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Dendronized polymer as building block for layer-by-layer assembly: Polyelectrolyte multilayer films for incorporation and controlled release of water-insoluble dye

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Abstract

The multilayer films of the carboxylic acid terminated Fréchet-type dendronized polymer (denpol) and poly(diallyl-dimethylammonium chloride) (PDDA) were fabricated using the electrostatic layer-by-layer (LbL) assembly technique on planar substrates. The influence of pH and ionic strength of the polyelectrolyte dipping solutions on the fabrication of the PDDA/denpol multilayer films has been investigated in detail. AFM images showed that pH of the polyeletrolyte dipping solutions can obviously influence the surface morphology and roughness of the denpol layer in the multilayer films. We also use a preassembly method for incorporating water-insoluble molecule of pyrene into interior of denpol, and then fabricate the PDDA/pyrene-loaded denpol multilayer films. Moreover, we demonstrated that the loaded pyrenes can be released from the LbL films, which can be controlled by ionic strength of immersing solutions. Interestingly, the pyrene-released multilayer film can be used to reload pyrene when immersing the pyrene-released film into a saturated aqueous solution of pyrene.

Keywords: Controlled release; Dendronized polymer; Layer-by-layer assembly

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1. Introduction

Layer-by-layer (LbL) assembly technique has been a versatile and inexpensive method for fabricating multilayer thin films with tailored structure and composition [1–3]. Numerous substances, such as oligo-charged dyes [4–7], inorganic compounds [8,9], polyelectrolytes [10], photoreactive species [11], thermoresponsive materials [12,13], colloids [14,15], biomacromolecules [16–21] and water-insolube polymer [22–26], have been assembled successfully into the multilayer films to achieve the material functionalization, such as controlled release, separation, drug delivery, and optical or electronic properties. Recently, a new strategy for fabricating functional multilayer films based on a combination of preassembly for incorporating water-insoluble molecules and LbL assembly has attracted special interest [27–31]. For example, Glinel and co-workers reported on the buildup of the multilayer films of poly-(ethyleneimine) (PEI) and carboxymethylpullulan (CMP) derivatives, which can trap the hydrophobic dye, Nile Red in the procedure of preassembly, and systematically studied the loading and the release behavior of the films [27]. Zhang et al. described the use of block copolymer micelles as building blocks for the incorporation of water-insoluble photochromic species and the fabrication of the multilayer films by LbL assembly of the block copolymer micelles of poly(styrene-*b*-acrylic acid), incorporating azobenzene and PDDA [29].

Dendronized polymers (denpols) can be considered as a new kind of comb polymers, consisting of a polymeric backbone with the dendrons being attached to each repeat unit, and have attracted high interest in recent years [32–36]. Based on the concept of ‘‘unimolecular container’’ [37], denpols exhibit

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more steady structures and possess efficient solubilizing power to guest molecules in solution [38]. To our best knowledge, the reports on the LbL assembly of denpol haven't been found. Moreover, it can be also anticipated that the host–guest property of denpol could be retained by control of polyelectrolyte interaction. In this paper, we used the water-soluble carboxylic acid terminated Fréchet-type dendronized polymer (see Fig. 1) to construct multilayer films with poly(diallyl-dimethylammonium chloride) (PDDA), and investigated the influence of pH and ionic strength of the polyelectrolyte dipping solutions on the formation of the multilayer films. Moreover, we attempted to fabricate the multilayer films of PDDA and the pyrene-loaded denpol, and wondered if the incorporated pyrene can be released from the multilayer films and pyrene can be incorporated again into the multilayer film under some conditions.

2. Experimental section

2.1. Materials

The structure of denpol used in the present work is shown in Fig. 1. The styrene-type dendritic macromonomer was synthesized by condensation of 3,5-bis(methyl benzoate-4′-methyleneoxyl)benzyl bromide with 4-vinylbenzyl-3′,5′-dihydroxybenzyl ether. After radical polymerization, the resultant dendronized polymer underwent hydrolysis. Water-soluble denpol with peripheral carboxylic acid groups was obtained, and the molecular weight (M_w) was 339 300 [37,39,40]. The detailed synthesis procedure and characterization of the denpol will be published elsewhere. PDDA (M_w 250 000) and pyrene (purity > 99%) were obtained from Aldrich Co. The chemical structures of the polyelectorlyte monomer units are shown in Fig. 1. Ultrapure water (Millipore) with a resistivity of more than 18 MΩ cm was used in all experiments. All other Chemicals are purchased from Beijing Chemical Reagent Co and used without further purification.

