Recent explorations in electrostatic multilayer thin film assembly

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Abstract

New developments in the area of electrostatic layer-by-layer assembly are reviewed, with emphasis on work in the past two years. Advances in fundamental understanding of polyelectrolyte adsorption is addressed, including the use of new probes and experimental techniques which examine final structure, film interpenetration, and control of thickness. Both theoretical and experimental studies of adsorption of weak polyelectrolytes have been addressed. The role of secondary interactions such as hydrogen bonding or dispersion forces on these parameters is a more recent area of focus. Molecular scale order has been achieved in layered films to produce noncentrosymmetric films; further control of the ordering of molecular side groups in these systems could lead to new and interesting electrical and optical properties. Finally, it has been shown that polyelectrolyte multilayers may be templated onto a number of surfaces; these materials can be patterned onto surfaces to make three dimensional microstructures, or grown on a sacrificial colloidal template to form encapsulant membranes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Electrostatic layer-by-layer assembly; Polyelectrolyte adsorption; Ionic self assembly; Polymer thin films; Patterned thin films

1. Introduction

The past decade has seen the use of non-covalent interactions as a key tool to the construction of new molecular and supramolecular architectures that cover a range of length scales. In the area of polymer thin films, the most influential area of growth in the use of non-covalent interactions is electrostatic layer-by-layer assembly, which was first introduced by Decher in 1991 [1,2]. This technique, which is based on the alternating adsorption of multiply charged cationic and anionic species, has experienced an explosion of growth in both application and theoretical and experimental advances. The popularity of the method is due to the ability to create highly tailored polymer thin films with a nearly unlimited range of functional groups incorporated within the structure of the film. This flexibility is achieved through the use of a simple, yet elegant adsorption process that is highly inexpensive, and readily accessible. The area has progressed to include the incorporation of electro-active polymers, organic dyes, semiconductor quantum dots, electrochemically active species, and a wide variety of proteins and other biosystems [3–5].

As the area of layer-by-layer (LBL) assembled films enters its 10th year, the impact on the use of layer-by-layer electrostatic adsorption in the polymer thin film area has become even more evident. New applications and a greater knowledge and control of the structure of the assembled films have been the thrust in this still-expanding research field. Closer examinations of the interactions within these systems have brought out the diversity of structures, film morphology and surface properties achieved by altering shielding and adsorption conditions. As shown

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1The reviews by Decher and colleagues [3,4] and Knoll [5] cover more comprehensively the developments from 1990 to 1997.
schematically in Fig. 1, electrostatic interactions between the polion in solution and the surface are the key to the final structure of the polion layered thin film; however, secondary, shorter range forces also play a role in determining the film thickness, the final morphology of the film, the surface properties, and in some cases, can determine whether or not stable multilayers form at all. These secondary interactions can also play a role in the selective deposition of polymers on surfaces, the formation of acentric polar structures, and the nature of permeation and ion transport within the film. An understanding of these interactions, as well as an ability to combine polions with other charged systems such as particles or low molar mass diampiphiles, lead to the development of new ordered systems, dimensional polymer structures and patterns, selective membranes, and a range of functional organic and organic–inorganic hybrid composite thin films.

In the past 2 years, a number of new advances have contributed to both the fundamental understanding of polion thin film assembly, and the use of these materials in the formation of mesoscale multifunctional materials systems. This review will address advancements gained from 1998 to the present. Areas that will be covered include fundamental studies, particularly gains made in understanding the role of electrostatics in combination with secondary interactions such as hydrophobicity, hydrogen bonding and dispersion forces in these systems. The incorporation and control of nano-to-micro scale particles in thin film composite architectures will also be covered, including the possibilities introduced by the incorporation of inorganic or organometallic functionalities. Finally, new approaches to the construction of two- and three-dimensional objects utilizing layering techniques will be addressed, and the use of electrostatic interactions, sometimes coupled with weaker non-specific interactions in directed assembly, will be discussed. Relevant examples of new applications and potential uses of multilayer films will also be addressed.

