

BASE-INDUCED RELEASE OF MOLECULES FROM HYDROGEN BONDING DIRECTED LAYER-BY-LAYER FILM*

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Abstract On the basis of hydrogen bonding directed layer-by-layer (LbL) assembly we have fabricated two multilayer systems, poly(acrylic acid) bearing spironaphthoxazine (PAA-SO)/poly(4-vinylpyridine) and carboxyl-terminated polyether dendrimer (dendrimer-COOH)/poly(4-vinylpyridine). UV-Vis spectroscopy indicates that either PAA-SO or dendrimer-COOH can be released from the corresponding multilayer assemblies upon immersion in a basic aqueous solution. Furthermore, the rate of molecule release can be controlled either by changing the pH value or by adjusting the layer structure.

Key words Layer-by-layer assembly, Hydrogen bonding, Molecule release

INTRODUCTION

Since the first report by G. Decher *et al.*, the layer-by-layer (LbL) self-assembly technique, which is based on the electrostatic interaction of oppositely charged polyelectrolytes, has been paid more and more attention as an effective way to fabricate ultrathin organic films^[1]. The potential applications of this technique have been explored in very diverse areas, such as (bio) sensors, light-emitting diodes, optical storage devices, separation membranes and so on^[2–4]. The popularity of the LbL method is due to its simplicity, speed, versatility and the systematic control of the structure and thickness of the resulting film on the nanoscale^[2–4].

In addition to electrostatic interaction, other weak interactions, such as hydrogen bonding, have also been employed as the driving force for the LbL assembly^[4]. For example, in 1997, almost at the same time, Rubner *et al.* and Zhang *et al.* reported a new concept of assembling a LbL film using hydrogen bonding^[5,6]. The concept was developed further by Cao *et al.* by combining hydrogen bonding directed layer-by-layer assembly with post-chemical reaction^[7]. Recently, Zhang *et al.* have further investigated the structure variation of hydrogen bonding directed poly(acrylic acid) (PAA)/poly(4-vinylpyridine) (PVP) LbL film in a basic aqueous solution and developed a new route for fabricating microporous films^[8]. It involved a two-step variation process. The first step was that one component of the multilayer film, PAA, dissolved in the basic solution and the other component of the film, PVP, remained on the substrate. The second was the reconfiguration of the PVP chains in the basic solution, which resulted in a microporous film.

Herein we report our studies on the molecule release process from the hydrogen bonding directed LbL film in a basic aqueous solution. The molecules assembled as H-donor, which will be released in a basic aqueous solution, are poly(acrylic acid) bearing spironaphthoxazine (PAA-SO) and carboxyl-terminated polyether dendrimer (dendrimer-COOH), respectively (see Scheme 1). The polymer assembled as H-acceptor with the

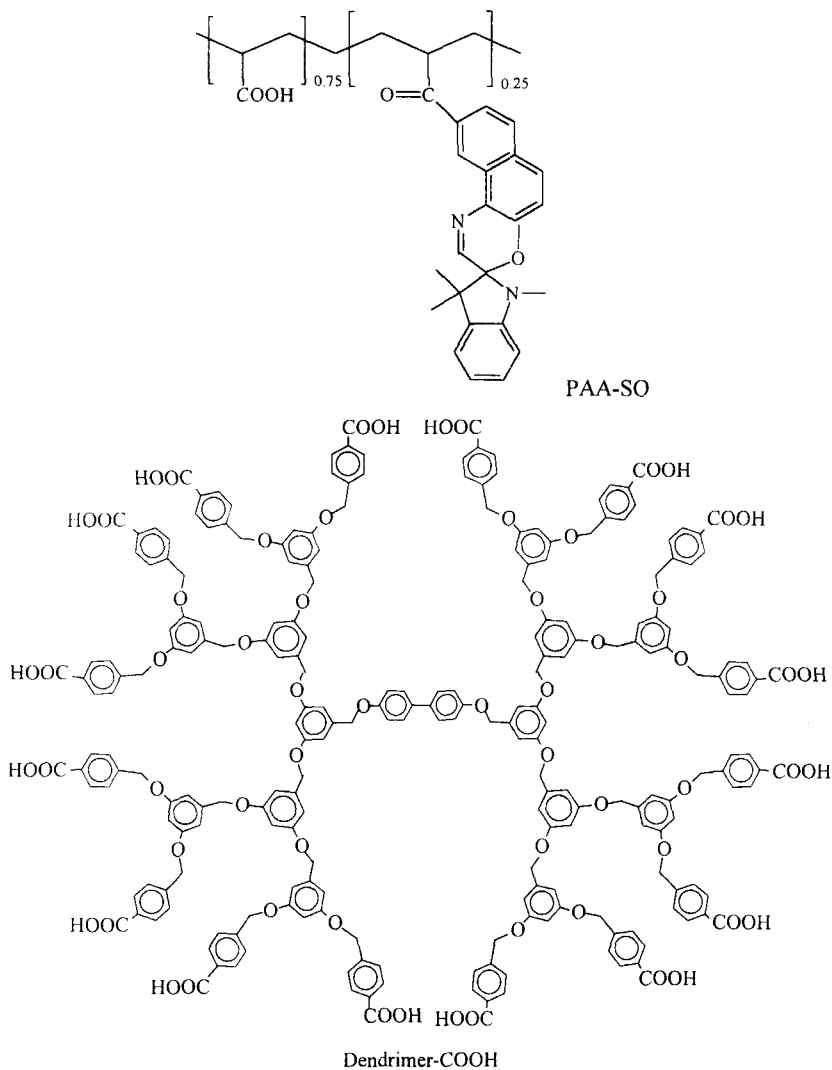
* The research was funded by the Major State Basic Research Development Program (Grand No. G2000078102), Key Project of Ministry of Education, and the National Natural Science Foundation of China.