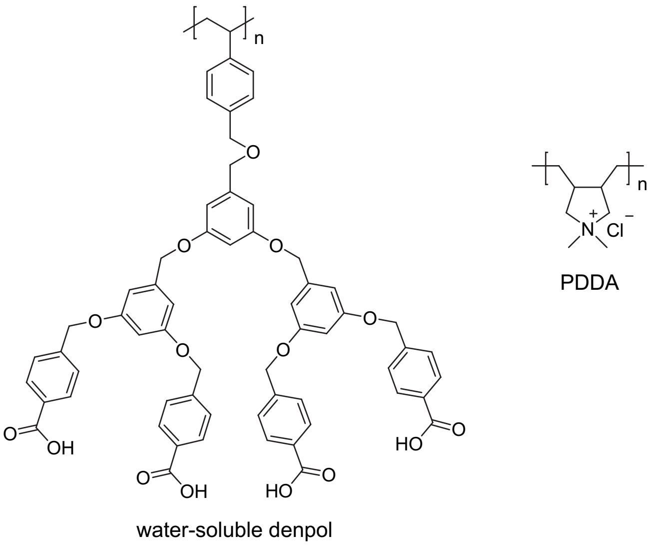


Fig. 1. Chemical structures of water-soluble denpol and PDDA.

2.2. Substrates preparation

Quartz slides and silicon wafers were cleaned by 3:7 (vol%) H_2O_2/H_2SO_4 (piranha solution) at 100 °C for ca. 40 min, followed by sonication in Milli-Q water for 1 h, and then extensively rinsed with Milli-Q water. (Caution: piranha solutions are very aggressive, corrosive solutions, and appropriate safety precautions should be utilized including the use of acid resistant gloves and adequate shielding.) After these cleaning procedures, the substrates were completely hydrophilic and kept immersed in Milli-Q water until used.

2.3. Preparation of multilayer films

All polyelectrolyte solutions were prepared by dissolving the polymers in ultrapure water at a concentration of 0.2 mg/mL. The pH of the polyelectrolyte solutions was adjusted using 0.01 M HCl and KOH, and ionic strength was adjusted using NaCl. Preparation of the pyrene-loaded denpol solution was shown as follows. An excess amount of pyrene was sonicated at 50 °C for 2 h in the above denpol aqueous solution ($pH = 8$) and allowed to stay at room temperature for 48 h. The resulting saturated solution of pyrene was filtered with 0.45 μm filters. In accordance with the UV absorbance and molar absorption coefficient of pyrene in saturated solution, the amount of pyrene incorporated into the denpol was determined as around 1.2 wt% [37].

Multilayer films were fabricated on precleaned substrate by sequential deposition of polyanions and polycations. Hydrophilized substrates was first immersed into PDDA aqueous solution for 10 min and washed with Milli-Q water. After the deposition and washing processes, the slide was dried with a nitrogen stream. Then the resulting substrate with a single layer of PDDA was immersed into a solution of denpol or pyrene-loaded denpol for 10 min to add a polyanion layer, and subsequently followed by washing and drying procedures. By repeating the above two steps in a cyclic fashion, the PDDA/denpol or PDDA/pyrene-loaded denpol multilayer film was fabricated. A film obtained by dipping the substrate n times in the solutions of polycation and polyanion, respectively, will be denoted by $(\text{polycation/polyanion})_n$ in the following.

2.4. Release and reloading experiment

The $(\text{PDDA/pyrene-loaded denpol})_{10}$ films deposited on quartz slides were immersed into a NaCl aqueous solution at room temperature, which was frequently replaced by a fresh one to ensure constant release conditions. For the reloading experiment, the pyrene-released film was exposed to the saturated aqueous solution of pyrene, and after 2-h immersion the pyrene-re-loaded film was washed with Milli-Q water to remove the dye molecules weakly adsorbed on the surface and dried with a nitrogen stream. The release behavior, monitored by Fluroscence spectroscopy, was studied as a function of immersion time.

2.5. Instruments

UV–vis spectra were obtained on a Shimadzu model UV-1601PC spectrometer. Fluorescence spectra were recorded on a Varian Cary-Eclipse spectrophotometer at room temperature. The excitation wavelength used throughout the experiments was 330 nm, and the excitation and emission slit widths were adjusted to 20 and 10 nm, respectively. The quartz slides were placed perpendicular to the beam using a slide holder to maintain the same position during each measurement. Atomic force microscopy (AFM) images were taken with a commercial instrument, Nanoscope IV. The tip involved was Si_3N_4 cantilever (Park Scientific, CA) with a nominal spring constant of 0.06 N/m for tapping mode. The AFM images of the denpol in film were obtained with tapping in air. Samples were prepared on precleaned silicon wafers (as described earlier).

