverage, and 150% of the polymer amount in the first layer is required to saturate the surface [24]. The larger adsorbed amount of polyion is attributed to segments of adsorbing chains, which entangle into the precoated layers (see figure 5). Thus, also here, one third of the adsorbing segments are required to compensate surface charges of the previous layer. Since this first third does not alter the ζ-potential significantly, it can be assumed to be buried and interdigitated into the preformed layers. The charge reversal at ζ equal to zero is reached at a polymer concentration of two thirds of the saturation concentration, and in total, 150% of the coverage of a hard surface is required for saturation of the ζ potential [24].

Thus, with the above papers agreeing on a fraction of 1/3 for the system PAH/PSS, it becomes clear that the first third of the segments is required to compensate internal charges, involving a deep interpenetration into the multilayer. The rest of the charges are then compensating surface charges of the previous polyion layer, and forming loops and tails extending into the solution and creating the charge overcompensation, which leads to the reversal of the ζ-potential.

Since regular layer growth requires charge neutrality, if the factor $1/3$ applies for each adsorption step, it follows that about $1/3$ of the charges have to remain compensated by counterions, or remain uncomplexed. In a binding study of charged dyes to multilayers, a fraction of $1/3$ of polyion charges were available as binding sites, which confirms the above model [60–62]. Additional evidence for the complexation is provided by x-ray reflectivity

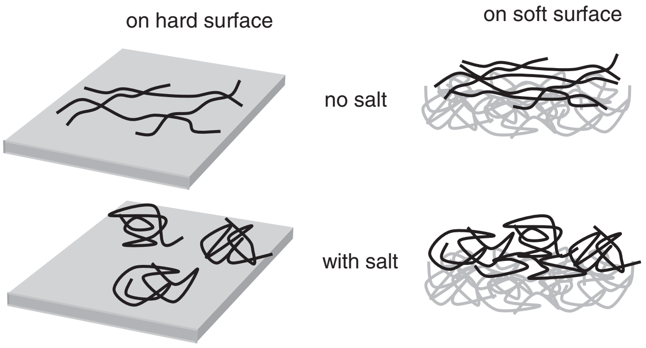

Figure 5. A sketch of the structure of a polyion adsorption layer: flat adsorption from water solution and coil-shaped adsorption from salt solution. Intercalation into precoated layers in the case of adsorption to a soft surface leads to a higher surface coverage [24].

experiments, where an increased density in the complexation region of two subsequent polyion layers was found, while the first layer close to the surface and the loops of the second layer regions are less dense [63].

However, it can be expected that the fraction of charges compensated by the corresponding next layer will depend strongly on the molecular architecture of the polyion pair involved. Other polyion pairs might complex with $1/2$ of the segments, or even asymmetric assemblies involving small ions are possible. In salt solution, the degree of interdigitation appears to be somewhat lower [24]. This can be explained by the adsorption of a coil-shaped structure in contrast to rod-like chains in the absence of salt (see figure 5), which implies a reduced accessibility of the outer layer segments to the next adsorbing layer chains.

Not only do the Coulomb interactions play a role in polyelectrolyte adsorption, but additional contributions such as van der Waals interactions or hydrogen bonds can also contribute substantially. For example, the adsorption of a weakly charged negative polyelectrolyte to a negative silica surface has been demonstrated [64, 65]. In this case, hydrogen bonds of the uncharged segments provided the interaction, while the charged segments can be expected to be contained in flexible loops pointing away from the surface.

3.5. Adsorption to ‘soft’ charged surfaces: models of multilayer growth

It should be pointed out that in the previous section only the interaction of an adsorption layer with the previously deposited one has been considered. Real systems seem to be far more complex than that: while the theoretical models describing adsorption to hard surfaces suggest a modest charge overcompensation, much thicker layers have been observed experimentally [39, 66]. In conclusion, the charge of the terminating layer is extended over several layers, i.e. the excess charge is penetrating into the multilayers. This results in more charges being required, and a larger layer thickness.

Phenomenological approaches describe the adsorption in terms of the segment distribution along the surface normal. Schlenoff and Dubas [35] employed two parameters, a charge overcompensation level and its decay length into the multilayer region, to describe the excess charge of the terminating layer as distributed over several layers beneath. Within this model modest charge overcompensation levels were sufficient to explain large thickness increments. In a similar model, Ladam *et al* described the dependence of three different zones on the distance from the template surface [41], including a precursor zone, which is influenced by the initial surface charge. Both models account for the increase of layer thickness with salt concentration.

For flexible chains, describing the adsorption by taking into account the complexation with the pre-deposited polyion layers, Castelnovo and Joanny derived a Debye–Hückel model for multilayer formation [34]. Charge overcompensation is explained by a partial complexation of the second layer with the loops of the first one. Scaling laws for complex formation at the surface are obtained from a description in analogy to a mean field description of bulk complexes. The outermost layer exhibited loops extending into the solution and carrying the excess charge. As a result of the interpenetration and complexation in each adsorption step, the interdigitation of subsequent layers can be understood.

In conclusion, the adsorption of a polyion layer to preformed multilayers differs greatly from adsorption to hard charged surfaces. An important process is the entanglement into the outer multilayers, since this drives the complexation and determines the segmental distribution width of each layer.