2. Advances in understanding: weak vs. highly charged systems

Until recently, a primary focus of fundamental studies on layer-by-layer adsorption was the behavior of highly charged strong polyelectrolyte chains, which can be shielded by altering ionic strength. Shielding and surface charge density effects on layer thickness and stability can be achieved in weak polyelectrolytes such as polyacids or polybases, by varying the pH and thus, affecting the relative amount of charge along the backbone. In the past 2 years, seminal works on the effects of pH on assembly of weak polions [6,7] have been published. It was found that by varying pH for the polycation and polyanion, surface charge, interpenetration between layers, and layer thickness can be dramatically altered. The most significant thing about this work is the ability to fine tune not only layer thickness, but the very nature of the polymer film, from degree of interpenetration to...
surface composition, based solely on pH. In experiments utilizing polyacrylic acid (PAA) and poly allyl amine hydrochloride (PAH) as polyanion and polycation, respectively, it was found that intermediate regimes of the PAA pH can result in very thick layers of both PAH and PAA over a broad range of PAH solution pH. Dramatic transitions in film thickness with pH have been observed over a narrow 0.5 pH range. In some cases, the film layers were so thick that the wetting angle and surface charge reflected the dominance of the topmost polyelectrolyte at the surface, unlike the highly mixed top surfaces found with thinner layers. By careful selection of pH conditions with weak polyelectrolytes, large differences in surface properties are obtained.

The effects of non-specific, hydrophobic or other interactions has been mentioned by a number of researchers as possible reasons for differences in adsorption on different types of charged substrates, or with different counterions. Kotov [8] has presented a simple free energy analysis to address and quantify the contribution of hydrophobic interactions in LBL adsorption. In this analysis, the free energy of adsorption of a positively charged polyelectrolyte to a negatively charged polyelectrolyte surface is considered to consist of several independent contributions, including the release of small counterions, partial removal of the hydration shell around both positively and negatively charged polyelectrolytes, and the formation of the polyelectrolyte complex. Finally, a free energy is associated with the liberation of structured water molecules around hydrophobic portions of the polyelectrolytes, and the gained short-range van der Waals interactions between these hydrophobic regions. The resulting analysis suggests that without the added effects of hydrophobic interactions at the surface, typical polyelectrolyte systems would not adsorb at all. This study also examines experimental evidence in the literature of LBL adsorption by Netz and Joanny [17].

Perhaps one of the fastest growing areas in the use of LBL techniques is the incorporation of electroactive and electro-optical moieties into the films. For
this reason, there has been an increasing interest in the use of these films for non-linear optical devices, hole and ion transport, and other applications in which the ordering of the chromophore itself can be critical to final properties. For this reason, perhaps one of the bigger challenges for the electrostatic self assembly community is the determination of a set of rules defining the requirements for ordered assemblies in these multilayer systems. Earlier work by Decher [1,2] determined that bolaform amphiphiles met certain requirements for perpendicular adsorption, leading to surface charge reversal, when a rod shaped molecule with aliphatic spacers and charged end groups was used. More recent studies of dye systems indicate that a large range of dyes do not necessarily fit this profile, but may form ordered films; this is particularly true of side chain polymer chromophores. The use of rigid side groups connected to a polymer main chain can enhance the tendency of the chromophores to align with respect to each other due to confinement effects, in much the same way that rigid low molar mass molecules will often exhibit liquid crystallinity when attached to a polymer main chain by an alkylene spacer group. In particular, a great deal of work has been done recently on polymers with non-linear optical chromophores. Balasubramaniam et al. [18] has constructed thin films of non-linear optical systems consisting of charged polymers with an azobenzene chromophore, and no alky spacer. These systems were the first reported to illustrate non-centrosymmetric ordered thin films without poling. Lenahan et al. [19] and Heflin et al. [20*] have also investigated the layer-by-layer adsorption of several commercially available polydyes. Tilt angles determined from SHG measurements range from 26 to 39°, suggesting that a moderate amount of molecular scale order has thus far been achieved in these films. Perhaps what is more fascinating is the presence of non-centrosymmetry in these films, which implies that these chromophores adsorb with some preference for a parallel orientation of dipoles relative to each other, rather than the usually preferred anti-parallel arrangement. In general, in these systems, SHG measurements indicate non-linear response in the range of 5–10 pM/V, comparable to poled polymer systems. Studies by Tripathy and others illustrate that the relative stability of these films is much greater than those of poled polymers, which may undergo relaxations following processing, due to the ionically cross-linked, interpenetrated network; further improvements on the signal from these systems could result in very interesting alternatives to current organic NLO materials.

