



Short communication

Sugar-sensitive dendrimer films as a sacrificial layer for the preparation of freestanding multilayer films

Fumiya Sato, Jun-ichi Anzai *

Graduate School of Pharmaceutical Sciences, Tohoku University, Aramaki, Aoba-ku, Sendai 980-8578, Japan



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ABSTRACT

Multilayer thin films composed of poly(vinyl alcohol) (PVA) and phenylboronic acid-bearing poly(amidoamine) dendrimer (PBA-PAMAM) were used as a sacrificial layer for constructing freestanding polyelectrolyte films consisting of poly(styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH). Freestanding (PSS/PAH)₁₅ films were successfully released from substrate by exposing composite (PVA/PBA-PAMAM)_n/(PSS/PAH)₁₅ films ($n = 5$ and 10) to sorbitol solutions under mild conditions at pH 7.0–9.0. The film release was accelerated in solutions of higher sorbitol concentrations at pH 9.0 as well as in solutions with lower concentration of NaCl. The results were rationalized based on the scission of boronate ester bonds between PBA-PAMAM and PVA in the (PVA/PBA-PAMAM)_n layer due to a competitive binding of sorbitol to PBA-PAMAM.

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1. Introduction

Layer-by-layer (LbL) thin films have been studied for the construction of sensors [1,2], bioactive surfaces [3,4], stimuli-sensitive systems [5,6], and so forth. LbL films are prepared by an alternate deposition of materials such as synthetic polymers [7,8], biopolymers [9,10], and carbon nanomaterials [11] on the surface of a solid substrate. Thus, nanometer-sized thin films with defined internal structures can be constructed on solid substrates.

Recently, freestanding LbL films have attracted much attention because of their potential use in biomedical devices [12–14]. They can be prepared by dissolving sacrificial LbL layers inserted between the film and solid substrate. In this protocol, stimuli-sensitive LbL layers that decompose in response to external stimuli, such as pH changes, temperature, salts, and photoirradiation, have been used as sacrificial layers. Hydrogen-bonded LbL layers have been extensively used for this purpose because they decompose at neutral pH [15,16]. For example, Ono and Decher have constructed freestanding LbL films using hydrogen-bonded LbL layers consisting of poly(acrylic acid) (PAA) and poly(ethylene glycol) (PEG) [15]. The sacrificial layer was constructed on a silicon substrate at pH 2.0 and the surface of the resulting PAA/PEG layer was further coated with LbL films made of poly(allylamine hydrochloride) (PAH) and poly(styrenesulfonate) (PSS). The PAH/PSS LbL film was released from the substrate by immersing the (PAA/PEG)/(PAH/PSS) film-coated silicon substrate in water at neutral pH as a result of decomposition of the PAA/PEG sacrificial layer in water. A drawback of hydrogen-bonded sacrificial layers is that they must be constructed at acidic

pH to stabilize the hydrogen bonds, which limits their applicability in the construction of freestanding LbL films containing acid-sensitive materials, such as proteins. In general, freestanding LbL films are released from the substrate under rather severe conditions such as high salt concentration [17], temperature changes [18], the use of redox reagents [19], and UV light irradiation [20]. In this context, Rubner and co-workers have recently used sacrificial layers composed of lectins (e.g., jacalin) and glycoproteins (e.g., mucin) to construct freestanding LbL films under mild conditions [21]. The jacalin/mucin sacrificial layer decomposed as a result of competitive binding of sugar to jacalin and the whole process was carried out at pH 7.4. Thus, sugar-sensitive LbL films have been proved useful as sacrificial layers for the preparation of freestanding LbL films under physiological conditions.

