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Self-assembled polyelectrolyte multilayers

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Abstract

Recent developments in the field of self-assembly of polyelectrolyte multilayers are presented and discussed. Fundamental studies of multilayers on planar or colloidal supports have in the past few years advanced from structural studies towards questions of the internal composition, dynamics, hydration, and interactions in multilayers. This is accompanied by new theoretical concepts and models for the multilayer assembly. Furthermore, in the past years the development of coating procedures onto colloidal templates instead of planar substrates has had a large impact on the field, leading either to the formation of new types of nanostructures, such as hollow shells with large application potential or colloid coating offered additional possibilities for fundamental multilayer studies involving volume methods. Finally, permeability studies are today an essential tool in providing an understanding of transport processes in these semi-permeable membranes, which are essential for applications such as drug encapsulation or membrane separation.

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1. Introduction

In the past decade the field of nanostructured material formation has progressed significantly. Self-assembly processes of polymers involving electrostatic interactions can be used to build-up multilayered materials with unique properties. A decade ago, Hong and Decher demonstrated the basic principle, i.e. the alternating exposure of a charged substrate to solutions of positive or negative polyelectrolytes, respectively [1]. Provided that each adsorption step leads to charge inversion of the surface, the subsequent deposition finally results in a layered complex, stabilised by strong electrostatic forces. Such self-assembled polyelectrolyte multilayers (PEMs) have proven versatile materials with respect to the incorporation of different charged compounds or nanoobjects. As building blocks for example inorganic nanoparticles, functional polymers, proteins, orientable chromophores, biopolymers such as DNA, or mesogenic units inducing local order have been used, as described in previous reviews [2–5].

The versatility of the multilayer formation process with respect to the variety of materials which can be used as building blocks, and furthermore the possibility of combination with other assembly procedures results in a high application potential in a broad range of different areas of materials development. Applications of planar layers involve the use as matrix materials for functional or biological molecular entities, e.g. for sensor applications, or as separation membranes, or as tailored surface modification. A major impact on the range of potential applications has been the coating of colloidal particles employing the technique of layer-by-layer assembly [6]. Subsequent removal of the core leads to the formation of very stable, hollow polymeric shell structures [7]. Such hollow, thin-walled microcapsules have attracted particular interest from the viewpoint of applications in encapsulation, for example as drug carrier systems, or microreactors.

PEMs are furthermore of fundamental physical interest, since they form two-dimensionally stratified layers, which are growing step-by-step into the third dimension. This leads to a behaviour being dominated by internal interfaces, and differing largely from the corresponding volume material properties. The amorphous nature of PEMs is another typical feature: while the properties of ordered monomolecular layers can easily be dominated by the amount and nature of a few defects, in disordered systems the overall amorphous nature not only deter-

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mines their properties, but also makes them less sensitive to details of the preparation process.

Theories describing PEMs today range from phenomenological descriptions of layer structure and segment distribution to mean field and scaling approaches. While the structural aspects of PEMs, e.g. the dependence of layer thickness on preparation conditions, or the internal interdigitation of adjacent layers are nowadays rather well understood, currently studied questions involve the presence of small ions in PEMs, local dissociation of weak polyelectroytes in layers, and the swelling behaviour, i.e. the amount of water and the local hydration. Of particular interest are permeabilities of planar layers or hollow capsules with respect to small ions, solvents or macromolecules.

In this review, four areas of major recent developments in the field of multilayer assemblies will be discussed. First, new developments in theoretical views of PEMs are presented. In the second part, as the main breakthrough in preparation, the deposition of PEMs onto colloidal templates with subsequent removal of the colloid is reviewed. In the third part, novel results concerning the internal composition of PEMs are given, focussing on questions of the ion content and intrinsic vs. extrinsic charge compensation. In the case of weak polyelectrolytes, the dissociation equilibrium has been investigated. Furthermore, the swelling in water or other solvents provides crucial knowledge about internal local properties. Finally, in the last part, focus is put on the properties which today appear to be the most crucial for currently developed applications of colloidal as well as planar multilayers: the permeability of multilayers for polymeric, or small molecules, for solvents or ions. Polyelectrolyte capsule permeability studies form the basis for the understanding of the release properties. On the other hand, also in planar membranes permeabilities are the essential parameters for ion or solvent separation applications.