Lindsay et al. [21] introduced an interesting twist in the development of acentric ordered films. To create a polar, acentric layered film with high chromophore density, this group combined a cationic polyether with a side chain NLO chromophore with an anionic main chain polymer with polar functional groups. The charges on each polymer were carefully placed so that assembly of the film would result in an ionically bound larger scale dipolar structure, as shown in Fig. 2. The assembly of a polar film was dependent on the nature of the surface; hydrophobic surfaces were required to form a film, which exhibited a non-linear response. It is thought that the polycation rearranged over the 50-min adsorption time to allow cationic groups to wet the interface with water, and hydrophobic end groups on the side group to arrange at the substrate, thus encouraging acentric order. Unfortunately, polar order appeared to decay beyond 10–20 bilayers, perhaps as surface effects became less important. What is important about this work is the use of two different molecular architectures to form a supramolecular polar system which assembles based on ionic interactions. Similar strategies might be used for a number of other layer-by-layer applications in which specific molecular scale arrangements must be accomplished.

It is apparent that order may be achieved in side group polyion systems, despite the random nature of adsorption for dilute solution. Interactions between side groups, including dispersion forces, ion-dipole and van der Waals interactions, are fundamental, and charge placement along the backbone or chromophore may also be critical to the directed assembly of ordered thin films. Main chain liquid crystalline ionomers have been used to examine the effect of
rigidity along the main chain in the structure of adsorbed films alternated with an amorphous polyanion. Such studies may lead to interesting developments in films with highly anisotropic structure within the plane of the film. An investigation of the nature of adsorption of liquid crystalline polyelectrolytes in layer-by-layer assembly is also currently underway; initial results suggest that placement of charge along the polymer backbone rather than on the chromophore can result in arrangements independent of solution pH or shielding. In these cases, the chromophore orientation is not directed by ionic attraction to the underlying or top polyanion layer, leaving the chromophore relatively free to take on arrangements, which essentially satisfy the packing requirements of liquid crystals. Chromophores containing charged groups exhibit ordering that is dependent on pH and the nature of the underlying polyanion layer (P.T. Hammond, unpublished results). In general, it appears that a second important parameter is the tether length, or spacer group between the polyanion chain and the chromophore in systems in which charge is placed on the polymer backbone; longer tethers allow a greater amount of decoupling from the arrangements of the polyanion backbone, thus allowing chromophore orientation in layers. It is important to keep in mind that in all systems reported, only averaged tilt angles have been reported, and order parameters have been fairly low. Optical measurements indicate a general trend toward orientation, rather than a highly ordered system.

Low molar mass bipolar amphiphiles also present promise in creating ordered layer-by-layer thin films. For example, recent work has been presented on charged azobenzene amphiphilic systems. Saremi and Tieke found two types of ordering resulting from co-adsorption with polyamines such as PAH, and strong polyelectrolytes such as poly(diallyl dimethyl ammonium chloride) (PDAC). In the first case, UV-visible absorption studies indicated that highly crystalline layers of azobenzene chromophores were arranged perpendicular to the surface; these highly ordered films did not undergo a trans-cis photoisomerization on exposure to UV light. On the other hand, films co-adsorbed with PDAC resulted in less ordered, smectic layers analogous to liquid crystal packing order. These systems did undergo photoisomerism, presumably due to the additional free volume provided in the film layers. In more recent examinations, Hong et al. has shown that similar azobenzene amphiphiles vary in the degree of order and the tilt angle with respect to the plane normal in multilayer films. Apparently, increased shielding of the ionic charge results in thicker bilayers of polyvinylsulfate and a trimethylammonium amphiphilic azobenzene salt. The tilt angle of the azobenzene group with respect to the normal decreases with increasing ionic strength, resulting in chromophores oriented normal to the surface. Both studies suggest that ordering is related to the formation of aggregates of the chromophore in dilute solution; however the relative arrangement of these aggregates, and the amount of free volume available for the photoisomerization process, are highly dependent on adsorption conditions. In general, additional shielding seems to promote rearrangements of the chromophore, which may be based on the preferred orientation of the hydrophobic portions of the molecule within the surrounding polyanion multilayers. These findings imply that secondary interactions can play a predominant role in orientation if electrostatic contributions are lessened in these systems. The search for control in the molecular scale order of multilayer films is still a fairly untapped area, and new investigations may open the way toward novel and interesting applications; some of these avenues would include hole transport, photorefractive, and optical switching or modulating devices. The layer-by-layer process offers high film stability and a straightforward and inexpensive processing technique with the added advantage that the need for poling might be eliminated.