3. Results and discussion

Our initial experiment concentrated on the LbL assembly of PDDA and denpol. In general, a 10-min immersion ensures that the deposition of polyelectrolyte reaches saturation. The $(PDDA/denpol)_{10}$ multilayer film were fabricated by alternately immersing a quartz slide into the PDDA and denpol solutions at pH 6 followed by UV–vis absorption. Fig. 2 shows the UV–vis spectra obtained for the $(PDDA/denpol)_{10}$ film after each adsorption step. The absorption bands at ca. 228 and 275 nm are identified as the π–π* and n–π* transitions of the phenoxy and carbonyl groups in the denpol, respectively. As shown in the inset of Fig. 2, the absorbance of quartz-supported multilayer film at 228 nm was plotted as a function of layer number in a linear fashion basically except for the first three bilayers, which is very similar to the result reported in literature [30].

To investigate the effect of the pH of PDDA and denpol solutions on the LbL assembly of the multilayer film, a series of dipping solutions with various pH were applied to fabricate 10-bilayer multilayer films, and the deposition behavior of the denpol in multilayer fabrication was monitored by UV–vis spectra. Fig. 3 displays the absorbance at 228 nm of these (PDDA/denpol multilayer) films as a function of the pH of the dipping solutions. A quick survey revealed that the deposition amount of the denpol is dramatically influenced by the pH of the polyelectrolyte dipping solutions. The similar behavior has been found in the fabrication of the PDDA/poly-(acrylic acid) (PAA) multilayer films with various polyelectrolyte solutions' pH [41,42]. Similar to the mechanism of the PDDA/PAA multilayer fabrication, the absorbance trend of the PDDA/denpol multilayer films might be rationalized in the following manner.

As shown in Fig. 3, when the pH of the PDDA dipping solution is held constant, the absorbance of the multilayer films decrease with the increase of the pH values of denpol solutions. It is known that the denpol with dendrons of the second generation adopts a semi-flexible rod conformation [43]. Because of abundant carboxylic acid groups peripherally, denpol becomes highly charged polyanion and possesses an expanded molecular conformation at higher pH conditions. The peripheral carboxylic acid groups become partially protonated in the solution with relatively low pH, in which case the denpol molecule prefers to adopt a curled conformation. When the denpol molecules deposit on an oppositely charged surface, these molecules are believed to maintain the same conformation as that in solution. Based on the interlayer charge compensation and the curled conformation of denpol, larger deposition amount should be found at lower pH of the denpol dipping solution.

Moreover, when the pH of the denpol dipping solution is held constant, the absorbance of the multilayer films increase with the increase of the pH of the PDDA solutions (Fig. 3). Since PDDA is a strong basic polyelectrolyte and has a high positive charge at all pH values, it is considered that the polycation property of PDDA may hardly be affected by the pH of the solution [44]. According to previous literature [45], the deposition amount of the polyelectrolyte depends primarily on

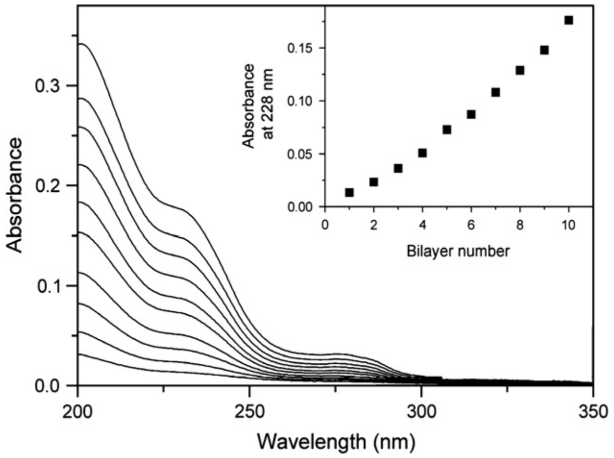


Fig. 2. UV–vis spectra of the $(PDDA/denpol)_{10}$ multilayer film, (inset) plotted as film absorbance at 228 nm versus the bilayer number. Both of the denpol and PDDA dipping solutions were adjusted to pH 6 using 0.01 M HCl.

