



Polyelectrolyte adsorption and layer-by-layer assembly: Electrochemical control

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ABSTRACT

Thin films formed via the adsorption or layer-by-layer assembly of charged polymers are important in many sensing, energy, and biomedical applications. When the underlying substrate is a (semi)conductor, the opportunity exists to influence film formation and film properties through an applied electric potential. The recent literature on electrochemical influence of polyelectrolyte-based films is reviewed, with a focus on monolayer and multilayer film assembly and disassembly. Of particular interest are monolayer films grown to a tailored thickness on the 10–100 nm scale, and polyelectrolyte multilayer films controllably disassembled, upon application of a modest electric potential. Experimental observations are discussed in terms of governing factors such as interfacial pH and ionic composition, counter-ion correlations, charge regulation, dielectric discontinuity, and short-range polymer–polymer interactions. Recent modeling efforts are also briefly addressed.

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1. Introduction

Thin films composed of polyelectrolytes (charged polymers) offer exciting opportunities in many sensing, energy, and biomedical applications [1–4]. For example, polyelectrolyte films may be used as sensing elements (often with embedded enzymes or other catalytic species) [5–7], as solid electrolytes (in battery and fuel cell applications) [8–12], as gas phase separation membranes [13, 14], and as highly tunable cell substrates (in diagnostic and tissue engineering applications) [2–4, 15].

Thin, monolayer polyelectrolyte films may form spontaneously via solution adsorption, and thicker multilayer films may be formed by layer-by-layer (LbL) assembly, that is, the alternate adsorption of oppositely charged polymers [16, 17]. In many cases, polyelectrolyte films form on the surface of a (semi)conductor, and the opportunity exists for electric potential control over assembly/disassembly and physicochemical properties.

In this article, we review recent attempts to influence polyelectrolyte-based films through an applied electric potential. Although considerable interest has been directed toward ionic migration and electrochemical reactions within polyelectrolyte films [10, 18–24], the focus here is on cases where the film assembly and/or disassembly are controlled via

the electric potential. In Section 2, we introduce certain fundamental concepts regarding polyelectrolyte adsorption and LbL assembly. In Section 3, we review the recent literature on electric potential control of single layer adsorption, LbL assembly, and polyelectrolyte film disassembly. We discuss this body of knowledge in Section 4 in terms of governing factors such as interfacial pH and ionic composition, counter-ion correlations, charge regulation, dielectric discontinuity, and short-range polymer–polymer interactions – and provide concluding remarks in Section 5.

2. Polyelectrolyte adsorption fundamentals

The adsorption of linear polyelectrolytes has been the subject of numerous experimental [25–34], theoretical [35–50], and simulation [51–63] studies. The most studied variables are solution pH and salt concentration, with pH controlling polymer and surface charge (resulting from acid–base equilibria), and salt serving to screen electrostatic interactions and, under certain conditions, to lower effective charge by “condensing” onto the adsorbing surface or polymer chain. The following general picture results: when the charges of both polymer and surface are pH dependent, a maximum in adsorption is generally observed at a pH between the isoelectric points of the surface and the polymer. At higher (lower) pH, both surface and polyelectrolyte are negatively (positively) charged, thus inhibiting adsorption. Adsorption is also typically maximal at intermediate salt concentration. At low salt, polyelectrolytes tend to be extended in the bulk and to interact strongly with the surface, resulting in thin adsorbed layers of relatively

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low mass (per area). At intermediate salt, the polymers become more coiled due to charge screening, and the adsorbed layer mass and thickness increase. At high salt, the polymer competes less effectively with the smaller charged species for surface sites, and the adsorbed amount is therefore lower.

The influence of an applied electric potential on the adsorption of charged macromolecules has been the subject of several previous investigations (see Section 3 and Refs. [24, 64–69]). Many of these studies note adsorption behavior in apparent violation of electrostatics, with proposed mechanisms involving pH, ionic composition, and solvent structure at the interface; and macromolecular conformation and charge heterogeneity.

Charge regulation is an important but subtle feature of polyelectrolyte adsorption. The idea is that polymer (as well as adsorbing surface) charge is not fixed, but rather may change (via (de)protonation) in response to changes in the local environment, such that the system may reach a lower overall free energy. For example, Sukhishvili and Granick have reported evidence that the charge of the first few adsorbing polycations is greater than the corresponding charge in the bulk, owing to a stabilization of positive charge by the negatively charged surface [29]. They also found that at a higher adsorbed density, the charge per molecule was reduced, probably due to electrostatic repulsion among adsorbed molecules. Measurable changes in surface charge have also been reported [32].

Another important and commonly observed feature is charge overcompensation, as occurs when the charge brought to the interface by the adsorbing polymer more than compensates the charge of the initially empty surface [36, 37, 70–72]. Charge overcompensation is thought to arise from a highly correlated structure of the strongly charged adsorbing species (it is not predicted by simple Poisson–Boltzmann type theories [70, 73]). Recent simulation evidence points to the key role short-range attractive interactions may play in charge overcompensation [74].