4. Nano- to microparticle composites: mesoscale assembly

Amongst the most rapidly expanding areas in materials science is the synthesis, functionalization and assembly of particles and particle arrays. Nanoscale inorganic particles such as quantum dots are known for their unique electrical and optical properties due to confinement effects. On the other end of the spectrum, polymer, silica and metallic submicron-to-micrometer sized spheres are of interest as ordered arrays for photonic bandgap applications. A major goal in the materials science community is the creation of hybrid composite structures in which functional nanometer-to-micrometer sized particles or other mesoscale objects are incorporated within organic films. Since the first incorporation of clay particles and silica microspheres using alternating sequential adsorption, several new developments have been presented.

Several studies have more closely examined the importance of particle–particle and particle–surface interactions on the adsorption of charged particles from solution. For example, the alternating deposition
of colloidal particles of opposite charge has been studied utilizing polystyrene latex particles functionalized with polyacrylic acid and quaternary ammonium groups [32]; in these studies, approximately 30% surface coverage was achieved in each deposition cycle, resulting in disordered but highly porous films. The porosity in such films might be of interest in the formation of high surface area thin films. The adsorption process for latex particles on planar charged surfaces has also been studied experimentally; in this case, repulsive interactions between particles must be overcome by attractive interactions between the particle and the surface to achieve dense particle coverage. This repulsion can be modulated by introducing ionic shielding effects or varying pH [31–33]. Serizawa et al. systematically examined the adsorption of 550-nm anionically-charged polystyrene latex particles on the surface of sulfonated polystyrene (SPS)/PAH multilayer films. The top surface of the multilayer film in all cases consisted of the final PAH layer. Measurements from Quartz Crystal Microbalance (QCM) indicated that the nanosphere adsorption was greatly influenced by the adsorption conditions of the multilayer film. If the multilayers were formed at low ionic strength, the amount of nanospheres adsorbed was also low, corresponding to only 6% surface coverage at 0 M NaCl. When the polyelectrolyte film was adsorbed at high ionic content, coverage increased to a maximum of 60% coverage at 2 M NaCl. These observations correspond to shielding effects observed with polyelectrolytes, and the authors postulate that free charged segments become available for binding to the spheres when the polyelectrolytes adsorb as partially shielded loops and trains on the surface [34]; an optimal ionic strength for adsorption is observed based on these principles, and the ultimate screening of the surface.

A number of functional particles and macroscopic systems have also been incorporated into these films in the past 2–3 years. These systems include the incorporation of Au nanoparticles to create conducting films [35,36] and iron magnetite particles [37], which have been characterized for their magnetic properties. A new approach to the incorporation of metal nanoclusters involves the use of Au clusters formed within the interiors of polyamidoamine (PAMAM) dendrimer molecules [38]. He et al. utilized the nanoporous regions of dendrimers to sequester Au ions, which were later converted to Au clusters. The metal clusters were completely protected by the organic dendrimer shell from aggregation and other solvent effects. Due to the amine groups on the dendrimer surface, the dendrimer could then be co-adsorbed with a polyanion, as shown in Fig. 3. LBL assembly of these films resulted in smooth, continuous polymer films with controlled film thickness; each layer contained densely packed gold particles of uniform size (5–20 nm). Single monolayers were generally formed on each adsorption cycle. This paper introduces new approaches to the incorporation of metals to form hybrid metal–organic systems, as well as the potential to use pre-formed macromolecular chemistry as the basis for assembly and reaction within the layers. Promising directions for the future include the incorporation of Pt and Pd containing...
clusters for catalysis applications, or other metals for magnetic or electro-optic applications.