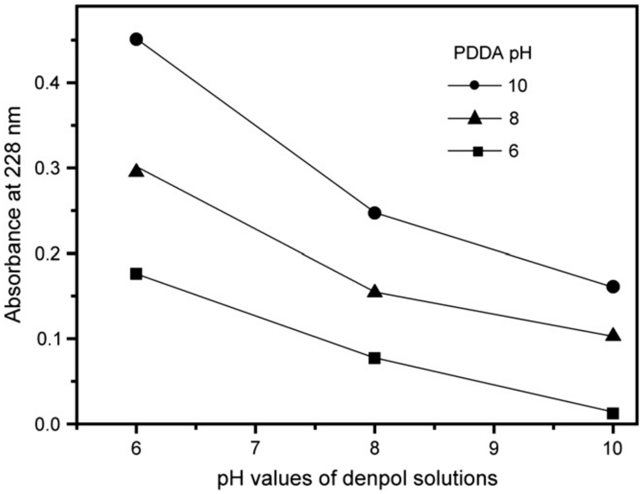


Fig. 3. Dependence of absorbance of a series of the $(PDDA/denpol)_{10}$ multilayer films at 228 nm on the pH of the polyelectrolyte solutions. The pH of the polyelectrolyte solutions was adjusted using 0.01 M KOH or HCl.

the charge density (or ionization degree) of the outmost layer and not on the thickness, conformation of the previously deposited polymer layer. Therefore, the change in trend of absorbance can be ascribed to the influence of the PDDA dipping solution pH on the ionization of the surface denpol layer of multilayer film, which was consistent with the observed fact of the PAH/PAA multilayer films to some extent [42]. That is to say, when the multilayer film with the outmost layer of denpol is immersed into the PDDA solution, the pH of the PDDA solution influences the ionization degree of the free carboxylic acid groups on surface of the multilayer film. Under relatively high pH, the denpol is highly ionized, and more PDDA with positive charges are deposited on the denpol surface to compensate these negative charges. Spontaneously, more PDDA results in more deposition amount of the denpol, when depositing denpol molecules on the PDDA surface in next deposition cyclic step.

To testify our assumption of the influence of the dipping solution pH on the deposition behavior of the denpol, atomic force microscopy (AFM) was employed to observe the surface morphologies of the denpol layer of the 1-bilayer and 10-bilayer multilayer films fabricated under various pH conditions. As indicated by AFM images in Fig. 4A and B, we can see clearly that there is obvious distinction in surface morphology between these two (PDDA/denpol)$_1$ films constructed by alternate deposition in different denpol dipping solutions at pH 6 and 8, respectively. AFM image in Fig. 4A displays many annular-like structures assembled on the surface uniformly, and the length and border widths of these annulations are around 50 and 8 nm, respectively, which can correspond with the size of individualized denpol molecules. However, AFM image in Fig. 4B shows some more spreading strip-like structures. These two surface layers observed in Fig. 4A and B are smooth and uniform with root-mean-square roughness of ca. 0.57 and 0.25 nm (over