2. Fundamental aspects and novel theoretical concepts

2.1. Salt influence on layer formation

The adsorption of PEMs from salt solutions of varying electrolyte concentration was the first approach to control layer thickness over a wide range [1]. Rather different power laws of the adsorbed amount or layer thickness in dependence of the salt concentration were found: while some authors reported a linear dependence on c_{salt} [8,9], others found the thickness to scale with c_{salt}^{α} with $\alpha = 0.5$ [10], or the adsorbed amount scaling with an exponent of 0.05–0.15 [11•].

2.2. The role of secondary interactions

Though the formation of PEMs is generally discussed as the consequence of the multiple electrostatic bonds causing a strong attraction, other attractive interactions can also contribute, such as hydrophobic interactions between polymer segments. Their influence on multilayer formation was studied by varying the deposition temperature under high salt conditions, where the electrostatic interactions are strongly screened. The layer thickness dependence on temperature reflects the effect of the hydrophobic interactions. With increasing temperature on approaching the precipitation temperature, a linear increase of the layer thickness was found [12•].

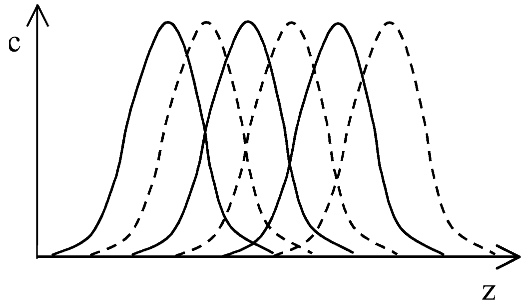

Fig. 1. Model of the segment distribution in multilayers along the surface normal. Dashed and full curves corresponding to polyanions and polycations, respectively. Redrawn according to Ref. [2].

2.3. Vertical segment distributions

In addition to the overall thickness, the question of subsequent layer interpenetration had attracted major interest. Experiments here were mainly performed by neutron reflectivity: only when superstructures with a distance of deuterated layers of more than $n > 2$ are formed, a contrast leading to interferences between reflections at internal interfaces can be observed. These results are consistent with a large overlap between the segments of adjacent layers. Since the segmental distribution of one layer is broader than the thickness, the interdigitation is large enough to result in a monomer density, which is constant along the z-axis for both polycation and anion. This behaviour has been termed 'fuzzy layers' in contrast to a 2D stratification of the layer [2], as it is for example found in Langmuir–Blodgett multilayers. The interpenetration can be described by segmental distributions of the layers along the surface normal, as shown in Fig. 1. Further techniques, such as energy transfer [13], surface force measurements [14], and electron transfer [15] were applied to determine the distribution widths, which can be viewed as internal roughness, and consistently yielded an interpenetration of one to 2.5 bilayers.

2.4. Monolayer adsorption

Theoretical descriptions of multilayer formation have first dealt with the charge inversion following monolayer adsorption to oppositely charged surfaces as a key step for multilayer formation. Joanny employed a self-consistent mean field approach for weakly charged, flexible chains for the extreme cases of high and low ionic strength: a slight charge overcompensation is found at low ionic strength for flat adsorbing chains, while at high ionic strength a strong overcompensation can be provided by loops and tails [16]. On the other hand, semiflexible chains of sufficiently high bending rigidity were described as flat adsorbing layers, where no mean field description applies. For this case, using scaling arguments, a phase diagram describing different charge reversal mechanisms in dependence of surface charge density and screening length was presented [17,18•].