3.6. Kinetics of multilayer formation

The complexation of polyions occurs simultaneously with the adsorption of each layer, due to the interactions with the charges of the previously deposited layer. The extent of interdigitation is determined during the process of the adsorption of each layer, whereas internal chains in PEMs are generally assumed immobile. For controlling the inner structure, therefore, the adsorption process of each single layer is of great interest and has been addressed experimentally as well as theoretically.

One way of viewing the adsorption–complexation process is a time dependent process at a polymer concentration large compared to the saturation concentration. In kinetic studies of multilayer formation the timescales vary greatly [15, 63]. A common feature is that the kinetics appears to be a two-step process with a fast adsorption occurring within seconds to minutes, and a much slower process, which can occur as slowly as over hours (see [15] and references therein).

The first kinetic step involves the transport of chains to the surface and a fast mass deposition [39, 63]. The rate of deposition is determined by the diffusion of polyion coils. Then at the surface chain rearrangements take place and mass deposition continues at a slower rate, until saturation is reached [63]. In this second kinetic step, slow chain rearrangements enable the diffusion of segments into the inner regions of the previously deposited layer. By mixing of positive and negative segments, the irreversible complexation of charges is finally achieved [9, 39]. For this process the flexibility of the outer region of a multilayered complex with respect to chain rearrangements, discussed in section 6, is of great importance.

Thus experimental proof of layer interdigitation is concluded not only from the properties of preformed multilayers, but is evident already during the formation process of the assembly. Finally, the question is which processes and which parameters are controlling the resulting properties of multilayers. The multilayer formation is apparently affected by both the kinetics and equilibrium properties. The transport of polyions to the surface takes place until a sufficiently repulsive ζ-potential is built up. Slower chain rearrangements allow for equilibration and the adsorption of additional chains. In this step, it is the flexibility of the last layers ensuring the interdigitation, and thus complexation. In conclusion, it is the repulsive interaction which limits further adsorption, while the efficiency of interdigitation and complexation determines the adsorbed amount in each layer.

4. Multilayers: structure and composition

In this section, the internal properties of polyelectrolyte multilayer assemblies are described, starting with structural aspects, and proceeding to implications for the local charge balance.

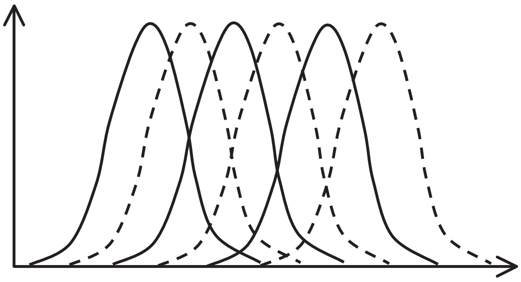

Figure 6. A model of the concentration of polyion segments in multilayers along the surface normal, as suggested by Decher [55]. Dashed curves: polycation layers; solid curves: polyanion layers.

4.1. Layer interpenetration and segmental distributions

The simplest structural model for subsequently deposited layers is a stack of well separated layered building blocks with defined interfaces between subsequent layers. Experimental evidence of such internal interfaces is, however, hard to obtain, apparently since the internal interfaces are not well resolved: neither in x-ray reflectivity experiments could a Bragg peak arising from the bilayer repeat unit be observed, nor did neutron reflectivity in layer systems containing one deuterated polyion moiety lead to Bragg reflections. A layered arrangement within the polyanion/polycation repeat unit thus does not seem observable. Only after the formation of superstructures with the distance between deuterated layers exceeding *several* monolayers, could reflectivity experiments detect internal structure: a Bragg peak in x-ray reflectivity was observed for superstructures of the type $(\mathrm{ABCB})_N$ containing a mesogenic unit on polyion C [10], and in neutron reflectivity experiments, Bragg peaks were observed for several types of superstructures [67, 68].

Such reflectivity data are consistent with a large overlap between the segments of adjacent layers. Since the segmental distribution width (FWHM) of one layer is larger than the distance of layers of the same polyion, the interdigitation is large enough to result in a monomer density in the multilayer arrangement which is constant along the z-axis for both polycation and polyanion. This behaviour has been termed ‘fuzzy layers’ in contrast to sharp internal interfaces [55]. The interpenetration can be described by segmental distributions of the layers along the surface normal, as shown in figure 6. Different techniques have been applied to determine the distribution widths, which can be viewed as internal roughness, yielding fairly consistent results: energy transfer experiments resulted in 1–2.5 bilayers [69], surface force measurements on PSS/PAH in 1.5–2.5 bilayers [70], electron transfer of viologen in (PSS/PAH) in 1.5–2.5 bilayers [71]. Only in a few cases of polyions carrying mesogenic side groups could a bilayer repeat unit be observed, since the interpenetration is reduced by the presence of rigid layer components [9].

It can be assumed that the interdigitation is driven by the complexation of positive and negative charges, since a close vicinity of polyion segments is energetically favoured. A further question is whether a constant segment density profile of each polyion type is accompanied by a complete complexation, or whether there are still free, uncomplexed charges remaining in the layer assembly; this question is treated in section 4.3.

There is evidence that the multilayer structure of the first layers differs from that of the last deposited layers [41]: this was described by different regions in a multilayer system, where a precursor zone of about six layers is affected by the substrate properties, then in a core zone the growth is very regular and all charges are compensated. Finally, in an outer zone the chains have a more loop-like conformation, and this is the zone in which the excess charge of the last layer is distributed [41]. Experimental evidence for different zones was given by diffusion measurements of probe molecules through multilayers, where in an outer zone of about 10 nm diffusion coefficients were enhanced by two orders of magnitude, which was attributed to a less dense complexation of the multilayers [72].