Charge overcompensation is the basis for the electrostatically driven layer-by-layer (LbL) assembly of polyelectrolytes [16, 17]. So long as each alternating layer reverses the overall interfacial charge, a driving force exists for adsorption of the next layer [75]. New layers form through ionic binding between an incoming polymer and oppositely charged polymers within the film. Salt concentration and pH exert an influence similar to that in monolayer adsorption: solution pH near the isoelectric point of one of the polymers, and high salt concentration, results in weaker binding and extended polymer conformations (and hence thicker layers). Certain polyelectrolyte multilayer systems maintain a truly layered structure, as demonstrated by neutron reflection [76, 77]. In other cases, significant interlayer diffusion occurs. Schaaf, Voegel and co-workers have shown, in general, the thickness of striated LbL systems scale linearly with layer number, while that of strongly “intermixed” LbL systems scale exponentially with layer number [78, 79].

3. Electric potential control of polyelectrolyte films

3.1. Electric potential enhanced polyelectrolyte adsorption

We begin by reviewing work by Bearinger, et al. [80], and Brusatori, et al. [81, 82], who extended the technique of optical waveguide light-mode spectroscopy (OWLS) – an optical method yielding precise, kinetic macromolecular adsorption data – to allow for measurement under an applied electric potential. Earlier experimental work (see Section 2) had focused mainly on ex situ techniques; the development of OWLS was significant in opening the door to in situ kinetic analysis, and hence a new level of mechanistic description. Bearinger, et al. considered a block copolymer of (cationic) poly(L-lysine) and poly(ethylene glycol), together with an indium tin oxide (ITO) substrate, and found adsorption to significantly increase with applied potential: the adsorbed amount after 15 min increased from about 150 ng/cm² [2] for potentials in the range 0 to 0.8 V to about 500 ng/cm² [2] for potentials in the range 1.2 to 1.5 V (versus a Ag reference electrode) [80]. Adsorption was irreversible (reversible) in the former (latter) voltage range. The authors

attributed this behavior to a weaker, more vertically aligned polymer layer at higher potential.

Brusatori, et al., considered the adsorption of (negatively charged) albumin and (positively charged) cytochrome c onto ITO [81, 82]. They observed the initial adsorption rate of albumin, but not cytochrome c, to increase with electric potential, in agreement with simple electrostatics. However, the rate and extent of adsorption at higher coverage increased with electric potential for both proteins, suggesting weaker surface binding, more vertical surface alignment, and perhaps multilayer formation at higher potentials.

Ngankam and Van Tassel employed OWLS to study polycation adsorption onto ITO under an applied electric potential, and discovered that under certain condition, adsorption could become continuous, i.e. asymptotically linear (or nearly linear) in time over hours (see Fig. 1) [83]. Under open circuit (or a sub-threshold) potential, adsorption occurs rapidly until saturation is reached. This is the expected result, easily explained by charge accumulation at the interface suppressing subsequent adsorption. However, past a certain threshold potential, a continuous regime may occur, where adsorption is slow (compared to the upper limit imposed by the rate of transport to the surface) but steady, and saturation may be avoided over the time scale of hours. Continuous adsorption occurs over a fairly broad range of conditions, although the detailed kinetics depend on polymer chemistry, salt concentration, and pH.

An important clue toward the mechanism of continuous polyelectrolyte adsorption under an applied potential is the observed zeroth order kinetics with respect to bulk polymer concentration, suggesting surface events to be rate limiting. The question then becomes whether the surface events involve a change in interfacial charge, or whether they are purely structural. To answer this question, a series of multi-step experiments was performed, whereby continuous adsorption was halted for a period of time through a buffer rinse, and then the system was exposed to a polymer of identical or opposite charge to that adsorbed initially. (During the rinse, the adsorbed layer continued to evolve in terms of structure and charge.) The results, summarized in Fig. 2, indicate an increased (decreased) rate of adsorption when the second polymer is oppositely (identically) charged to the first layer, suggesting the magnitude of layer charge to spontaneously diminish in the absence of adsorption. The mechanism of continuous adsorption thus appears to involve a gradual loss of layer charge, enabling the additional adsorption of charged polymer, such that overall interfacial charge remains essentially constant.

The authors proposed a mechanism based on polymer–polymer binding, enabled by suppressed electrostatic repulsion due to a

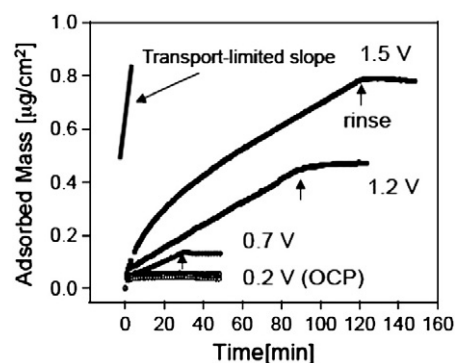


Fig. 1. Mass versus time of poly(L-lysine) adsorbing onto indium tin oxide at various applied potentials (relative to a standard hydrogen electrode, OCP = open circuit potential.) The adsorbing solution is 0.4 g/L poly(L-lysine hydrobromide) of MW 70,000–150,000 in flowing (surface shear rate ca. 1 s^{-1}) 10 mM HEPES buffer of [NaCl] 100 mM and pH 7.4. Buffer rinses appear at times marked by upward arrows. Detection is made using optical waveguide lightmode spectroscopy (OWLS). Note that the asymptotic (nearly linear) slopes (i.e. prior to the rinses) are considerably smaller than the transport limited slope (shown at upper left); the kinetics of continuous adsorption are therefore limited by events at the adsorbing surface.

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