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Invited lecture presented at the China-Canada Bilateral Polymer Symposium, 2002, Tianjin, China

Received March 3, 2003

above two polymers is poly (4-vinylpyridine) (PVP). The assembly and molecule release process of the PAA-SO/PVP and dendrimer-COOH/PVP multilayer film were monitored by UV-Vis spectroscopy. Furthermore, the influence of the LbL film structure on the release rate of PAA-SO is demonstrated. We envision that release of molecules from the multilayer film may have potential applications in advanced material science^[9].



Scheme 1

EXPERIMENTAL

The synthesis of poly(acrylic acid) bearing spironaphthoxazine ($M_w = 1.1 \times 10^4$, the content of SO is about 25 mol%), carboxyl-terminated polyether dendrimer ($M = 4196.5$) and poly(4-vinylpyridine) ($M_w = 1.8 \times 10^5$) has been separately described in previous publications^[10, 11, 12]. The copolymer of *p*-(hexafluoro-2-hydroxylisopropyl)-*R*-methylstyrene and styrene (PSOH) was kindly provided by Prof. Jiang (Fudan University)^[13, 14]. UV-Vis spectra were carried out on a Shimadzu 3100 UV-Vis-near-IR recording spectrometer.

The LbL films were assembled on a quartz substrate, which was modified with (4-aminobutyl)-dimethylmethoxysilane (Aldrich) yielding a NH_2 -tailored surface before assembly. The LbL films were fabricated by alternating immersion of the NH_2 modified substrate in PVP (1mg/ml) methanol solution and PAA-

SO (1 mg/mL) THF solution or dendrimer-COOH (4 mg/25 mL) methanol solution for 10 min. Rinsing in a pure solvent was needed, three times (1 min each) after each step. To investigate the influence of a basic aqueous solution on the hydrogen bonding multilayer film, the resulting LbL films were immersed in a NaOH aqueous solution. After rinsing in water and drying by N_2 gas, the samples were stored under ambient conditions prior to measurements.

RESULTS AND DISCUSSION

The PAA-SO/PVP Multilayer

The assembly process of the PAA-SO/PVP LbL film was monitored by UV-Vis spectroscopy. Figure 1 shows the UV-Vis spectra of the LbL film of PAA-SO and PVP with different number of layers. The absorption bands appearing at 241 nm and around 340 nm are separately assigned to indole ring and naphthoxazine ring absorption in PAA-SO^[15]. The shoulder around 256 nm is attributed to the pyridine absorption of PVP. As shown in the inserted figure, the absorbance at 241 nm increases linearly with the number of layers, which indicates a uniform assembling process.

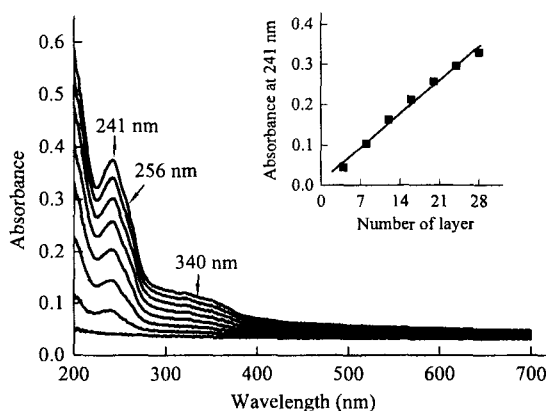


Fig. 1 UV-Vis absorption spectra of the LbL films of PAA-SO and PVP with different numbers of layers (from bottom to top) 0, 4, 8, 12, 16, 20, 24 and 28. The inserted figure shows the absorbance at 239 nm versus the number of layers.