4.2. General views of polyelectrolyte multilayers

An interesting question in view of the mechanisms of layer formation is whether the resulting multilayer composition and structure is determined either by the kinetics of the adsorption and interdigitation processes, or whether equilibrium properties dominate.

The latter would suggest complete equilibration following each monolayer deposition. However, though equilibration processes are involved, a complete equilibration of complexed chains, which would result in a random conformation, is clearly not achieved. Layered complexes are not in thermodynamic equilibrium, since their formation never occurs spontaneously in solution, but only following a given preparation protocol. In addition, according to the above discussion of the kinetics, a number of properties are determined rather by the number and accessibility of the polyion charges of the previous layer, and are not well described by thermal equilibrium.

Therefore, the structure of PEMs has to be considered as partly determined by the preparation history, and partly by equilibrium aspects. One can separate these influences according to the different length scales: while the overall chain structure cannot equilibrate, and on a length scale $>$ some nanometres nonequilibrium applies, on a shorter length scale the structures can be considered equilibrated. This picture agrees with the fact that two-dimensional stratification is clearly present. Thus on a local segment scale the multilayers can be considered equilibrated, and in fact they show very similar molecular properties as compared to three-dimensional volume complexes, which are spontaneously formed in solution. This had been proven, for example, concerning the vicinity and complexation of opposing charges, as shown by solid-state NMR [22]. There, PDADMAC/PSS multilayers were investigated by ultra-fast MAS-DQF 1H spectra, a method which is sensitive to the respective distance of weakly coupled protons. The results showed that the spacing of positive and negative charges in PSS/PDADMAC layers is identical to bulk complexes. Therefore, on a local segmental scale, the charge complexation is identical.

In addition, IR spectra showed similar shifts of the IR absorption due to complexation in layered complexes as in volume complexes [66, 73]. PEMs can therefore be considered as ‘layered complexes’ of locally the same interactions as in soluble complexes, but exhibiting a higher segment density and a remaining 2D stratification of chains.

Inspired by their strong hydration and by their swelling properties, PEMs can be viewed as rather soft materials, i.e. as dense hydrogels [15] or as cross-linked gels. In such a picture, the cross-linking density, or the mesh size, is controlled by the charge distribution along the chain [74, 75]. Such models are very successful in explaining the permeabilities of different PEMs for small molecular probes.

On the other hand, PEMs have been described as a glassy, quasi-frozen state [34, 76], which suggests a rigid and compact layer structure. In a phase diagram the glassy state of the layered complex is considered in equilibrium with a solution complex phase. This phase diagram describes PEMs as a glassy state at low ion concentration c_{ion}, ‘liquid-like’ at higher c_{ion}, and uncomplexed at very high c_{ion}, making the assumption of thermodynamic equilibrium [77].

A crucial point for refining such pictures and models of multilayers are dynamic studies, as discussed in section 6.

4.3. Stoichiometry and charge balance

Strong polyelectrolytes, carrying a charge on each monomeric unit, are the simplest case of polyions used for multilayer build-up. Their fraction of charged segments is constantly $f = 1$, if counterion condensation can be neglected. In multilayers, the internal layers are electrically neutral [66, 73]. The macroscopic neutrality can on the one hand be fulfilled by intrinsic charge compensation, i.e. a layered complex being formed with an exact 1:1 stoichiometry of polycation and polyanion charges, involving ion pair formation with the previous layer until all of its charges are complexed. Alternatively, a fraction of these charges might remain uncomplexed and extrinsically compensated by counterions present in the multilayer. Therefore, questions of the polyion composition of multilayers are of large interest. The possible presence of counterions has been answered controversially at quite different levels of precision. We discuss here first the stoichiometry concerning the polyion complexes, and then review the question of incorporated counterions.

Extrinsic compensation might be the case for those polyion segments, which are sterically not accessible to the charges of the next adsorbing layer. For example, while the stoichiometric ratio is about 1 for PAMA/PSS [78], it is 2.7 to 3.2 for PSS/PVP [78], which can be explained by a flexible position of the charge at the end of each side group for both PAMA and PSS, leading to a good matching of the charges on complexation. The PVP charge is more ‘hidden’, i.e. close to the backbone, and therefore less accessible for complexation, which leads to a higher factor f [78].

In addition, the screening length κ^{-1} in the layer can influence the charge compensation. For κ^{-1} small compared to the layer extension, $\kappa^{-1} < \delta$, polyion charges can remain uncomplexed and extrinsically compensated by small counterions. If the opposite is the case, i.e. $\delta < \kappa^{-1}$, uncompensated polyion charges might remain, creating a layered arrangement of positive and negative excess charge. Indeed, a model employs the idea of locally charged layers, in contrast to the above discussed models of locally neutral complexes [76].

The possible presence of counterions has been discussed controversially in a number of investigations dealing with intrinsic versus extrinsic charge compensation [14, 15, 55]: intrinsic charge compensation is claimed, since according to neutron reflectivity and radioanalytical studies no substantial amount of counterions was found in multilayers [66, 68]. It can be assumed that the majority of counterions of each polyion chain are removed during the adsorption or the subsequent washing [45, 66], since it is entropically more favourable for small ions to be solubilized in the aqueous phase.