2.5. Multilayer formation

The adsorption of a polyion layer to preformed multilayers differs largely from adsorption to rigid, charged surfaces. An important process is the entanglement into the outer multilayers, since this is driving the complexation and determining the segment distribution width of each layer. Electrophoretic fingerprinting [19] as well as spin relaxation and Zeta-potential studies [20] followed the formation of a polyion layer on an oppositely charged polymeric support: the results show that about one third of the charges of the terminating layer are complexing with the underlying polyion layer, the remaining charges are compensated by counterions, which can be released on adsorption of a next layer. In X-ray reflectivity experiments, an increased density in the complexation region of two subsequent layers was found, while the first layer close to the surface, and the loops of the second layer regions are less dense [21].

Based on such a complexation, Castelnovo and Joanny derived a Debye–Hückel model for multilayer formation [22••], concentrating on flexible chains. 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 shown in Fig. 2. As a result of the interpenetration and complexation in each adsorption step, the interdigitation of subsequent layers can be understood.

A simple phenomenological approach was given by Schlenoff and Dubas, who 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, i.e. the excess charge is penetrating into the multilayers [23••]. Within this model modest charge overcompensation levels were sufficient to explain large thickness increments. Both models account for the increase of layer thickness with salt concentration. Ladam et al. had described three different zones in dependence on the distance from the template surface [11•], including a precursor zone, which is influenced by the initial surface charge.

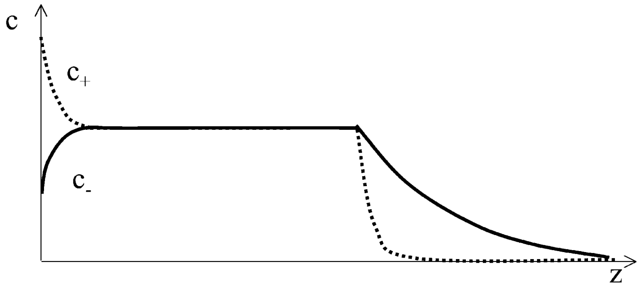

Fig. 2. Concentration profile of polycations (dashed curve) and polyanions (full curve) in the first two layers adsorbed to negatively charged substrate. Redrawn according to Ref. [22••].

2.6. Kinetics

The kinetics of multilayer formation have been addressed as well (Refs. [21,5] and references therein), and though the time scales vary largely, a common feature is a two-step process, suggesting that fast adsorption is followed by slow rearrangements at the surface: the first kinetic step involves the transport of chains to the surface by diffusion, so that adsorption due to electrostatic forces can take place. Subsequent slow chain rearrangements enable the diffusion of segments into the inner regions of the previously deposited layer. By mixing of positive and negative segments, finally the irreversible complexation of charges occurs [9,24]. The flexibility of the outer region of a multilayered complex concerning chain rearrangements was demonstrated in binding studies of charged lipids, which were strongly attracted to both, positively or negatively terminated multilayers [25].

2.7. Instability/dissolution

The complexation of a polyion layer with the previous one can even be so strong, that it leads to desorption of a soluble complex [26••]: though first an increase of the adsorbed amount occurred, typically after several minutes the adsorbed amount decreases again, consistent with the dissolution of a complex. Kovacevic et al. have explained this behaviour as equilibrium between a solid polyion complex phase and soluble complexes in solution, as viewed in the phase diagram, Fig. 3. The 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. The addition of polyions or salt to the 'liquid-like' phase then leads to a shift

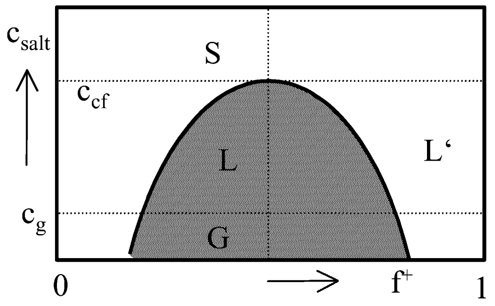

Fig. 3. Phase diagram of PEMs in dependence on fraction of positive polyion charges and salt concentration, redrawn according to Ref. [26••]. Grey region, layered complexes; G, glassy state; L, liquid layered complex; L′, soluble complex; S, soluble single chains.

into the soluble complex phase L′, and thus causes layer dissolution [26••].

