Multilayering of a pseudo polyelectrolyte (PVPh) with a strong polyelectrolyte (PDMAC) from aqueous media

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ARTICLE INFO

ABSTRACT

The introduction of pseudo polyelectrolytes (pPE) into the field of multilayer thin films has recently been achieved with the successful combination of poly(4-vinylphenol) (PVPh) with the weak polyelectrolyte (WPE), polyallylamine hydrochloride (PAH). This paper examines the stretching of this limit by exploring the extremes of using the pPE with the strong polyelectrolyte (SPE), poly(diallyldimethylammonium chloride) (PDMAC). UV–Vis absorbance and atomic force microscopy (AFM) topography data reveal a linear growth trend in film thickness that depends critically upon the assembly pH. At an assembly pH of 11.0 the multilayer was five times thicker compared to that assembled at pH 12.0. AFM topography images also show that the surface roughness of the films increases as the assembly pH decreases.

1. Introduction

In the field of materials science there is a push towards progressively smaller, ordered, multifunctional, cheap, and easily tailored systems [1]. For 20 years multilayering of polyelectrolyte systems have been of interest in many technological and scientific areas [2–6]. Initially, polyelectrolyte multilayered systems were fabricated by mixing dilute solutions of a polycation and polyanion together. The resultant films exhibited very distinctive physical properties based upon their ionic nature [2]. However, this technique made producing thin, uniform coatings for multilayering purposes difficult [2]. Due to this inconsistency, a novel layer-by-layer deposition process, introduced by Decher, allowed polyelectrolyte systems to be created one layer at a time by repeatedly dipping surfaces into a polycation, and then a polyanion solution [7]. This allowed for thin, uniform polyelectrolyte systems of many different materials to be created. Numerous studies have been reported on the effects of a strong polyacid and polybase system, adding a salt to the polyelectrolyte aqueous solutions to help control the thickness of the adsorbed layers [8].

The layer-by-layer deposition process was extended from strong polyelectrolytes (SPE) to weak polyelectrolyte (WPE) systems. Multilayer films have been fabricated with WPE, such as poly(acrylic acid) (PAA) and poly(allylamine hydrochloride)

(PAH) and the effects of changing the pH of the system on the thickness of the layers has been measured [9–15]. It was revealed that by changing the assembly pH of the multilayering system, it was possible to create very thick or very thin bilayers based on the pK_as of the polyelectrolytes used [9–15]. It was also shown that polyaniline can be assembled in multilayers with several different polymers including poly(vinyl pyrrolidone), poly(vinyl alcohol), poly(acrylamide), and poly(ethylene oxide) which all contain functional groups that are capable of hydrogen bonding with polyaniline [16]. This result demonstrated that along with molecular weight, solution pH, and polymer type, hydrogen bonding also plays a role in influencing the thickness of the self-assembled weak polyelectrolyte layers [16].

Recently, the creation of thin films of pseudo polyelectrolytes (pPE) assembled in a layer-by-layer fashion was accomplished [17] by incorporating the pPE, poly(4-vinylphenol) (PVPh) into a multilayer system with the WPE, poly(allylamine hydrochloride) (PAH). The basis for the assembly was that phenol is considered a very weak acid (p$K_a \sim 10$), therefore polymers of 4-vinylphenol would be pPE. In addition, phenol is capable of hydrogen bonding through its hydroxyl group and the electron cloud of the phenyl ring [18,19] which can be exploited when creating multilayer systems. The introduction of very weak polyelectrolytes from aqueous media has been accomplished not only with the PVPh/PAH system [17], but with a few other cases; such as with carbohydrates [20], poly(ethylene oxide) [21], and polyamides [22]. The success of multilayering PVPh with PAH [17] encouraged us to explore the

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limits of this novel system. We decided to explore how the PVPh would behave when assembled with the SPE poly(diallyldimethylammonium chloride) (PDMAC) (Fig. 1). It was anticipated that due to the pH independent charge of the PDMAC, the layers would be thinner compared to their counterpart, PAH/PVPh system. What was discovered was this was not always the case. At certain pH values the layer thickness was virtually identical, suggesting that PVPh dominates the assembly.

2. Experimental

2.1. Multilayer film assembly

Using freshly piranha-washed quartz slides, polyelectrolyte multilayer films were assembled using a 2 mM poly(diallyldimethylammonium chloride) (PDMAC, Aldrich, M_w < 100,000) aqueous solution containing 100 mM NaCl (VWR) at the desired assembly pH, and a 2 mM poly(4-vinylphenol) (PVPh, Aldrich, $M_W \sim 8000$) with 100 mM NaCl solution of the same pH, via the layer-*by*-layer deposition technique. The first layer was created by dipping a quartz slide in the PDMAC solution for 10 min, which was followed by three consecutive washing with purified water (Millipure, Milli-Q) for 1, 2, and 2 min, respectively. The second layer was adsorbed by dipping the slide into the PVPh solution for 10 min and washing again in the same manner. This alternating dipping pattern was continued until the desired number of layers was reached. For multilayer systems comprised of three polymers, a 2 mM polyallylamine hydrochloride (PAH, Aldrich, MW $\sim$ 15,000) with 100 mM NaCl was used.