On the other hand, with intrinsic compensation, macroscopic neutrality requires a 1:1 stoichiometry in the layers—which is not supported by the stoichiometric ratios discussed above. In fact, a number of investigations report on substantial fractions of 30% of the polyion charges being free for binding of ionic dyes into the layers [60–62], a number which agrees well with the details of the layer formation process described in section 3. However, the fact that counterions are not detected in such large concentrations seems to contradict the above view. It can be speculated whether for example rearrangements of the chains can lead to a degree of complexation, which can easily vary under different conditions.

The question of the presence of counterions in the multilayers is also of relevance for ion exchange and ion transport. In electrochemical experiments, the internal counterion concentration was so low that there were virtually no exchangeable ions [79]. The ion transport is then mediated by salt ions when layers were swollen in salt solutions. This was termed a ‘reluctant’ ion exchanger [79]. Large selectivity values were reported for the transport of different anions [80] and cations [74], and the permeability for ions was dependent on the solution pH [81] and on internal layer chemistry [82].

Interesting in the context of the polyion stoichiometry are studies of layer formation from strongly asymmetric pairs of polyions. Employing polyions with a reduced charge density along the chain, i.e. consisting of charged and uncharged co-monomers, it was observed that a minimum charge density is required for polyelectrolyte adsorption [78, 83, 84]. The influence of the charge density on multilayer formation was investigated employing PDADMAC with varying charge densities f [85–87]. A threshold for layer formation at about 50% charged monomers is found. Below this value, very flat layers adsorb and charge overcompensation is hard to achieve, independent of the salt concentration [85, 86]. Above the threshold charge density, layer growth is efficient and the thickness increases with salt concentration with an exponent of $1/2$ [85]. In this regime, lower charged fractions lead to larger thickness increments, an effect attributed to the chain conformation in solution [86]. At high charge density, Glinel *et al* [87] found a regime independent of the charge density, since counterion condensation dominates the effective charge density.

However, the picture of a minimum charge density is much too simplified, since multilayer deposition has been successful even at very low charge densities, if hydrophobic interactions contribute.

4.4. Weak polyelectrolytes: pH influence and stoichiometry

Weak polyelectrolytes offer the possibility of a variation of the charge along the chain, i.e. the fraction of charged segments, f, simply by varying the pH value during deposition. A reduced f has a similar effect as salt, since the self-repulsion of the chain in solution is reduced, which leads to a decrease of chain stiffness, and thus to an increased surface coverage [84].

Building multilayers from two weak polyelectrolytes, PAH and PAA, different regimes of layer growth are found, where the layer pair thickness either increases or decreases with f, depending on the pK_a value of both polyelectrolytes. The thickness increments vary over more than an order of magnitude depending on the solution pH, as the thickness per bilayer ranged from 5 to 80 Å [46, 47]. The findings can be explained by a dependence on the pH values in either deposition solution for different regimes: if the pH is only varied in the PAH solution, the contribution of PAA remains constant, and with an increasing charged fraction along the PAH chain, f, the adsorption is more flat and the layer thickness decreases. Therefore, if both polyions are fully ionized, very thin layers are formed. On the other hand, when only one of the polyelectrolytes is close to full dissociation, very thick layers are also observed [46].

Another regime is formed in the pH range from 2.5 to 4.5, where PAH is fully dissociated and only the dissociation of PAA increases with increasing pH. This leads to a reduced layer thickness of PAA and an increased one for PAH, since the adsorption of PAH is controlled by the surface charge of the previous layer [46, 47]. In this regime, f of the adsorbing and σ of the pre-deposited layer are the relevant parameters. In conclusion, the two critical parameters controlling layer growth are the linear charge density of the previously adsorbed polyion, which determines the net surface charge, and the charge density on the adsorbing polymer [46, 47].

These variations of the charge along the chain also bear implications for the internal complexation in multilayers: for PAH/PAA, the number of nonionized carboxylic groups within the film and on the surface can be varied with pH [46]. This implies also that the cross-linking density depends on the deposition pH, as was shown for PAH/PSS [88]. The stoichiometry of PAH/PSS multilayers was further derived from ellipsometry data [89], with Manning condensation for PAH suggested to be responsible for extrinsic charge compensation and leading to deviations from a 1:1 stoichiometry. From pervaporation experiments, the cross-linking density in weak polyelectrolyte multilayers was optimized at a pH value corresponding to the average of the pK_a values of both polyions involved [88].

In conclusion, the multilayer formation is not only controlled by the absolute charge density of the polyion chains. More relevant seems to be how well the polyion pair is matched in charge density.

4.5. Secondary interactions and internal hydrophobicity

Multiple electrostatic bonds causing a strong attraction are generally discussed as being responsible for the formation and stability of PEMs. However, in order to explain the phenomenological behaviour of layer formation, not only the Coulomb attraction, but additional contributions to the free energy of complexation have to be considered. These involve secondary interactions, such as hydrophobic attraction of the chains, and also entropic contributions, such as the entropy increase of counterions as a consequence of their release. Furthermore, solvent molecules from the hydration shell can be released, further increasing the entropy on adsorption.