The interior regions of polyelectrolyte multilayer films have been shown to act as nanoscale reactors for the production of metallic or semiconductor particles in a study by Joly et al. [39]. By varying the linear charge density of polyacrylic acid in PAA/PAH multilayers, free acid groups remain available within the film for the complexation or ionic binding with metal ions. Silver and lead sulfide particles with 1–2-nm diameters were created within the multilayers following a simple reduction step. Blocks of PAA/PAH and PAH/SPS polion bilayers were used to create alternating regions of particle rich layers and passive film, as shown in Fig. 4. Further developments in this area are anticipated to lead to the creation of alternating layers of pure metal/polymer composite films.

Colloidal particles may also be adsorbed onto non-planar surfaces; this has been demonstrated by Dekoutchaev et al. [40*] in the adsorption of nanoscale metal colloid particles onto the surfaces of polystyrene latex beads onto which ionic multilayers were adsorbed. In this work, particles on two differing length scales are assembled to create novel catalytic surfaces. Polycation is adsorbed on the surface of 0.1–3-nm negatively charged polystyrene beads, followed by the adsorption of 20–30 Å Pd or Pt particles. A second polycation film is adsorbed on the surfaces of the metal particles. The film may be a passive protective covering, or may contain an electrochemical mediator in the catalysis process. The authors used polyelectrolyte films that can mediate the reduction of hydrogen and oxygen to form hydrogen peroxide. This application ties together the utility and ease of multilayer assembly processes with multiscale organization to achieve new organic–inorganic composite materials. There are limitless possibilities in the type of nanoparticle system that might be adsorbed onto particle surfaces. Luminescent core-shell particles have recently been created by adsorbing Cd-based nanoparticles into multilayers on similar latex spheres [41].

Numerous other metal and inorganic systems have been incorporated into layer-by-layer thin films, yielding interesting electro-optical properties or magnetic properties, including fullerene particles [42], iron oxide particles and magnetite polion composite multilayers may result in interesting materials for applications such as magnetic recording or memory [35,37,43].

5. New dimensions: two-dimensional and three-dimensional structures from layer-by-layer approaches

The LBL technique has provided a route to a large number of functional organic and organic–inorganic composite thin films. A number of applications for these films can be further enabled by the creation of two- and three-dimensional microstructures. In these cases, layer-by-layer systems move beyond the conventional realm of planar films and become the basis for patterned devices, encapsulant particles, and dimensional objects. The ability to direct the deposition of layer-by-layer films onto specific regions of a surface was introduced by Hammond and co-workers [44,45] as a means of creating patterned films. This approach eliminates the need for expensive photolithography, a process which is incongruous with the cheap costs associated with LBL, by utilizing surfaces with alternating charged and uncharged surfaces. To achieve a chemically patterned substrate, self-assembled monolayers may be microcontact printed [46,47] or applied to surfaces using writing or other techniques to form micron scale sized patterns. An ionizable surface group such as an acid terminated SAM (COOH) acts as a site for polion deposition, and an oligoethylene oxide (EG) or polyethyleneoxide surface acts as a resist to deposition of charged groups based on entropic and enthalpic penalties to adsorption in aqueous solution. The result is the build-up of uniform, regular microstructures on the surface. Feature sizes as low as 1 μm have been obtained; because the limits of this technique are bounded by the effective size of the macromolecules in solution, it is believed that much lower length scales might be achieved. More recent developments in this area include the selective deposition of weak polyamines and polyacids; a key finding is that the region of deposition of these LBL systems are highly influenced by secondary interactions and the molecular structure of the adsorbing polions [74*].
drophobic interactions in combination with hydrogen bonding with the oligoethylene glycol surface is believed to direct the polyamine, PAH, preferentially to the EG monolayer surface. Unlike PAH, linear polyethyleneimine (LPEI) has a hydrophilic, heteroatomic backbone which is thought to be hydrated at low pH values; repulsive interactions with the EG layer result in selectivity toward the COOH surface. Utilizing this knowledge, it is possible to direct specific polyion pairs to different regions of the surface. This can be demonstrated in the creation of lateral composite structures [48**], as shown in Fig. 5a. A new approach to printing on polyamine and other surfaces with oligoethyleneglycol functional oligomers has also been developed. It is possible to create multiply patterned heterostructures by printing oligoethylene glycol oligomers on the polyion patterned surface as shown in Fig. 5b. Utilizing this approach, three-dimensional heterostructures can be built on top of a surface, allowing the creation of complex systems such as transistors, or sensor arrays. Further development of these techniques should greatly expand the range of structures obtainable using electrostatic assembly, and broaden applications of these uniquely tailored thin films.