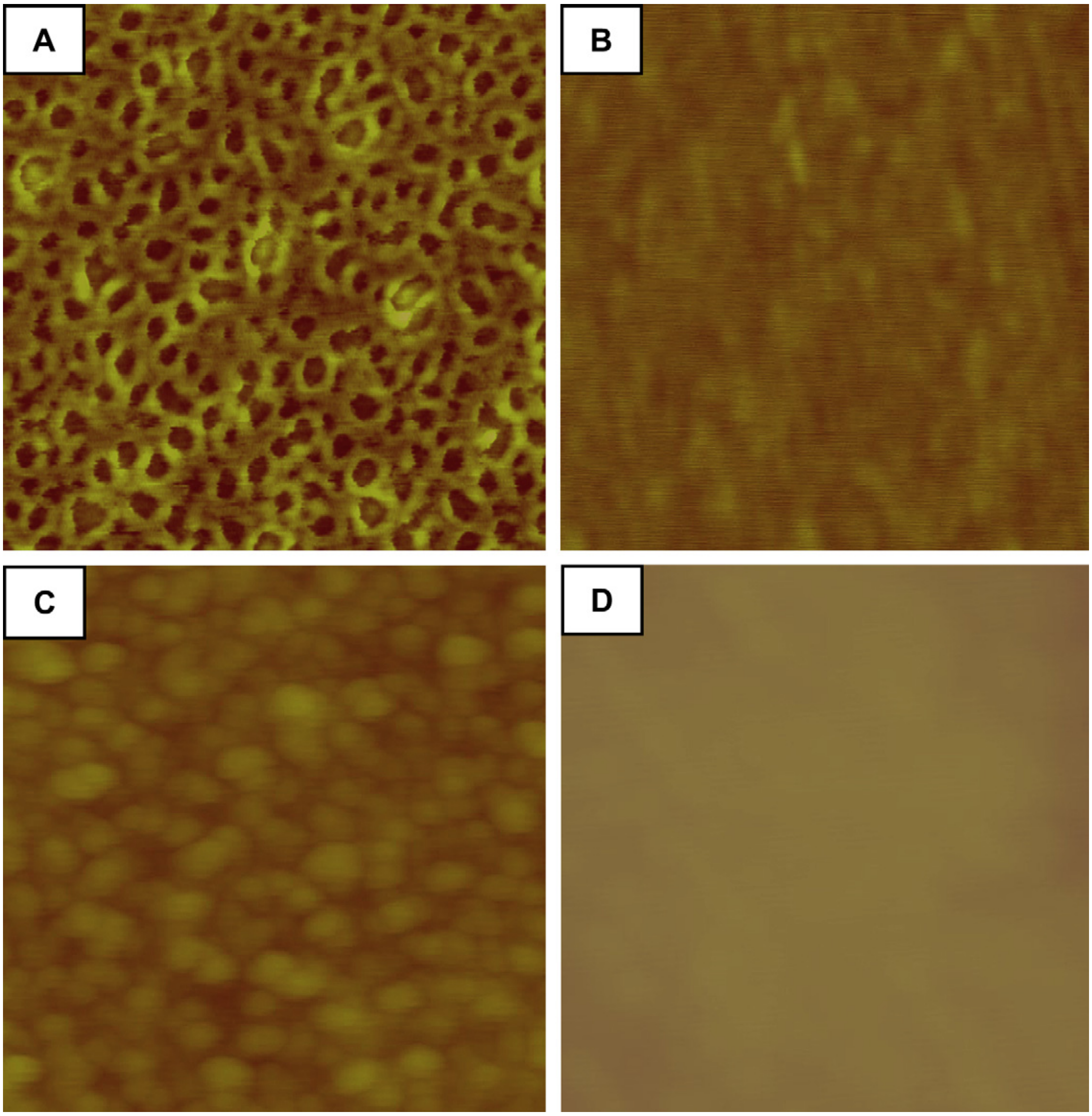


Fig. 4. AFM images of the outmost denpol layer in the (PDDA/denpol)$_1$ multilayer films ((A) both of the denpol and PDDA dipping solutions were adjusted to pH 6 using 0.01 M HCl, scale: 500 nm × 500 nm, (B) both of the denpol and PDDA dipping solutions were adjusted to pH 8 using 0.01 M KOH, scale: 500 nm × 500 nm), and the (PDDA/denpol)$_{10}$ multilayer films ((C) the pH values are same with these of (A), scale: 500 nm × 500 nm, (D) the pH values are same with those of (B), scale: 500 nm × 500 nm).

0.5 μm × 0.5 μm area) respectively. The AFM observation suggests that the denpol molecules will take a more curled or annular-like conformation under low pH condition and a strip-like one under high pH condition, namely the diversity of the surface morphology was ascribed to the different conformations of the denpol under various pH conditions [2].

As shown by AFM images in Fig. 4C and D, the surface morphologies of the 10-bilayer PDDA/denpol multilayer films, constructed by alternate deposition in denpol dipping solution at pH 6 and 8, respectively, are also observed. The grain-like morphology of the outmost denpol layer in the (PDDA/denpol)$_{10}$ multilayer film (pH 6), with a grain size of ca. 40 nm, was observed in Fig. 4C. However, no special morphology was found on the surface of the (PDDA/denpol)$_{10}$ multilayer film (pH 8) in Fig. 4D. The latter 10-bilayer multilayer film was smoother than that of the former, with the root-mean-square roughness of ca. 2.54 and 5.01 nm (over 0.5 μm × 0.5 μm area). Since there is no clear interface between layers in multilayer films, which results from the interfacial overlap, it is difficult to observe the single molecule morphology similar to that of the 1-bilayer films. However, it should be concluded that the pH values of the polyelectrolyte dipping solutions obviously influence the morphologies and roughness of LbL films.