The commonly employed polyions typically consist of a hydrophobic hydrocarbon chain as the backbone, while the charges are attached to side groups. Thus, the polyelectrolytes exhibit a pronounced amphiphilic character, and hydrophobic interactions have to be taken into account. In addition to the backbone, especially the large ring structures such as in PSS or PDADMAC are rather hydrophobic.

While on the one hand hydrophobic groups might cause steric problems, partly preventing ion complexation [15], they can on the other hand enhance the adsorption; in his theoretical approach, Kotov takes into account ionic and hydrophobic interactions [90]: the Gibbs free energy of film formation, ΔG_{SA}, is calculated from estimates of different contributions, such as the entropy of ion release, or solvent release from the hydration shell, and furthermore hydrophobic interactions. According to such calculations, for a number of polyion pairs hydrophobic interactions are essential for multilayer formation [90].

Recently, Büscher *et al* [45] performed a systematic study of the influence of hydrophobic interactions on multilayer formation by varying the deposition temperature. Under conditions where the electrostatic interactions are strongly screened (high salt concentration), the secondary interactions dominate. The layer thickness dependence on deposition temperature then reflects the influence of the hydrophobic interactions, thus their role can be followed. With increasing temperature on approaching the precipitation temperature, a linear increase of the layer thickness was found [45].

If weak forces are dominating the adsorption, this also has implications for the stability; thus, a less robust regime with an increased roughness and instability of the layers is formed after preparation at elevated temperature [45]. However, under the practical conditions commonly employed, PEMs are rather dominated by strong electrostatic attractions, while the hydrophobic parts of the chain influence the internal properties, for example the internal hydrophobicity, which is further described in the context of swelling experiments in section 5.

5. The response of multilayers to external conditions

For a number of practical applications, such as in controlled release or in separation technology, it is of interest whether the properties of PEMs can be changed by varying the external conditions, since controllable and tunable properties are required. This concerns for example the control of permeation by external parameters. In addition to this, the response of PEMs to external parameters can be analysed in terms of basic information on their internal material properties. For example, swelling experiments provide insight into the interactions within PEMs, and thus for example on the internal hydrophobicity.

5.1. Hydration and swelling in aqueous solutions

PEMs are strongly hydrated and even in the ‘dry’ state, that is, at ambient conditions in air, they contain a substantial amount of water. Early determinations of the water fraction in multilayers against air involved x-ray reflectivity [32], neutron reflectivity [33] and FTIR spectra [73]. The data result in 6–8 water molecules per ion pair for PSS/PDADMAC [73] or PSS/PAH [33], respectively, which corresponds to a weight fraction of water in the layers of the order of 10–20%. This water fraction is of great importance for the internal dynamics and stability of the interacting layers, since the coupling of the charges between subsequently deposited layers is directly controlled by the local solvent environment, that is, the water of hydration.

Multilayers exhibit a pronounced swelling behaviour, for example in the dependence on the humidity for layers in contact with air [91], or in the dependence on the salt concentration for layers immersed in aqueous solutions [17, 32, 92]. Brought into contact with water, the layer thickness of dry layers increases substantially, e.g. PSS/PAH multilayers swell by 20%–40% [33, 93, 94]. The water uptake is controlled by the internal interactions between polymer segments versus those between polymer and water molecules. In a swelling study of PSS/PAH, a Flory–Huggins parameter for the interaction of multilayers with water molecules was extracted, which corresponded to that of hydrophobic polymers [94].

Multilayers prepared from salt-free solutions and then immersed into salt solutions show further swelling relative to their thickness in salt-free solution. Small salt ions penetrate into the layers and compete with the polyion charges for binding sites, so that they can release polyion bonds and the degree of complexation decreases. Such a release of a fraction of the polyion bonds leads to a more flexible layer arrangement, which allows for hydration water uptake. For example, in repeated immersion cycles, an increase of the multilayer thickness in NaCl solutions, and a decrease after H_2O immersion, was detected [32].

In addition, salt solutions affect the film roughness due to segmental rearrangements: an equilibration of the layers was detected as a decrease of the roughness in concentrated salt solutions [32, 92]. While on the one hand this can be interpreted as an annealing process, on the other hand, porous films can be formed by subsequent exposure of multilayers to solutions of different salt content [95, 96].

Swelling properties furthermore demonstrate differences for different polyion pairs: for example the swelling ratio in NaCl solutions increases over two decades in the series PSS/PAH, PSS/PDADMAC, PAA/PDADMAC [92]. These large differences for the different polyion pairs are attributed to the fact that swelling involves salt as well as hydration water uptake. The association of polymer segments is less strong for PAA/PDADMAC, allowing strong swelling, whereas a strong complexation for PSS/PAH leads to a low swelling ratio. From this, conclusions on the internal hydrophobicity are obtained [92].

All these findings show that in spite of their high degree of complexation and their stability, PEMs can undergo large rearrangements, provided that the strength of the electrostatic interactions is reduced, as is the case in salt solutions. Similar findings apply for the variation of temperature, as described in section 4.5.

5.2. Surface potential driven properties

The alternating deposition of polycations and polyanions causes alternating external conditions for the preformed multilayers, since the surface potential of the terminating layer varies between positive and negative values. For a number of properties reversible variations with the surface potential of the terminating layer can be observed. Surface properties such as the ζ-potential are evidently determined by the terminating layer, therefore ζ is reversibly alternating; see figure 4. For example, also water contact angles alternate depending on the number of layers deposited, reflecting the surface energy of the terminating layer [47].