In the present study, we used sugar-sensitive LbL films composed of phenylboronic acid-bearing poly(amidoamine) dendrimer (PBA-PAMAM, Fig. 1) and poly(vinyl alcohol) (PVA) as a sacrificial layer for constructing freestanding PSS/PAH films. It is reported that alternate deposition of PVA and PBA-PAMAM affords LbL films through boronate ester bonding between 1,3-diol units in PVA and PBA residues, and the films decompose in response to sugars under mild conditions because of the competitive binding of sugars to PBA-PAMAM in the film [22]. The response of the PBA-PAMAM-based LbL films to sugar was higher than that of LbL films consisting of PBA-bearing linear polymers. These results suggest that PVA/PBA-PAMAM films could be used as sacrificial layers for the construction of freestanding LbL films triggered by sugars. The advantage of using synthetic materials (e.g., PVA and PBA-PAMAM) over proteins such as lectin is that possible problems arising from the contamination of proteins in freestanding films for biomedical use can be circumvented. In addition, PAMAM dendrimers are promising as component for the construction of stimuli-sensitive LbL films in view

* Corresponding author.

E-mail address: jumanzai@mail.pharm.tohoku.ac.jp (J. Anzai).

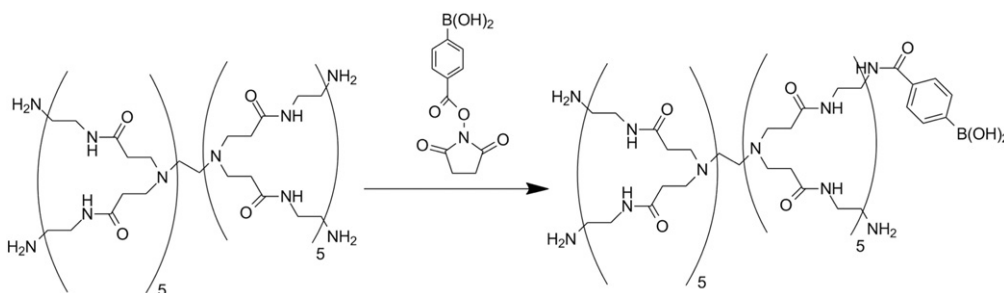


Fig. 1. Synthesis of PBA-PAMAM.

of the fact that dendrimers (e.g., 4th generation PAMAM dendrimer) bind small molecules to form inclusion complexes. In fact, dendrimer-based LbL films have been studied as scaffold for drug delivery systems [23,24]. We report here that PVA/PBA-PAMAM films can be used to prepare freestanding PSS/PAH films in the presence of sorbitol under mild conditions.

2. Experimental

2.1. Materials

PBA-PAMAM was synthesized according to a reported procedure [22]. Briefly, PAMAM (4.0th generation, ethylenediamine core, Sigma-Aldrich Co., St. Louis, MO) was reacted with *N*-hydroxysuccinimide ester of 4-carboxyphenylboronic acid [22] in water for 12 h at room temperature. PBA-PAMAM was purified by dialysis in water using a Spectra/Por®6 dialysis membrane (molecular weight cut-off: 3500; Spectrum Lab. Inc., Rancho Dominguez, CA). Thus, a PBA-PAMAM sample was obtained in which PBA residues were attached to 32 mol% of the primary amino groups in PAMAM, as determined by the UV absorption spectrum. PVA (average molecular weight: 22,000) was purchased from Wako Chemical Co. (Osaka, Japan) and used without further purification. All other reagents used were of reagent grade, which were obtained from commercially sources.

2.2. Preparation of LbL films

LbL films composed of (PVA/PBA-PAMAM)_{*n*}/(PSS/PAH)₁₅ layers (*n* = 5 and 10) were prepared on the surface of a quartz slide (50 × 50 × 1 mm³), which had been cleaned in a mixture of sulfuric acid and chromic acid. The inner (PVA/PBA-PAMAM)_{*n*} layers serve as a sacrificial layer, while (PSS/PAH)₁₅ layer is released as freestanding film. A quartz slide was immersed in 0.1 mg mL⁻¹ PVA solution (10 mM 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid, HEPES, pH 8.0) to deposit the first PVA layer and rinsed in buffer solution for 5 min. The PVA film-coated quartz slide was subsequently immersed in 0.1 mg mL⁻¹ PBA-PAMAM solution (10 mM HEPES, pH 8.0) for 15 min to deposit PBA-PAMAM. After being rinsed, the second PVA and PBA-PAMAM layers were similarly deposited. The procedure was repeated to build up the (PVA/PBA-PAMAM)_{*n*} films. (PSS/PAH)₁₅ film was further deposited on the surface of the (PVA/PBA-PAMAM)_{*n*} layer using 1 mg mL⁻¹ PSS (10 mM HEPES, pH 8.0) and 1 mg mL⁻¹ PAH (10 mM HEPES, pH 8.0) solutions. The deposition and rinsing times in the preparation of the (PSS/PAH)₁₅ layer were 5 and 1 min, respectively. The deposition of the films was monitored by recording UV-visible absorption spectra of the film-deposited quartz slide.