We also found that adding salt to the polyelectrolyte dipping solutions can best control deposition amount of denpol. A series of PDDA/denpol multilayer films were fabricated using the PDDA and denpol dipping solutions containing varying concentrations of NaCl. Fig. 5 shows that the deposition amount of denpol remarkably increases at higher salt concentration of polyelectrolyte dipping solutions. These phenomena are similar to previously reported deposition behavior of the multilayer films based on poly(amidoamine) dendrimer (PAMAM) and PSS [46]. Due to the high electrostatic screening at high salt concentration, the two kinds of polyelectrolyte molecules adopt a curled conformation, which result in larger denpol deposition amount per bilayer. Remarkably, excessively high salt concentration leads to some decrease of deposition amount, which is likely ascribed to the more curled conformation of these polyelectrolyte molecules at higher salt concentration, thus resulting in a lower number of contact point with the oppositely charged surface.

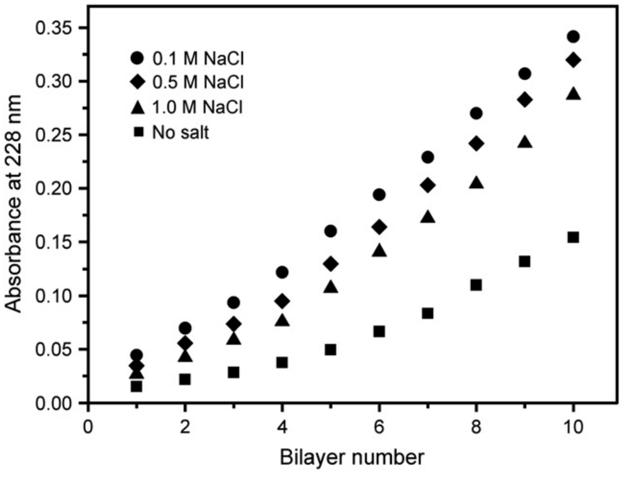
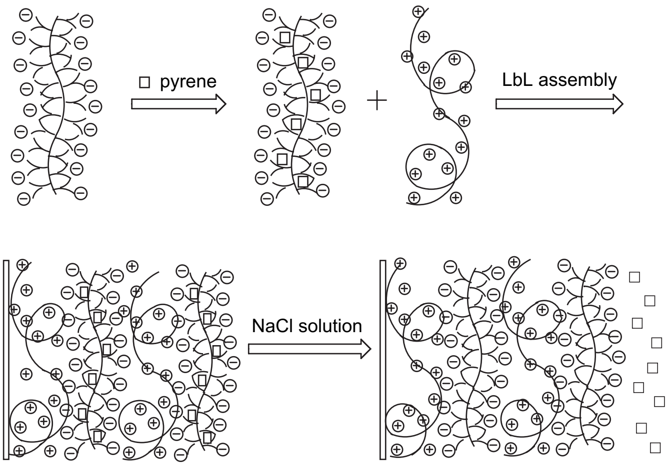


Fig. 5. Dependence of the growth of a series of (PDDA/denpol)$_{10}$ multilayer films on ionic strength of the polyelectrolyte solutions, plotted as film absorbance at 228 nm versus bilayer number. The pH values of the dipping solutions were adjusted to 8, and the ionic strength was adjusted using 0.1, 0.5 and 1.0 M NaCl, respectively.



Scheme 1. Schematic representation of a combination of preassembly and LbL assembly.

Similar to Fréchet-type dendrimer [37], pyrene could be incorporated into the interior of the water-soluble denpol on the basis of the hydrophobic and π−π interaction in aqueous solution. Therefore, it should be anticipated that the pyrene-loaded denpol can be assembled as building block, and then pyrene can be incorporated into the multilayer film. As shown in Scheme 1, the incorporation of pyrene into the multilayer film was performed using a combination of preassembly and LbL assembly. The polyelectrolyte dipping solutions, used to fabricate the (PDDA/pyrene-loaded denpol)$_{10}$ multilayer film, were adjusted to pH 8 and contained 0.1 M NaCl. The LbL assembly of the multilayer film was monitored by UV−vis and fluorescence spectra. Unsurprisingly, as shown in Fig. 6, the UV−vis spectra of the (PDDA/pyrene-loaded denpol)$_{10}$ multilayer film possess the same pattern and increased fashion