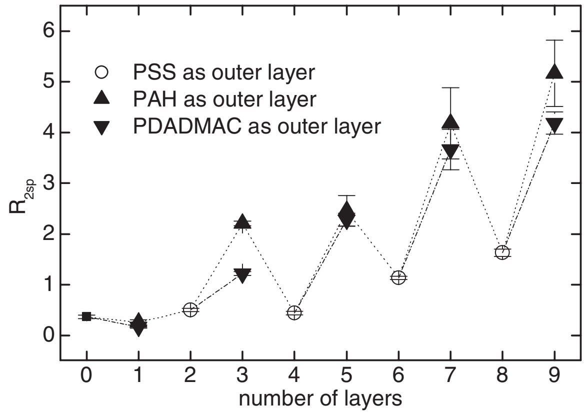

Figure 7. The specific spin relaxation rate of protons in coated colloid dispersions. Inner layers: PSS/PAH. An alternating average water mobility is driven by the surface potential.

Concerning internal multilayer properties, however, a variation with the surface potential of the terminating layer is not directly evident. As discussed in the models of section 3, the excess charge is positioned only in the outer region of the multilayer arrangement. However, these charges create an electric potential, which decays into the multilayer assembly. Depending on the sign of charge of the terminating layer, this potential alternates and can have an influence on the internal electrochemical properties.

For example, the average dissociation of carboxylic groups in multilayers was increased by a terminating polycation layer, and decreased by a terminating polyanion layer, as shown by IR spectroscopy [97]. Weak PEMs thus adjust their charge density depending on the local electrostatic environment. For one weak polyelectrolyte layer of PMA embedded into a multilayer system of strong polyelectrolytes the degree of dissociation depends on the charge of the terminating layer [50]. Such effects were studied in the dependence of the amount adsorbed in the terminating layer [50, 98]. These data formed the experimental basis of a model proposed by Finkenstadt, which describes the dependence of the internal dissociation on the outer potential [76].

Furthermore, reversible variations of the hydration water dynamics in PSS/PAH multilayers have been observed in the dependence of the potential of the terminating layer [23]. The method of solvent spin relaxation offers the possibility to sensitively monitor the average mobility of the water in aqueous dispersions; thus the hydration of polymer-coated layers can be studied [24].

For PSS/PAH layers an alternating variation of the average water mobility in its dependence on n is observed. As is shown in figure 7, these variations of water mobility can be obtained with different terminating polycations and are thus driven by the surface potential rather than the nature of the terminating layer. The data were discussed in terms of a range of possible underlying mechanisms, such as swelling, dissociation changes, or water structuring depending on the surface potential [23]. In the present case, the dissociation of the weak polyelectrolyte component PAH is not the driving force for the effect, since in a positive potential the immobilization increases, see figure 7, whereas for a dissociation effect the proton immobilization should rather decrease and lead to a reduced R_{2sp} in a positive potential. Currently, a variation of the internal porosity and its effect on the local hydration water mobility are discussed as a mechanism [99].

In this context it is interesting to note that in addition to weak polyelectrolytes, also strong polyelectrolyte pairs, where dissociation changes are not expected, can be affected by the outer potential. This is demonstrated by a second harmonic generation (SHG) efficiency alternating with the number of layers, n [100]. In addition, water mobility variations are detectable for a pair of strong polyelectrolytes (PSS/PDADMAC) as well, though with a far lower amplitude than for PAH/PSS [99].

A notable feature in all surface potential driven experiments is the fact that the decay length of the electric potential of the outer layer is rather large. In the dissociation experiments, it was estimated to ten layers [50], while in the water swelling experiments no levelling off of the swelling amplitude is observed up to 12 layers, which implies a decay length of at least 20 nm. Such large decay lengths again indicate a negligible counterion content in PEMs, as well as a large internal Debye length.

It has to be concluded that in addition to the water amount and the degree of dissociation of weak polyions, other parameters such as the porosity or the local water structure can be modified by the surface potential and affect the average mobility. In fact, the porosity of PEMs, which can easily be changed by external conditions, is currently discussed as a major parameter controlling permeabilities [95, 96, 101].

5.3. The influence of the external pH on internal properties

In PEMs brought into contact with solutions of a defined pH value, the distribution coefficient of free protons between the solution and the layer interior determines the internal, local pH value. The local pH value, which might differ from the external pH, then controls the dissociation of weak polyions in the layers. In addition, the pK_a value of a weak polyion in PEMs can be shifted relative to the solution value because of the local electrostatic environment, which might stabilize either the protonated or the deprotonated form. A shift of the local pK_a relative to the solution value was shown incorporating pH-sensitive dyes into PEMs [102]. Thus, the dissociation of weak polyelectrolytes in multilayers can be varied by changing the external conditions even after deposition [102, 103].

The dissociation equilibrium of PAH affects water mobility data as well, as shown in figure 8, where the dependence of the water immobilization in PSS/PAH multilayers on the solution pH is given. Data are given for 9 and 10 layers, respectively. The difference between the two curves gives the amplitude of the alternating behaviour of figure 7 as the difference between PEMs with a terminating polycation (PAH) or polyanion (PSS) layer, represented by the grey arrow.