The potential for creating three-dimensional microstructures with controlled, ultrathin thickness has also been investigated by Ghosh et al. [49**] in the patterned assembly of alternating polyanhydrides and polyamidoamine dendrimers utilizing chemically patterned surfaces as templates. In this layer-by-layer process, the ionic interactions are replaced with covalent bonds and cross-links formed at high temperature between the multiple functional groups of the multiply branched dendrimer and the anhydride groups to form polyamide networks. These structures have been used to corral cells on patterned surfaces. Huck et al. [50**] have recently illustrated that these types of structures can be used as effective etch resists, and may actually be removed from the surface by etching away an underlying gold layer, obtaining dimensional micron sized objects with excellent mechanical integrity. The formation of covalently cross-linked structures can be an added advantage when considering the mechanical stability of these systems.

Of particular importance is the recently demonstrated ability to create multilayers on colloidal templates, which can later be removed to create hollow multilayer film shells [51–53**]. This has been accomplished by Caruso et al. utilizing a range of polyanion systems, including simple polyelectrolytes [51], metal-organic systems [53**] and proteins [54]. The particles, which range in size from 2 μm to 70 nm, can include polystyrene or melamine-formaldehyde resin particles. Once assembly is accomplished, the melamine-formaldehyde particles can be removed following LBL assembly on the surface, utilizing an acid etch, and leaving only the outer shell intact. A TEM image of such a hollow sphere in its collapsed state is shown in Fig. 6. These shells may be re-dispersed in water, and behave much like small particles in solution. Different sets of polyelectrolyte bilayers may be used to engineer the properties of the colloidal particles, and the interiors may be used as microreactors or drug delivery vehicles. The concept of templating layer-by-layer films onto mesoscale objects is one which brings the assembly process from the two-dimensional thin film world to the realm of three-dimensional objects.
An important aspect of layer-by-layer assembly is its universal application to organic and inorganic materials. The formation of mesoscale heterostructures can be extended to nano- to microscale particle assemblies. For example, charged silica and polystyrene latex microparticles have been selectively adsorbed onto patterned polyelectrolyte multilayer films. The packing of the spheres on the surface, and the region of preferred adsorption were altered by changing ionic strength, pH and the addition of surfactant molecules, which enhanced interparticle interactions. The resulting densely packed patterned particles on the surface may be of interest in the development of low-cost photonic structures [55*]. The ability of directing charged particles or objects of a range of sizes leads to new possibilities in the coupling of functional organic systems with inorganic elements using electrostatic, hydrogen bonding, and hydrophobic interactions.

6. Other advancement areas

There are several other areas of new growth in the layer-by-layer assembly field, as well as important advancements in promising applications. Perhaps the greatest expansion in the field has been in the area of electro and photo-active thin films. In the past 5 years, several researchers have successfully demonstrated the use of this technique in the formation of electroluminescent polymers into layer-by-layer films [56,57]. An important new emphasis in the use of LBL films in such devices is the possibility of modifying surface properties at the electrode with a few bilayers of electro-active polyion film. In this case, the bilayers act to modify injection and transport at the electrode interface, rather than as an active layer in the film. By altering the composition of the first five bilayers of film in electroluminescent polymer devices, the luminescent device efficiency can be increased by 1–2 orders of magnitude, and the light output by an order of magnitude [58]. This concept can be used with bulk film organic electroluminescent devices by coating the indium tin oxide electrode with five to six multilayers of SPS/PPV (poly-p-vinylene precursor) or similar electroactive polymers to achieve greatly improved performance [59*].

More recent investigations have included electroactive cobalt phthalocyanine films [60]. Polyalkyl viologen films have been incorporated into thin films with various polyanions, to achieve systems, which exhibit electrochemically active redox behavior. Visible and UV-Visible dyes and photochromic systems continue to be of interest [61,62] as well as the photochromic azobenzene systems mentioned earlier [25–27].