PEMs have been viewed by some authors as rather soft materials, i.e. as dense hydrogels or as crosslinked gels with the crosslinking density being controlled by the charge distribution along the chain [27•,28••]. On the other hand, PEMs were described as a glassy, quasi-frozen state [22••]. Concerning the internal dynamics in multilayers, swelling and temperature changes reveal very slow rearrangement processes on the order of hours [25,29]. In fact, experimental evidence showed that multilayers are structurally similar to polyelectrolyte complexes in solution, for example concerning the vicinity and complexation of opposing charges, as shown by solid-state NMR [30•] or by IR spectra [31]. They are therefore as well 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.

3. Colloid coating and hollow shells

3.1. Preparation of coated colloids

Instead of planar substrates, colloidal particles have been coated as well, employing a method of alternating addition of polycations and polyanions with intermediate washing and centrifugation steps to remove excess polyions [6,7]. Alternatively, a protocol using ultrafiltration was developed [32]. This enabled the multilayer coating of curved surfaces in the size range of 50 nm to several micrometer (Fig. 4). Successful deposition of PEMs to colloids is typically monitored by electrophoresis and single particle light scattering [6,33••], as also shown in Fig. 5. Similar to planar PEMs, a large variability of possible building blocks was demonstrated, for example employing biopolymers [34], inorganic nanoparticles [35], or multivalent ions [36].

3.2. Shell formation by core removal

Multilayer coating of colloidal surfaces not only laid the basis for applying volume methods, such as NMR, to PEMs [20,30•,37•]. Followed by core removal, it further led to the pioneering development of hollow capsules consisting of spherical, closed thin multilayer films, which form novel materials with a large application potential. The first approaches in core removal followed the idea of using not fully crosslinked polymeric particles, which are low pH degradable [7,33••]. Such hollow capsules are semi-permeable: while small molecular species can penetrate them, they are impermeable for larger molecular weight compounds [7]. The capsule interior can provide chemical conditions different from free solution; as for example exploited in polymer synthesis in the interior [38••], in organic and

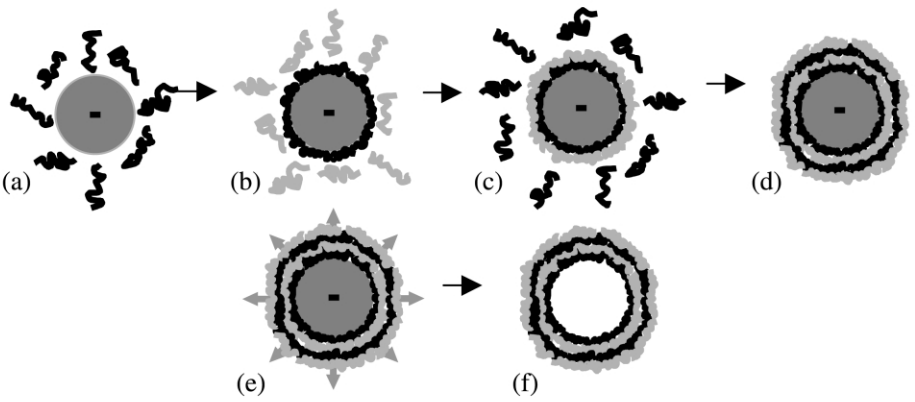

Fig. 4. Polyelectrolyte coating of colloidal particles with polycations, steps (a) and (c), and with polyanions, steps (b) and (d). Subsequent removal of the core (e) leads to the formation of hollow shells (f).