In the range of $\mathrm{pH} = 6$–9, it is clearly seen that the swelling amplitude decreases with increasing pH. With increasing pH the dissociation equilibrium of the internal PAH layers is shifted towards the dissociated form: $NH_3^+ \rightarrow NH_2 + H^+$. The free protons may leave the multilayers, and under the assumption of positive excess charges in the multilayer, their concentration would be reduced. Thus the variations in water mobility can be assumed to be driven by the surface potential, while their amplitude is controlled by the density of excess polyion charges in the multilayers, which decreases with increasing pH [99].

5.4. Swelling in solvent mixtures and internal hydrophobicity

Swelling experiments of multilayers in water/alcohol mixtures provide information on the uptake of hydrophilic or hydrophobic solvent molecules from mixtures and thus serve to probe the internal hydrophobicity in layers. For example, a deswelling can be observed in ATR-FTIR spectroscopy, where an increasing polymer segment density is a measure for solvent release [104].

Further attempts to characterize the internal hydrophobicity of PEMs involve probe molecules such as pyrene: from pyrene fluorescence spectra, the dielectric properties of

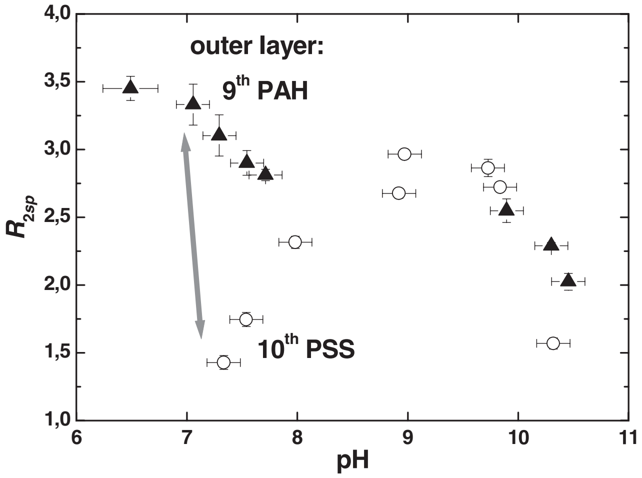

Figure 8. The dependence of water spin relaxation rates on pH value for a positively and negatively terminated layer, respectively.

Table 1. Specific relaxation rates of the alcohol C–D resonance, R_{2sp}^{CD}, for *n* layers in water/alcohol mixtures, representing the average solvent immobilization in layers and thus the hydrophobicity of the layers.

R_{2sp}^{CD}	PDADMAC/PSS	PAH/PSS
Methanol	0.9	1.2
Propanol	0.7	3.3

various polycation/polyanion combinations in *dry* layers were investigated, where PAH/PSS multilayers exhibit a lower internal polarity as compared to PDADMAC/PSS [105]. Studying various polycation/polyanion combinations by the fluorescence of incorporated pyrene probes, the internal polarity increases in the order PEI/PSS, PAH/PSS, PAH/PAA, PDADMAC/PSS [105].

In addition, the average solvent mobility in alcohol/water mixtures was studied by spin relaxation: the water and alcohol uptake into the layers was investigated by separately monitoring the 2H spin–spin relaxation rate R_2 of both molecules separately [99]. The specific relaxation rate R_{2sp} is given in table 1 for the C–D spins, i.e. the alcohol signal in a propanol/water and methanol/water mixture, respectively. R_{2sp} is proportional to the fraction of alcohol molecules immobilized in the PEMs, and further dependent on their order and mobility.

The alcohol is most strongly immobilized in PAH/PSS layers. These immobilize propanol more strongly, while PDADMAC/PSS layers have a slightly higher affinity for methanol. These results indicate a more hydrophobic nature of PAH/PSS layers, which is consistent with the conclusions obtained from pyrene spectra, and with the results from salt swelling (section 5.1). The water signal from the O–D spins is far more difficult to interpret, since it is subject to exchange processes of the deuterons with the alcohol O–D group, and furthermore also with polyelectrolyte exchangeable protons in the case of PAH.

Swelling experiments in water/alcohol mixtures studied by ATR-FTIR spectroscopy result in integrated band areas as a measure of the polymer segmental density [104]. For poly(acrylate)/poly(L-lysine) (PAC/PLL) multilayers, *deswelling* in H_2O/ethanol mixtures has been observed. The polymer segment density increases with increasing ethanol amount [104], and reaches values about twice as high as in pure water. Thus, ethanol is a bad solvent for these multilayers.

A useful parameter as a concept describing the hydrophobicity of the monomeric units is given by the number of carbon atoms per charge on the monomer, F. As can be seen from the structures in figure 1, it is $F = 8$ for PDADMAC or PSS and $F = 3$ for PAH, assuming fully dissociated chains for the latter. For multilayer assemblies, from the respective values of F, the number of ion pairs per carbon, ρ_C, can be calculated [75]. From such a picture, however, it is expected that PAH/PSS films ($\rho_C = 0.091$) are more hydrophilic than PDADMAC/PSS ($\rho_C = 0.063$). However, all the techniques discussed here deliver substantially different parameters. IR experiments yield the polymer segment density and are not sensitive to the composition of the water/alcohol mixture within the layers. NMR experiments provide estimates of the internal solvent composition, but only relative to the composition of the free phase. Pyrene data rather reflect the dielectric constant, and thus the polarity, and polarity values might be enhanced for PDADMAC due to its steric properties: close access of polyanion charges to the quaternary nitrogen atom is prohibited by the spatial requirements of the methyl groups. Therefore, PDADMAC/PSS layers can exhibit a larger charge separation and thus a larger polarity, while at the same time being more hydrophobic in terms of the parameter F as compared to PAH/PSS.

