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Layer-by-layer assembly of poly (*N*-acryloyl-*N*'-propylpiperazine) and poly (acrylic acid): Effect of pH and temperature

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Abstract

Layer-by-layer assembly technique was applied to fabricate multilayer films of poly(*N*-acryloyl-*N*'-propylpiperazine) (PAcrNPP) and poly (acrylic acid). The film buildup was followed by Quartz Crystal Microbalance, and the effect of temperature and pH on the layer-by-layer assembly was investigated. Below the lower critical solution temperature of PAcrNPP, the adsorption amount increased with increase of temperature. As the pH of dipping solutions was systematically varied from 2.0 to 7.5, adsorption amount of polymers initially increased and then decreased. The relationship between adsorption amount and degree of ionization of polymers was discussed. When an eight-bilayer film was alternately exposed to HCl aqueous solution (pH = 3.5) and neutral water (pH = 6.5), the film showed pH-response, which could be the result of polymer rearrangement.

Keywords: Multilayer film; Thermo-responsive polymer; pH response; Degree of ionization; Conformation

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1. Introduction

The layer-by-layer assembly technique has played an important role in materials and surface science since 1991 [1–3]. The technique applies the alternate adsorption of complementary species to construct multilayer films in a cyclic fashion. In early works, multilayer assemblies were constructed on the basis of electrostatic force [3–7], and recently it has been demonstrated that a secondary interaction, such as hydrogen bonding [8–10], charge-transfer complexation [11], hydrophobic interactions [12] and host–guest interactions [13], can also act as the driving force. Polymer multilayer films have been constructed and studied with regard to temperature [14,15], ionic strength [16,17], or pH [18,19] responsivity and their ability to load/release small molecules [20–22] in a triggered fashion.

In recent years, water-soluble, stimuli-responsive polymers have aroused a great deal of interest owing to their potential applications in smart materials [23]. Lyon and co-workers reported layer-by-layer assembly of thermo-responsive polymer poly(*N*-isopropylacrylamide)-co-acrylic acid (PNIPAAm-co-AA) and poly(allylamine hydrochloride) (PAH) [24]. Akashi and co-workers demonstrated a thermo-responsive layer-by-layer assembly of poly(vinylamine-co-*N*-vinylisobutyramide) (PVAm-co-NVIBA) and poly(acrylic acid) (PAA) using sequential chemical reactions [25]. After these reports, a number of other systems have also been examined, such as PNIPAAm-co-AA/PVAm [26], poly(styrenesulfonate)-co-PNIPAAm/PAH-co-PNIPAAm [27], poly(*N*-vinylcaprolactam)/poly(methacrylic acid) (PMAA) [28], poly(vinyl methyl ether)/PMAA [28], PNIPAAm/PAA [29], and poly(styrene-alt-maleic acid)/poly(ethylene oxide) [30]. Multilayer thin films composed of these polymers showed a response to variations in temperature [29] or ionic strength [30].

In this article, we fabricated multilayer films using poly(*N*-acryloyl-*N*'-propylpiperazine) (PAcrNPP) and poly(acrylic acid) (PAA) as shown in Fig. 1. PAA is a pH-sensitive polymer [18,19]. PAcrNPP has low critical solution temperature (LCST) close to 37 °C [31], and it is also sensitive to pH value. Compared with PNIPAAm, PAcrNPP is a good polymer for layer-by-layer assembly because of its tertiary amino groups. We investigated the effect of temperature and pH on the layer-by-layer assembly, as well as the pH responsivity of multilayer films.

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2. Materials and methods

2.1. Materials

Poly(diallyldimethylammonium chloride) (PDDA, $M_w = 1.0–2.0 \times 10^5$ g mol^{-1}, 20 wt.% in water), poly(ethyleneimine) (PEI, $M_w = 5.0 \times 10^4$ g mol^{-1}), and *N*-propylpiperazine were purchased from Sigma-Aldrich and used as received. 3-aminopropyl-dimethylmethoxysilane was purchased from ACROS Organics. Synthesis and characterization of poly (acrylic acid) (PAA, $M_w = 2.3 \times 10^4$ g mol^{-1}) were described in Ref. [10]. Acryloyl chloride was distilled under reduced pressure and stored in a refrigerator. 1,4-Dioxane was refluxed and distilled under nitrogen over metallic sodium and was used fresh. Deionized water was used in all experiments.

2.2. Characterization

UV–vis absorption spectra were recorded with a Perkin-Elmer Lambda 800 UV–vis spectrometer using quartz slides as the substrates. Quartz Crystal Microbalance (QCM) measurements were carried out on KSV QCM-Z500 using quartz resonators. Fourier transform infrared (FT-IR) spectra were collected on a Bruker IFS 66V instrument. Scanning electron microscopy (SEM) was performed on a Shimadzu SSX-550 SEM after the surface of the polymer film had been coated with gold.