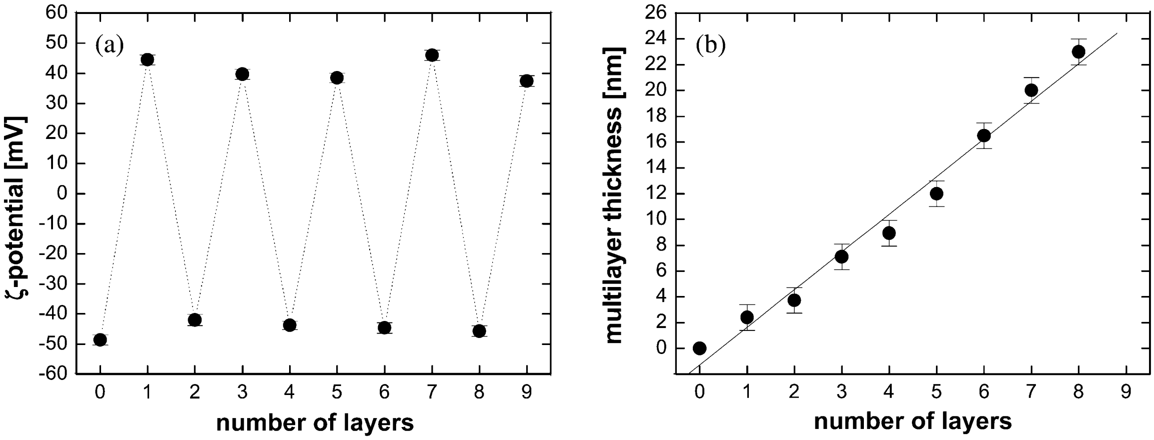

Fig. 5. Demonstration of successful alternate deposition: (a) zeta-potential alternating between positive and negative values in dependence of layer number; and (b) linearly increasing total layer thickness, as derived from single particle light scattering. Data for PSS/PAH on polystyrene latex, replotted from Ref. [37•].

inorganic crystal precipitation [38••,39], and in organic solvent inclusion [40•].

A major disadvantage was the incompleteness of core removal, and alternative templates, such as erythrocyte cells [7,33••,41], or several inorganic [35,42] or organic crystals [43,44••,45] were coated and dissolved. The variety of template materials offers the possibility of permeability studies to be performed during the process of template dissolution: for example, for coated fluorescein microcrystals the fluorescein release could be investigated by fluorescence measurements [44••]. Fluorescence microscopy experiments under the influence of osmotic pressure further formed the basis of studies of the mechanical properties of multilayer capsules, so that elasticity moduli could be derived [46••].

4. Internal composition and swelling

4.1. Strong polyelectrolytes

Chains carrying a charge on each monomeric unit are the simplest case of polyions used for multilayer buildup. The condition of macroscopic neutrality can either be fulfilled by intrinsic charge compensation, i.e. a layered complex being formed with an exact 1:1 stoichiometry of polycations and polyanions or charges might remain partially uncomplexed and extrinsically compensated by counterions. A number of investigations have dealt with these questions [2,4,5], and the possible presence of counterions has been discussed controversially: intrinsic charge compensation was claimed, since small counterions are removed during washing [12•,47]. Then, macroscopic neutrality requires a 1:1 stoichiometry in the layers. A theoretical model also assumed intrinsic charge compensation and a locally neutral complex [48••]. On the other hand, it had been argued and shown that the charge balance in PEMs involves both polyions and small ions [49••], since approximately 30% of charges are free for binding of ionic dyes into the layers [50,51].

4.2. Charge diluted chains

Following an earlier study [52] employing chains of charged and uncharged co-monomers in multilayers, the influence of the charge density along the chain on multilayer formation was investigated [53–56••]. The more recent studies employ PDADMAC with varying charge densities f along the chain, and find a threshold for layer formation at approximately 50% charged monomers. Below this value, very flat layers adsorb and charge overcompensation is hard to achieve, independent of the salt concentration [54,55]. Above the threshold charge density, layer growth is efficient and the thickness increases with salt concentration. In this regime, lower charged fractions lead to larger thickness increments, an effect attributed to the chain conformation in solution [55]. At very high charge density Glinel et al. found a regime independent of the charge density, since counterion condensation dominates the effective charge density [56••].