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Fig. 6. (a) TEM image of [(SPS/Fe(II)-MEPE)/SPS] coated melamine-formaldehyde particles of diameter 1.7 μm. (b) TEM and (c) AFM images of a five-layer polyelectrolyte shell obtained after decomposition of the melamine-formaldehyde template (used with permission from Caruso et al. [53**]).

3The papers by Ferreira et al. [56] and Gao et al. [57] are examples of earlier studies in electroluminescent studies with PPV precursors and with CdSe nanoparticles, respectively. Reviews by Decher and colleagues [3,4], Knoll [5] and Yoo et al. [6*] give more extensive descriptions of work in this area.
Investigations into the use of bio-specific interactions as the basis of self assembly that were initiated in the mid-1990s [63,64] have since expanded to fuller investigations of the kinetics and mechanisms of film growth within these multilayer films. For example, the highly specific binding between avidin or streptavidin with biotinylated polymers has been demonstrated and investigated [65*-67] as a means of alternating assembly. In a study by Anzai et al. [67], the effect of the polymer architecture in biotin functionalized polyamines on the loading of avidin in alternating multilayers of these two components was investigated. True monolayer adsorption can be observed with globular polyamidoamine dendrimers, whereas the use of branched polyethyleneimine led to loadings much higher than that of a single monolayer in each adsorption step. An advantage to this approach is the ability to form extremely stable, uniform films while maintaining the bio-activity of the enzyme. The specificity of the deposition approach also presents an opportunity to use biospecific interactions to direct molecules or sets of molecules to designated regions of a surface.

Formation of active and passive membranes with applications ranging from molecular separations to catalytic or enzymatic membranes has been an area of interest for layer-by-layer thin films; in this case, interesting properties might be derived from adsorption of a relatively small number of layers on a porous support. Among more recent developments, Krasemann and Tieke [68] and van Ackern et al. [69*] report that the formation of ultra thin asymmetric composite membranes on a commercial porous polymer support can be used for the separation of carbon dioxide from nitrogen. Perhaps more significant, large separation factors were also found in this study for pervaporation of ethanol–water mixtures, and promising results were found in ion-selective transport of monovalent vs. divalent cations. Sixty layer pair films of PAH/SPS were used to separate sodium from magnesium ions based on electrostatic repulsive forces within the film; separation factors — a ratio of permeation rates of the ions — of up to 100 were observed in these membranes [70]. Sun et al. [71*] have demonstrated the incorporation of horseradish peroxidase alternating with quaternized polyvinylpyrrolidine in multilayer thin films; the resulting films exhibited catalytic effects in the reduction of hydrogen peroxide.

Surface modifications have been demonstrated using polyelectrolyte complexes. Charged polyelectrolyte surfaces have been found to act as anti-fouling agents on membrane surfaces during protein separations [72], and the basic studies of the influence of solution parameters on the interactions between partially charged polyelectrolytes on polyelectrolyte surfaces have been undertaken [73]. Ultimately, the use of just two to 10 bilayers of adsorbed polyelectrolyte in the modification of surface wetting properties, adhesion, or other surface properties such as surface conductivity or ion transport may be the key to the application of layer-by-layer films in industry for the near future. An excellent example of this principle is found in the use of LBL films for altering charge transport in devices, as noted above electroluminescent devices. An industrial use has also been found for surface modification to improve wettability of contact lenses; the high stability of the polyelectrolyte complex formed resists surface rearrangements in these thin films.

7. Conclusions

The use of electrostatic layer-by-layer thin films has continued to experience an accelerated growth in the past 2 years, as a greater understanding of the effects of adsorption conditions, polyelectrolyte structure, and surface interactions has been gained. A better fundamental understanding has been gained in general in this area, with more in-depth analysis of the adsorption process, and new experimental techniques to probe the structure of multilayer films; the adsorption of weakly charged polyelectrolytes has also been more thoroughly investigated, yielding a greater appreciation for the control that might be gained in manipulating adsorption conditions.