2.2. UV–Vis monitoring

The growth of the multilayered films was monitored using a Perkin-Elmer (Lambda 650) UV/Vis spectrophotometer.

2.3. AFM – topography and thickness

AFM topography images of polymer thin film samples were obtained using a Digital Instruments Nanoscope IIIa operated in tapping mode using a Si tip (300 kHz, 40 N/m). Polymer thickness was determined by making a scratch (1 cm by $\sim$100 μm) through the polymer film to the underlying glass substrate with a razor blade. Six cross sections were made across the scratch in the acquired AFM image. This provided six height profiles each with three data points. The 18 height measurements were averaged to yield the film thickness.

3. Results and discussion

For this study we examined the assembly pH values of 11.0, 11.5, and 12.0. It was previously noted that at pH 10.5 and lower, the PVPh tends to precipitate out of solution as more ambient CO_2 dissolves into the solution increasing the acidity and protonating this pPE [17]. As with the PAH/PVPh system previously reported

[17], we initially monitored film growth using UV–Vis spectroscopy. The PDMAC/PVPh system clearly revealed three distinct absorption peaks centered at $\sim$200, 225, and 280 nm which had been previously observed [17,23]. Fig. 2 illustrates the multilayer growth for PDMAC/PVPh assembled at pH 12.0 for 10, 20, 30, 40, and 50 layers, whereby the absorbance increased with each subsequent layer. A linear increase at all three adsorption peaks with each PVPh additional layer was observed for assembly pH values 11.0, 11.5, and 12.0 systems. Fig. 3 illustrates the linear trend at 200 nm.

As with the PAH/PVPh system [17], the absorbance of the multilayer system decreases as the assembly pH increases (Fig. 3). The lower absorbance at higher pH values suggests that the charge on the PVPh increases, hence less PVPh is required to interact with the highly charged PDMAC surface. At the lower pH values there would invariably be larger PVPh Gaussian electrostatic blobs [24], hence more of the phenol to absorb the UV–Vis lightwaves. These Gaussian electrostatic blobs are due to the chains not being fully stretched and thus are described as elongated chains divided into subunits [25]. The trend with pH also implies that there should exist a similar trend in film thickness, which was confirmed using atomic force microscopy (AFM). The surface morphology of the multilayer system was much rougher at lower pH values than at higher suggesting that indeed larger Gaussian electrostatic blobs are present. (Fig. 4).

Fig. 2. Absorption spectra for PDMAC/PVPh multilayer system assembled at pH 12.0.
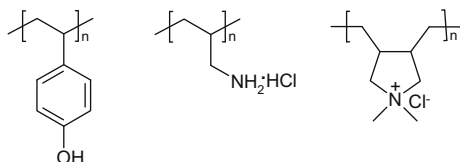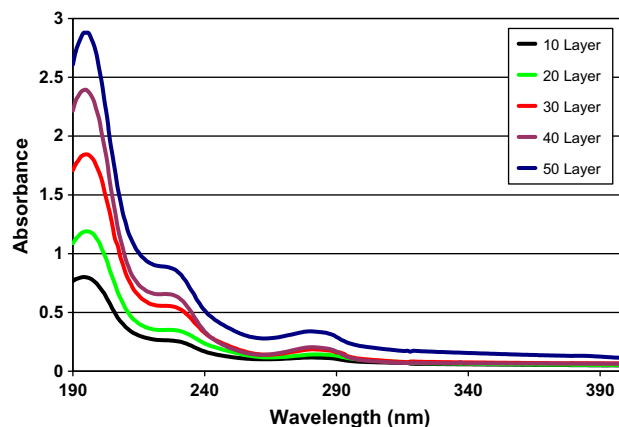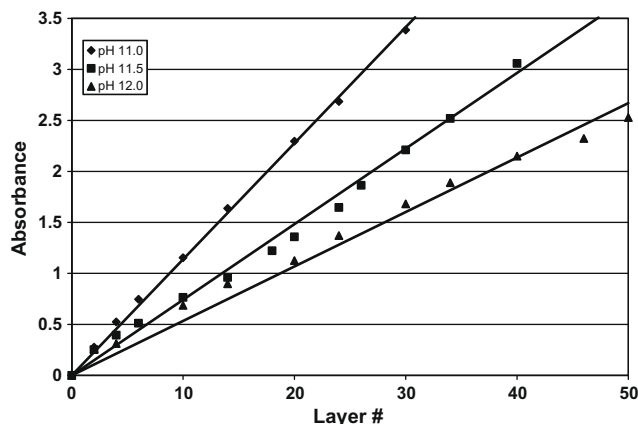
Fig. 1. From left to right, chemical structures of poly(4-vinylphenol) (PVPh), polyallylamine hydrochloride (PAH), and poly(diallyldimethylammonium chloride) (PDMAC).

Fig. 3. Absorption at 200 nm of the PDMAC/PVPh multilayer system assembled at pH 11.0, 11.5, and 12.0.