4.3. Weak polyelectrolytes

Of particular recent interest have been multilayers assembled from weak polyelectrolytes, where the degree of ionisation in solution—and thus the multilayer properties—can be adjusted by the solution pH value. Building multilayers from two weak polyelectrolytes, it was shown that within a certain range of pH values the pH of either polyion solution independently influences layer thickness increments [57]. Thickness increments can vary over more than an order of magnitude, where two fully ionised chains led to very thin layers, and large layer thickness values were observed when one of the polyelectrolytes was close to full dissociation [58••]. Different regimes of layer formation were identified, where the thickness increment was either controlled by the surface charge of the previous layer, or by the charge of the adsorbing polyion chain [57,58••].

The stoichiometry of PAH/PSS multilayers was concluded from ellipsometry data [59], 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 crosslinking density in weak PEMs was optimised at a pH value corresponding to the average of the pK_a values of the polyions involved [60].

In dependence of external conditions, the dissociation of weak polyelectrolytes in multilayers can be varied after deposition. This was exploited for triggering the loading and release of charged dyes into and from weak polyion films, since the internal dissociation responded to external pH conditions [61].

Measurements of the local pK_a value in multilayers were recently achieved by incorporating pH-sensitive dyes. The local pK_a of a weak polyion in multilayers was shown to be shifted relative to the solution value, and the dissociation was additionally affected by the salt concentration [62••].

4.4. Surface potential driven properties

The alternating deposition of polycations and polyanions causes alternating external conditions for the preformed multilayers. Several recent approaches demonstrated properties reversibly varying with the surface potential of the terminating layer: IR spectroscopy showed that the dissociation of carboxylic groups in multilayers was increased by a terminating polycation layer, and decreased by a terminating polyanion layer [63]. Xie and Granick systematically investigated such effects in dependence of the amount adsorbed in the terminating layer [49••,64]. Weak PEMs thus adjust their charge density in dependence of the local electrostatic environment. This explained charge regulation and the response to external parameters such as pH or electric field. These data formed the experimental basis of a model proposed by Finkenstadt, which describes the internal dissociation in dependence of the outer potential [48••].

Furthermore, the water mobility in multilayers was oscillating in dependence of the surface potential, as observed by water spin relaxation measurements. The data were discussed in terms of dissociation changes, swelling or water structuring in dependence of the surface potential [37•]. A notable feature in all surface potential driven experiments was the large decay length of the electric potential [37•,49••]. It is interesting to note that in addition to weak polyelectrolytes, also strong polyelectrolyte pairs were affected by the outer potential, as demonstrated by an SHG efficiency alternating with layer number [65].

4.5. Swelling in humid air or aqueous environment

Swelling properties of PEMs in water, salt solutions or binary solvent mixtures are not only relevant for the internal properties, that can be concluded from such data, e.g. the number of ion binding sites or the internal hydrophobicity. The swelling properties are of further substantial interest for release or separation applications, see Section 5. Earlier determinations of the water amount in multilayers against air involved X-ray reflectivity [66], neutron reflectivity [8] and FTIR spectra [31]. Recent studies systematically explored the water swelling in humid air and aqueous environment and extracted a Flory–Huggins parameter for the interaction of multilayers with water molecules, which corresponded to that of hydrophobic polymers [29].

Dubas and Schlenoff determined the swelling of PEMs exposed to salt solutions and found drastic differences in the dependence on salt concentration, from which they concluded on the internal hydrophobicity of various polyion combinations [67•]. The multilayers swell in the presence of the salt solutions, while multilayers prepared from salt solutions were swelling in water [10,11•]. In addition, salt affected the film roughness: while Dubas and Schlenoff showed an annealing of roughness in concentrated salt solution [67•], Fery et al. formed porous films by subsequent exposure of multilayers to solutions of different salt content. Porosity could alternatively be induced by a change of the environmental pH [68].