The release process of PAA-SO from the PAA-SO/PVP LbL film in a NaOH solution was monitored by UV-Vis spectroscopy. As shown in Fig. 2, after immersion in a NaOH aqueous solution ($pH = 13$) for 30 s, the absorbance of PAA-SO decreases greatly and the maximum of the peak shifts from 241 nm to 250 nm. On prolonging the immersion time, the absorption intensity of PAA-SO decreases continuously and the peak shifts to longer wavelengths concomitantly. For comparison the accumulated spectra of PVP layer is shown, which indicates that the maximum of PVP absorption lies at 259 nm. Both the intensity decrease and the maximum shift of PAA-SO indicate that in the basic aqueous solution the PAA-SO of the multilayer dissolves in the solution. And the comparison of the spectra of the films after immersion and the accumulated spectrum of PVP layer shows that PVP still remains on the substrate. This variation of the hydrogen bonding directed LbL film in the basic solution may be caused by ionization of carboxylic acid of PAA-SO in the basic solution, which leads to the destruction of the interaction, mainly via hydrogen bonds, between the neighbor layers. The PAA-SO consequently dissolved in the solution, and PVP remained on the substrate for its poor solubility in a basic solution^[8].

The effect of the pH value of the immersion solution on the release process was explored. Figure 3 shows the intensity change of the PAA-SO absorption with the immersion time in solutions with different pH values. It indicates that in the acidic or neutral solutions the LbL film is stable, yet in the basic solutions the PAA-SO

release rate increases with the pH value of the solution. This result further supports our above suggestion that the destruction causes the release of PAA-SO. In acidic or neutral conditions, the carboxylic acid group is not ionized and the hydrogen bonds between PAA-SO and PVP still remain, so no PAA-SO is released. The reason for the increase of release rate with pH value is that in a solution with higher pH value, the ionization degree of PAA-SO would be greater, resulting in weaker interaction within the multilayer and better solubility of PAA-SO in the solution.

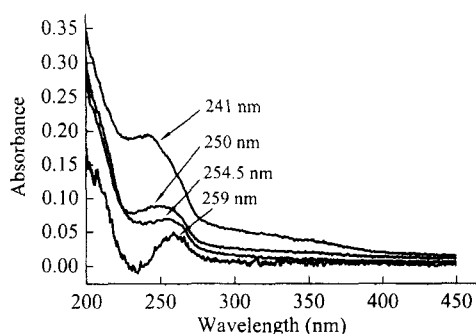


Fig. 2 UV-Vis absorption spectra of (from top to bottom) the 9-bilayer PAA-SO/PVP film, the 9-bilayer PAA-SO/PVP films after 30 seconds and 60 min immersion in a pH = 13 solution and the accumulation of PVP layer

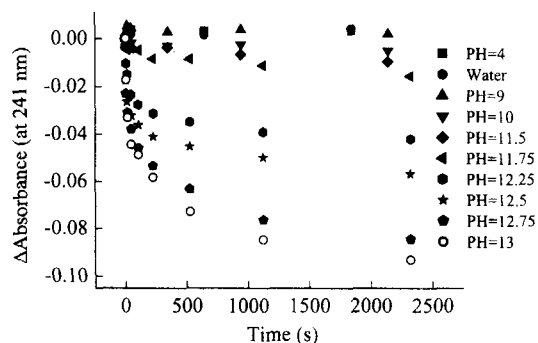


Fig. 3 The decrease of absorbance at 241 nm of 9-bilayer PAA-SO/PVP films versus the immersion time in NaOH aqueous solutions with different pH value

The Dendrimer-COOH/PVP Multilayer

The assembly process of dendrimer-COOH and PVP multilayer film was followed by UV-Vis spectroscopy, as shown in Figure 4. The band appearing at 233 nm is the mixture absorption of PVP and dendrimer-COOH, and the shoulder around 281 nm is mainly attributed to the dendrimer-COOH absorption. Following the absorbance at 233 nm, we find a linear increase with the number of bilayers, which shows a uniform assembly process of dendrimer-COOH and PVP. The dendrimer-COOH release process was studied similarly to that in the PAA-SO/PVP system. Figure 5 shows the decrease of absorbance at 281 nm of dendrimer-COOH/PVP films vs. the immersion time in the NaOH aqueous solutions with different pH values. Similar to the PAA-SO/PVP system, the release rate of dendrimer-COOH increases with the pH value of the immersion solution. All these results imply that the base-induced molecule release from a hydrogen bonding directed LbL film can be universalized.