Incorporation of particles has been a particularly important area of research in the recent past, as the variety of functional objects that may be placed in multilayer films has increased; such particles include polyelectrolyte–inorganic hybrid structures and inorganic metal sulfides and oxides. In the meantime, the number of investigations into electro-optical applications and dye chromophore systems has steadily increased, and this method has outpaced several other more traditional areas of thin films with regard to growth in the electro-optical field. Further investigation into the formation of ordered systems utilizing the principles of liquid crystal molecular design may prove fruitful in understanding how to induce order in these systems; an understanding of the effect of charge density and placement on the polymer is also critical to this goal.

In the past couple of years a better appreciation of the role of and balance between electrostatic forces and secondary interactions has been of major importance. These interactions have been utilized to alter the layer thickness or surface properties of the polyelectrolyte multilayer film. Experimental and theoretical analyses have revealed the importance of dispersion forces in the formation of stable multilayer films. Such interactions have also been fundamental to the
selective deposition of poliains and the formation of patterned polymeric microstructures and lateral composite structures on surfaces. In general, the introduction of patterning and templating of these thin films has led to creative approaches to creating three-dimensional structures, including the formation of hollow microparticles and core-shell structures. Upcoming challenges include the integration of these techniques into commercial applications. New frontiers remain in the ability to create and control the formation of dimensional structures, to explore the many possibilities in their functionalization and use, and in the ultimate creation of new mesoscale systems with these materials.

References and recommended reading

- of special interest
- of outstanding interest


[7] Shiratori S, Rubner MF. pH Dependent thickness behavior of sequentially adsorbed layers of weak polyelectrolytes. Macromolecules 2000 (in press). This paper addresses the effects of pH on the layer thickness, degree of interpenetration and wetting properties of polycryllic acid/poly allyl amine. Large variations in the nature of the thin films is obtained with pH variation of each polyion solution.


An important paper which addresses the importance of contributions of hydrophobic interactions between polyelectrolytes and the charged surface in the formation of stable layers.


This paper considers the effects of interactions between charged surfaces, polyelectrolytes and their counterions on the adsorption process, and the ion exchange process between small ions and polyelectrolytes. Experimental data are discussed with respect to theoretical considerations, and comparisons are made to polyelectrolyte complexes.


The non-equilibrium adsorption of polymer based on hydrogen bonding is addressed.


A new technique for the examination of the multilayer adsorption process and ion/polyion exchange utilizing charged fluorescent probes.


A scaling theoretical argument is presented for adsorption of polyelectrolytes on charged surfaces, charge compensation or over-compensation, and multilayer assembly.


This paper addresses the non-centrosymmetric, polar ordering of a polymer with charged non-linear optical side groups.


Examine the stability and growth of films with non-linear optical polymer chromophores. It is found that growth up to 100 bilayers is possible, while maintaining quadratic increases in second harmonic generation, suggesting acentric order throughout the structure of the film.


A novel polyeon structure is presented consisting of polycation and polyanion chromophores that form a single polar structure on formation of multilayers.


This paper presents the adsorption of nanoscale colloidal metal spheres on micron sized latex particles using the layer-by-layer process, as well as other techniques. Particles are interesting for catalysis applications.


Ionic shielding effects and polyelectrolyte-surface interactions are used to direct polyelectrolyte multilayers to specific regions of a chemically patterned surface, allowing the creation of complex polymeric microstructures.


Polyanhydrides are alternately layered with polyanimes, and resected at high temperature to produce covalently cross-linked, interpenetrated alternating multilayer films on a patterned surface. The resulting patterned films can be used to coral cells, among other applications.


Patterned polyanime/anhydride multilayers are used as etch resists for silicon/metal processing.


Latex or silica colloid particles are used as templates for the construction of multilayer films; afterward, the particle is etched or dissolved away, leaving the polyelectrolyte layer intact. The hollow microspheres created can be used for encapsulation and other applications.


This paper explores the use of patterned multilayers for patterned adsorption of closepacked monolayers of microspheres onto sur-
faces, illustrating the incorporation of polymer–microparticle composite microstructures.


This paper illustrates the enhancement of LED luminescence based on the use of assembled multilayers to improve transport properties at the electrode–polymer interface.


Explores separation properties of layer-by-layer membranes for a range of separation systems.