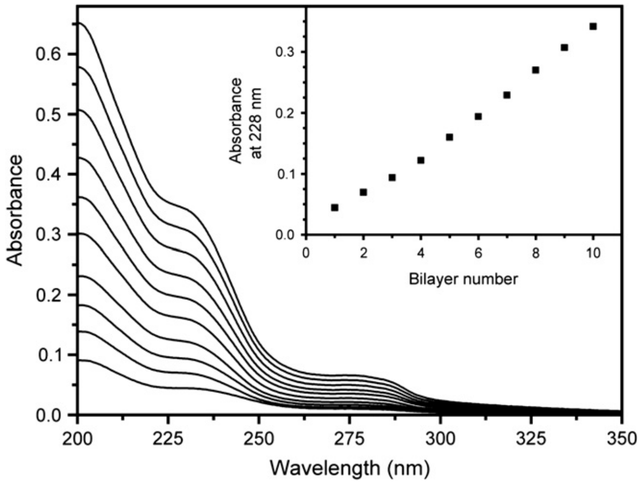


Fig. 6. UV−vis spectra of the (PDDA/pyrene-loaded denpol)$_{10}$ multilayer film, (inset) plotted as film absorbance at 228 nm versus the bilayer number. The dipping solutions were adjusted to pH 8, and contained 0.1 M NaCl.

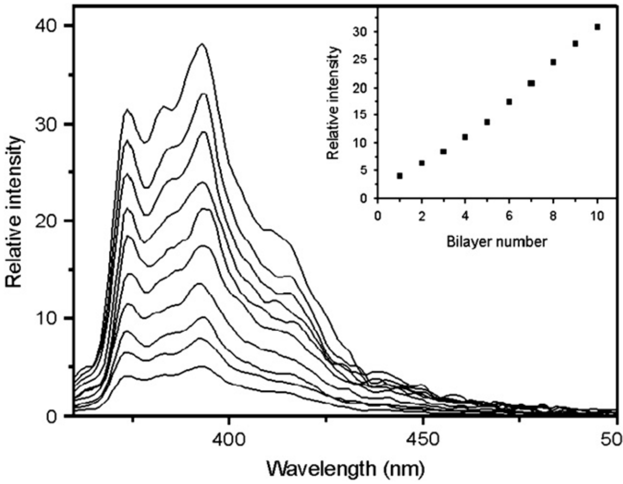


Fig. 7. Fluorescence spectra of the (PDDA/pyrene-loaded denpol)$_{10}$ multilayer film, (inset) plotted as relative intensity of fluorescence at 373 nm versus the bilayer number. The polyelectrolyte solutions were adjusted to pH 8, and contained 0.1 M NaCl.

as that of the PDDA/denpol multilayer film. Fig. 7 shows the fluorescence spectra, excited at 330 nm, of the multilayer film in each deposition cycle. The fluorescence band from 370 to 430 nm is attributed to the pyrene. Significantly, there is no pyrene excimer formed in the denpol by the absence of an emission band at ca. 475 nm. This result shows that the self-quenching of pyrene incorporated in the multilayer film is avoided in the present experiment, which may be attributed to the relatively lower concentration of pyrene and the ‘‘isolation effect’’ of the denpol.

Moreover, as shown in the inset of Fig. 7, the fluorescence intensity of pyrene at 373 nm basically increases in a linear fashion except for the first three bilayers, which corresponds to the data of the UV–vis spectra. The micropolarity at the incorporation sites of denpol could be reflected through pyrene fluorescence emission bands, typically the I_3/I_1 ratio of the fluorescence intensity of the first to the third vibrational peak, which is a good measure of assessing the medium polarity [47,48]. The fluorescence intensity ratio of two peaks at 373 and 387 nm in the PDDA/pyrene-loaded denpol multilayer films is around 0.95. Such a low ratio indicates that the pyrene molecules exist in a hydrophobic microenvironment of the LbL films. That is to say, the pyrene-loaded denpol can retain its host–guest property and pyrene, a water-insoluble molecule, can be incorporated successfully into multilayer films via a combination of preassembly and LbL assembly.

Since the incorporation ability of LbL films can be affected by the ionic strength of aqueous solution, we wondered if the incorporated pyrene could be released from the multilayer film depending on the ionic strength of the solution. For this purpose, the (PDDA/pyrene-loaded denpol)$_{10}$ film was immersed into NaCl aqueous solutions of various concentrations, and the release kinetics of pyrene from the film was monitored by fluorescence spectra (Fig. 8). It is clear that the amount of pyrene remaining in the film decreases with increasing immersion time, and the most pyrene molecules are released from the film within 100 s from the film. Moreover, higher ionic strength can accelerate the release of pyrene from the multilayer film. It is well known that the addition of salts makes the multilayer film looser (due to electrostatic screening) than before so as to make more tunnels and speed up the release process of pyrene from the multilayer film. This is the reason that the release rate of pyrene is much lower in pure water in which several hours have to be taken to achieve the full release of pyrene. Therefore, the release rate of pyrene can be controlled through varying the ionic strength of the solutions for immersion.