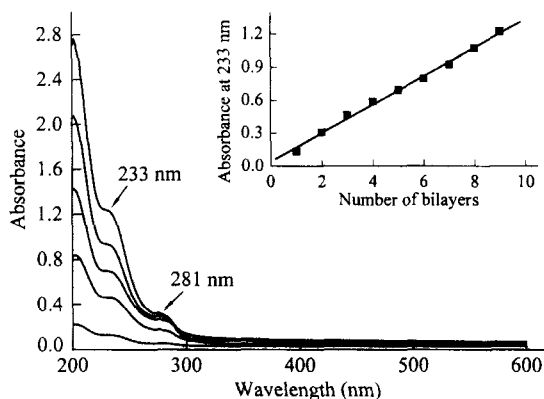


Fig. 4 UV-Vis absorption spectra of the LbL films of dendrimer-COOH and PVP with different numbers of bilayers (from bottom to top) 1, 3, 5, 7 and 9. The inserted figure shows the absorbance at 233 nm versus the number of bilayers

Controlled Molecule Release

We have realized furthermore a controlled molecule release from the hydrogen bonding directed LbL film by assembling the inert layers, which are stable in the basic solution, onto the resulting PAA-SO/PVP film. The PSOH/PVP multilayer film fabricated by LbL assembly through hydrogen bonding interactions has been investigated by Wang *et al.*^[13]. Because of their stability in basic solution we selected PSOH and PVP as the inert layers to assemble them onto the PAA-SO/PVP film. We have compared the PAA-SO release process from multilayer films of (PAA-SO/PVP)₉, (PAA-SO/PVP)₉PSOH and (PAA-SO/PVP)₉PSOH/PVP/PSOH, as shown in Figure 6. An obvious decrease of the release rate is observed after adding a PSOH layer on the PAA-SO/PVP film. With the increase of the number of inert layers, the release of PAA-SO becomes visibly slower.

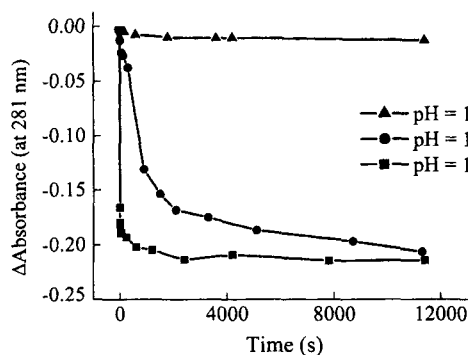


Fig. 5 The decrease of absorbance at 281 nm of 5-bilayer dendrimer-COOH/PVP films versus the immersion time in the NaOH aqueous solutions with different pH values

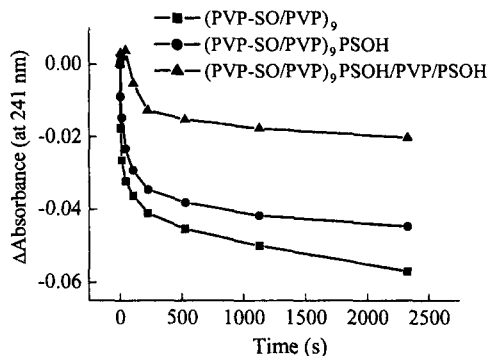


Fig. 6 The decrease of absorbance at 241 nm of (PAA-SO/PVP)₉PSOH and (PAA-SO/PVP)₉PSOH/PVP/PSOH films versus the immersion time in a pH = 12.5 NaOH solution

CONCLUSION

The base-induced release of PAA-SO and dendrimer-COOH from their hydrogen bonding directed LbL films was investigated by UV-Vis spectroscopy. We have found that the release rate of the molecules from the multilayer assemblies can be controlled by adjusting either the pH value of solutions, or the layer architectures.

REFERENCES

- 1 Decher, G., *Science*, 1997, 277: 1232
- 2 Bertrand, P., Jonas, A. and Laschewsky, A., *Macromol. Rapid Commun.*, 2000, 21: 319
- 3 Zhang, X. and Shen, J.C., *Adv. Mater.*, 1999, 11: 1139
- 4 Hammond, P.T., *Curr. Opin. Colloid & Interface Sci.*, 2000, 4: 430
- 5 Stockton, W.B. and Rubner, M.F., *Macromolecules*, 1997, 30: 2714
- 6 Wang, L.Y., Wang, Z.Q., Zhang, X., Shen, J.C., Chi, L.F. and Fuchs, H., *Macromol. Rapid Commun.*, 1997, 18: 509