2.3. Synthesis of N-acryloyl-N′-propylpiperazine (AcrNPP)

The preparation of *N*-acryloyl-*N*’-propylpiperazine followed a literature approach [31]. *N*-Propylpiperazine was obtained by neutralizing *N*-propylpiperazine dihydrobromide with 2 M NaOH aqueous solution, followed by extraction with chloroform. The chloroform layer was dried over anhydrous magnesium sulfate. It was then filtered and evaporated on a rotary evaporator. The *N*-propylpiperazine was used fresh, as it was prone to oxidation on storage. *N*-propylpiperazine (0.01 mol, 1.27 g) and triethylamine (0.01 mol, 1.0 g) were dissolved in 300 ml dry tetrahydrofuran (THF) in a Claisen flask. The flask was cooled in an ice bath and was maintained under an inert atmosphere by passing through dry nitrogen gas. Acryloyl chloride (0.01 mol, 0.94 g) dissolved in THF (30 ml) was added dropwise for 30 min. The contents in the flask were stirred vigorously, and the reaction mixture was allowed to equilibrate to room temperature, after which the reaction was continued for 10 h. Triethylamine hydrochloride was removed by filtration. The filtrate was concentrated on a rotary evaporator. The residue was subjected to column chromatography on silica gel with CH_2Cl_2 as the eluent. The fraction was collected and evaporated to dryness. Then a yellowy liquid was obtained with 40% yield. Proton nuclear magnetic resonance in $CDCl_3$: δ 0.91 (t, 3H,–CH_3), 1.52 (m, 2H,–CH_2–CH_3), 2.31 (m, 2H,–N–CH_2–C_2H_5), 2.43(t, 4H,–CH_2–N–C_3H_7), 3.57–3.75 (m, 4H,–CO–N–CH_2–), 6.56 (m, 1H,═CH–), 6.28 (dd, 1H, CH_2═, *cis*), 5.68 (dd, 1H, CH_2═, *trans*) ppm.

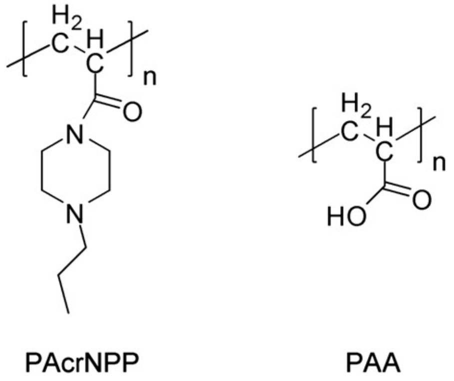

Fig. 1. Molecular structures of poly(*N*-acryloyl-*N*’-propylpiperazine) (PAcrNPP) and poly(acrylic acid) (PAA).

2.4. Synthesis of poly(N-acryloyl-N′-propylpiperazine) (PAcrNPP)

AcrNPP (5.6 mmol, 1.02 g) and 2,2′-azobis(2-methylpropionitrile) (0.02 g) were dissolved in 20 ml freshly distilled dioxane. The mixture was degassed by three freeze–thaw cycles. Polymerization was carried out at 70 °C for 24 h. The polymer was precipitated in anhydrous ether (400 ml), purified by reprecipitation and dried in a vacuum at 50 °C (yield 60%, yellowy powder). Intrinsic viscosity [η] was 2.3×10^{-2} l g^{-1} in *N*,*N*-dimethylformamide at 30 °C [31].

2.5. Preparation of multilayer thin films

Multilayer films were assembled on a variety of substrates, including quartz slides, CaF_2 plates, and Ag-coated quartz crystal microbalance (QCM) resonators. Quartz slides were cleaned with Piranha solution (98% sulfuric acid:30% hydrogen peroxide, 70/30 v/v). *Caution! Piranha solution is highly corrosive. Extreme care should be taken when handling Piranha solution, and only small quantities should be prepared.* Quartz slides were immersed in slightly boiled piranha solution for 30 min, followed by rinsing with water. Then the slides were modified with 3-aminopropyl-dimethyl methoxysilane, having an NH_2-tailored surface. QCM resonators were sonicated in ethanol and water, and dried by nitrogen gas. Then they were immersed in an aqueous solution of PDDA to adsorb a thin layer of PDDA. In the case of CaF_2, the surface was coated by adsorption of a thin layer of PEI.

The concentrations of the dipping solutions of PAA and PAcrNPP were both 0.42 g l^{-1}. The pH of PAA solution was 3.5 ± 0.1, and that of PAcrNPP solution was 7.5 ± 0.5. The pH of dipping solutions was not adjusted with HCl or NaOH, if not mentioned otherwise. The temperature of dipping solutions was maintained at 14.5 °C by water circulation, if not mentioned otherwise. A substrate was immersed into a PAA solution for 10 min and subsequently rinsed in three test-tubes with neutral water for 1 min each. In this way, the substrate was covered with a PAA layer. After each adsorption and rinsing, the substrate was blown dry with a gentle stream of N_2 for 20 s and dried in air for 3 min. The substrate was then immersed into a PAcrNPP solution, thus adding a PAcrNPP layer. Alternate adsorptions of