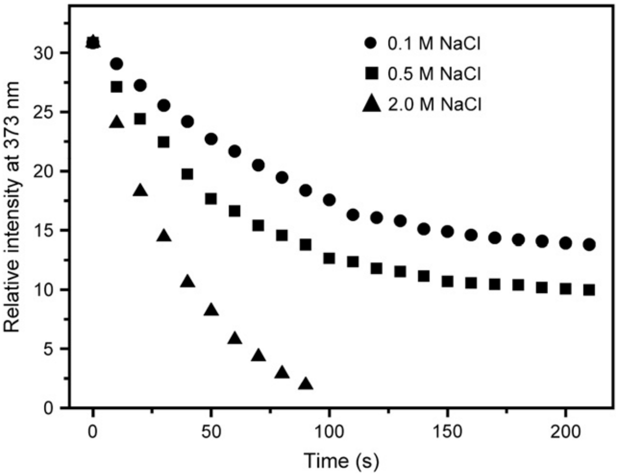


Fig. 8. Release kinetics of pyrene from the (PDDA/pyrene-loaded denpol)$_{10}$ multilayer film.

Spontaneously, we also attempted to immerse the pyrene-released multilayer film into a saturated aqueous solution of pyrene and after a 2-h immersion, a marked increase of the fluorescence emission intensity was observed, which can arrive to 80% original intensity of the film (curve c in Fig. 9). As shown in Fig. 9, both the original pyrene-loaded multilayer film (curve a) and the pyrene re-loaded multilayer film (curve c) possess

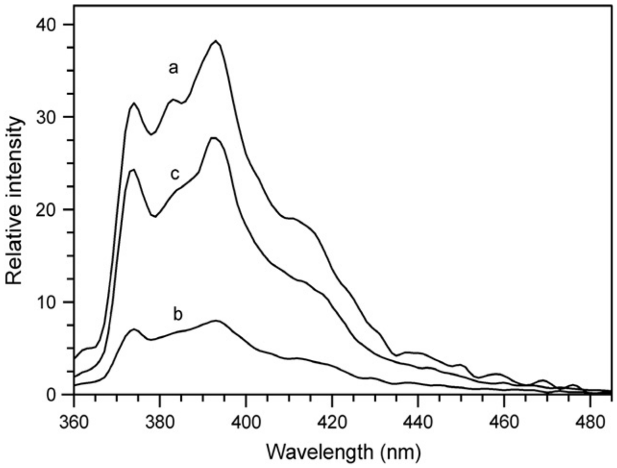


Fig. 9. Fluorescence spectra of the multilayer films under various conditions: (a) original (PDDA/pyrene-loaded denpol)$_{10}$ multilayer film, (b) the (PDDA/pyrene-released)$_{10}$ multilayer film after immersing the (PDDA/pyrene-loaded denpol)$_{10}$ multilayer film into a 2.0 M NaCl aqueous solution for 60 s, (c) the (PDDA/pyrene re-loaded)$_{10}$ multilayer film after immersing the (PDDA/pyrene-released)$_{10}$ film in a saturated aqueous solution of pyrene for 2 h.

similar fluorescence pattern. This result demonstrates that pyrene can be incorporated again into the multilayer film, however, the absorption efficiency of the film decreases to some extent.

4. Conclusion

In conclusion, the water-soluble denpol was employed as building block to construct the multilayer films with PDDA via LbL assembly. The influences of pH and ionic strength of the polyelectrolyte dipping solutions on the fabrication of the PDDA/denpol multilayer films have been investigated in detail. AFM images showed that pH of the denpol dipping solutions can obviously influence the morphology and roughness of the multilayer films. We also use a preassembly method to incorporate water-insoluble molecule of pyrene into denpol, and then fabricate the PDDA/pyrene-loaded denpol multilayer films via LbL assembly. Moreover, we demonstrate that the loaded molecules can be released from the LbL films, which can be controlled by ionic strength of immersing solutions. Interestingly, the pyrene-released multilayer film can also reload pyrene when immersing the pyrene-released film into a saturated aqueous solution of pyrene.

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