The selectivity of PEMs for water in pervaporation experiments of water/alcohol mixtures through multilayer membranes on porous supports increased with an increasing number of ion pairs per carbon in the polyion chains, that is with increasing hydrophilicity of the monomer units [75]. PAH/PSS layers for example exhibit a higher selectivity, that is preferential pervaporation for water as compared to methanol, but a lower flux as compared to PDADMAC/PSS multilayers. This was attributed to the local network structure of a multilayer assembly, with the mesh size being given by the distance of the charges, or the number of charges per atom. The more charges per carbon the layers contain, the smaller the mesh size and the lower the flux and the selectivity for water in pervaporation studies. This model employs geometric considerations only, while the molecular distribution of a binary solvent mixture in the multilayers or the internal hydrophobicity is not taken into account [75].

Altogether, the internal picture of PEMs is not yet consistent, probably since the different methods probe different parameters.

6. Dynamics: chain flexibility and local interactions

A crucial issue for refining models of multilayers is dynamic studies, for example clarifying the question whether PEMs should be considered as flexible networks, as glasses, or as solids. However, the experimental possibilities are limited and so far only few data are available. The majority of kinetic studies of equilibration processes following instant changes of external parameters, such as solvent or temperature, reveal very slow rearrangement processes, typically of the order of hours [94, 106].

Polymer chain diffusion in PEMs is extremely slow and has so far not been detected: a sample of partially deuterated multilayers was investigated by neutron reflectivity after equilibration for one year, and no differences from a fresh sample occurred. This implies that the spatial displacement is less than on the scale of the layer thickness [55]. Thus, the dynamics is frozen, probably due to the close vicinity of strongly interacting charges creating potential wells, and a glassy, quasi-frozen phase is formed [34].

Evidence of the complexation limiting the chain flexibility is given by a direct study of interactions between polyelectrolyte layer surfaces: a monolayer deposited on mica can be deformed and anneals, while a layered polyion pair does not anneal after deformation [107]. Therefore, the complexation of a polyion layer with pre-deposited layers has a large impact on the dynamics.

As already pointed out in section 3, describing the process of polyion adsorption and complexation, the outer part of a multilayer arrangement contains charged segments, which are compensated by counterions. This also has implications for the dynamics: while the inner layers are very stable and rigid due to the motional restriction of the multiple electrostatic interactions, the outer layer part is less dense and much more mobile. The flexibility of the outer region of a multilayered complex concerning chain rearrangements was demonstrated by performing temperature jumps, where a timescale of less than 1 h was needed for equilibration of the terminating layer [106].

Furthermore, flexibility of the outer layers is proven by the strength of the interaction with a model membrane consisting of charged phospholipid monolayers. Here, a strong interaction is found irrespective of the charge of the terminating polyelectrolyte layer; in comparison to a positively charged terminating layer, a negative one has similarly strong interactions with a negative lipid layer. Such results can only be explained by a complexation of the lipid layer with segments from the second last, positively charged polyion layer. This is evidence of a flexibility of the outer layer region, which is required for efficient complexation to take place [106, 108].

The high stability of PEMs, which is generally observed, is attributed to the large number of electrostatic interactions formed between polyions in subsequent layers. However, if the strength of these single interactions is decreased, the probability of desorption of a full polyion chain increases and the overall layer stability is affected. In fact, in cases of reduced polycation–polyanion interactions instable layers are found. One example is the swelling and reduction of the interaction strength in salt solution, which can eventually lead to layer deconstruction [31, 77, 109]. Kovacevic *et al* [77] have explained stability issues in terms of a phase diagram, which describes PEMs as a glassy state at low ion concentration c_{ion}, ‘liquid-like’ at higher c_{ion}, and uncomplexed at very high c_{ion}, making the assumption of thermodynamic equilibrium. The addition of polyions or salt to the ‘liquid-like’ phase then leads to a shift into a phase of soluble complexes, and thus causes layer dissolution. Such a model picture shows the sensitivity of the PEM stability on the strength of the interactions between single segments. The correlation of local interactions with overall multilayer properties is certainly a direction towards which further descriptions of PEMs should be developed.

7. Conclusion

The understanding of polyelectrolyte multilayers and the process of their formation have today reached a much higher level of detail as compared to the early phenomenological studies involving layer thickness and adsorbed amount as the main parameters. Today, the stoichiometry and the internal charge complexation are rather well understood. However, predicting overall material properties as a consequence of the internal composition and local interactions remains a challenging task, which still requires further investigations.

PEMs are complex materials with interesting properties on several length scales. On the segmental scale, they are complexed similarly to polyion complexes in solution. On a larger scale ($>$ nm) the two-dimensional stratification determines the layer structure.

In addition, the dynamics of PEMs extends over several orders of magnitude. The picture of rigid, glassy multilayers, which applies to most systems, seems to be very different for systems with exponential growth, which are very mobile. In particular the dynamic aspects and questions of equilibrium versus kinetically trapped structures deserve further investigation.

Interesting prospects are given by the possibility of understanding the internal interactions and their implication for overall layer composition and dynamics. If such an understanding is provided, controlled variations of internal interactions might in the future offer possibilities to tune dynamic properties.

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