2.3. Sorbitol response of (PVA/PBA-PAMAM)_{*n*} films

(PVA/PBA-PAMAM)_{*n*} films were deposited on one side of cleaned quartz slide (50 × 9 × 1 mm³) at pH 8.0 in a similar manner. The slide was placed in a quartz cuvette (optical path length, 10 mm) filled with a sorbitol solution. The slide was placed near the sidewall of the

cuvette in parallel to the light path so as to avoid blocking the incident light. The absorbance of the sorbitol solution was monitored at 242 nm with gentle stirring, which enabled us to estimate the amount of decomposed film components dissolved in the solution. All measurements were carried out at room temperature (ca. 23 °C).

2.4. Preparation of freestanding films

Quartz slides (50 × 50 × 1 mm³) coated with LbL films composed of (PVA/PBA-PAMAM)_{*n*}/(PSS/PAH)₁₅ layers (*n* = 5 and 10) were immersed in sorbitol solutions (pH 7.0, 8.0, and 9.0) and occasionally gently shaken to release the film from the substrate. The concentrations of sorbitol and NaCl in the bathing solutions were systematically varied.

2.5. Atomic force microscope (AFM) observation of LbL films

AFM images of the films were taken on AFM (SPM-9600, Shimadzu Co. Kyoto, Japan) in contact mode at room temperature in air. To estimate the thickness of LbL films, (PVA/PBA-PAMAM)₅ and (PVA/PBA-PAMAM)₅/(PSS/PAH)₁₅ films were prepared on a glass slide (diameter, 15 mm). The film-coated glass slide was dried for 24 h in a desiccator. Film thickness was determined by scratching the film-coated glass slide with a blade and scanning over the scratch.

3. Results and discussion

Fig. 2 shows the UV-visible absorption spectra of (PVA/PBA-PAMAM)₅/(PSS/PAH)₁₅ films. For (PVA/PBA-PAMAM)₅ layers, absorption bands at 242 nm originating from PBA-PAMAM increased with increasing numbers of PVA/PBA-PAMAM bilayers, confirming that the (PVA/PBA-PAMAM)₅ multilayers were deposited on the quartz slide. It is clear that the multilayer films were formed through boronate ester bonding between PVA and PBA-PAMAM [22]. A further increase in the absorption intensity of the spectra was observed at 222 nm when (PSS/PAH)₁₅ layers were deposited. The absorption band at 222 nm is ascribed to the aromatic ring of PSS in the films. The results showed

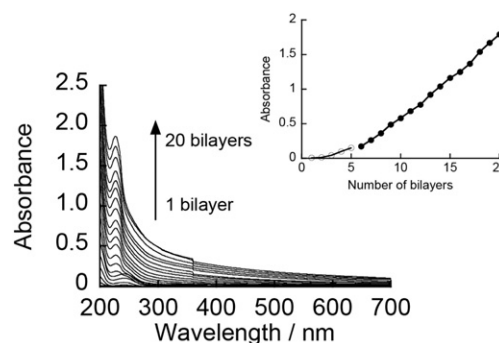


Fig. 2. UV absorption spectra of (PVA/PBA-PAMAM)₅/(PSS/PAH)₁₅ films. (inset) Absorbance of the films at 242 nm for the 1st–5th bilayers and at 222 nm for the 6th–20th bilayers as a function of the number of bilayers.

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