4.6. Internal hydrophobicity

Swelling of multilayers in water/ethanol mixtures was studied by ATR-FTIR spectroscopy, where a deswelling was observed, as the polymer segment density increased [69]. Such data provided information about the internal hydrophobicity. Another approach towards characterising internal hydrophobicity of PEMs was to employ probe molecules: from pyrene fluorescence spectra, the dielectric properties of various polycation/polyanion combinations were investigated and compared [70•].

5. Permeability and separation properties

5.1. Permeability of capsules

As described above, the permeability of multilayers is a crucial property with respect to the currently most promising applications of PEMs. Employing large capsules (>μm), permeability studies of dyes as model compounds could easily be performed by fluorescence microscopy [44••]. The rate of release of fluorescein from the capsule was a function of the number of layers. For most applications, a fast loading and a slow release process is desirable. Therefore, approaches have been made to tune the permeability by external conditions, and it was shown that it could be modified by pH [44••], ionic strength [71], temperature and solvent nature [43]. However, an overall understanding of permeabilities is up to now difficult to achieve, since not only molecular scale properties, but also lateral segregation and pore formation were determining the permeability. Salt and pH jumps during or after film formation induced porosity [68,72], where the lateral structures formed were regular pores [72]. While some authors claimed reversible pore formation processes at high ionic strength [71], or at low pH for a weak polyelectrolyte [73], others reported an irreversible pore formation of weak polyelectrolytes at low pH [68]. Therefore, for tailoring capsules with defined permeability, the dissolution process of the template, which involves drastic pH changes and large osmotic pressures in the capsule interior, is a very critical step.

5.2. PEMs as selective membranes for separation

Due to their extremely low thickness, and its homogeneity and tunability on molecular dimensions, PEMs are attractive materials as separation membranes for gases or dissolved species, such as ions or small organic solvent molecules. In separation applications, the general task is to develop materials, which provide a large permeation rate combined with a high selectivity. While the former is provided by the molecular dimensions of PEMs, the latter can be fine-tuned by the chemical composition.

5.3. Ions

Ion transport across multilayer films was studied by electrochemical methods [74]. Due to the low internal counterion concentration there were virtually no exchangeable ions, and the ion transport was mediated by salt ions, when layers were swollen in salt solutions. This was termed a ‘reluctant’ ion exchanger [74]. Large selectivity values were reported for different anions [75•] and cations [27•], and the permeability for ions was dependent on the solution pH [76] and on internal layer chemistry [77].

5.4. Solvent

Pervaporation of water/alcohol mixtures through multilayer membranes on porous supports provided additional insight into the internal properties: as a general rule, the water content in the permeate was higher than in the feed solution, and the selectivity increased with an increasing number of ion pairs per carbon in the polyion chains, that is with increasing hydrophilicity of the monomer units [28••]. Differences in the selectivity for water and the total flux between different polyion pairs could thus be attributed to the local network structure of the multilayer assembly, with the mesh size being given by the distance of the charges, or the number of charges per atom [28••].

6. Conclusion

PEMs are today, more than a decade after the initial development, a more exciting field of research than ever. A substantial broadening of the range of experimental techniques applied in their investigation has laid the basis for a more detailed understanding of their properties on the molecular scale, as opposed to a few years back, when still layer thickness and adsorbed amount were the main characterisation parameters. As the understanding of molecular details emerged, theories have now started to be developed and will be refined in the future. Colloid coating and core removal is probably the most important breakthrough of the past few years, and part of the field has shifted to chemical engineering tasks, optimising the constituent materials. On the other hand, fundamental investigations on capsule systems will also be of major importance, since the major tasks for the future remain the control of molecular properties by external parameters, in order to develop truly reversibly tunable materials for controlled release applications.

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•• of outstanding interest

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