Front. Chem. China (2006) 3: 329–333
DOI 10.1007/s11458-006-0024-y

RESEARCH ARTICLE

Tuo Xinlin, Chen Di, Wang Xiaogong

Preparation of azo polyelectrolyte self-assembled multilayers by using *N*,*N*-dimethylformamide/H_2O mixtures as solvents

Abstract *N*,*N*-Dimethylformamide (DMF)/H_2O mixtures were used as solvents to fabricate azo polyelectrolyte (PEAPH)/poly(diallyldimethyl ammonium chloride)(PDAC) self-assembled multilayers with the layer-by-layer electrostatic adsorption technique. PEAPH is a copolymer of acrylic acid and azobenzene-containing acrylate. The effect of the ratio of DMF to water on the multilayer growth, structure and surface morphology was studied in some details. Results show that DMF/H_2O mixtures are proper media for PEAPH/PDAC multilayer fabrication. The ratio of DMF to water in the mixture has significant influence on the multilayer structure and surface morphology. With the increase of DMF content, the multilayer thickness has a better linear growth relationship with the bilayer number, and the multilayer surface becomes smoother. Moreover, azo chromophores show less H-aggregation when the multilayers are fabricated from DMF/H_2O mixtures with higher DMF contents. These studies demonstrate that using organic solvent and water mixtures is an effective way to control the multilayer construction by adjusting the media properties. This method can be applied to multilayer fabrication of other water-insoluble polyelectrolytes.

Keywords azo polyelectrolyte, self-assembled multilayer, DMF/H_2O mixture

1 Introduction

Azobenzene-containing polymers (azo polymers for short) are promising for future applications in optical and photonic devices [1–4]. In recent years, using electrostatic layer-by-layer (ELBL) selfassembly to fabricate azobenzene-containing multilayer films has become an important method to control the optical properties of azobenzene-containing materials and adjust the compositions in nano-scale [5,6]. In a typical ELBL method [7,8], azobenzene–containing polyelectrolytes and the opposite-charged ions were dissolved in water, and the LBL deposition process was completed in aqueous media. In this process multilayer growth and structure control were performed by adjusting the ionic strength and pH of the media [9–11].

However, using aqueous media for ELBL self-assembly of azo polyelectrolyte often encounters some difficulties. One of them is the poor solubility of the polymers in water due to the hydrophobicity of azobenzene units [12,13]. The polyelectrolytes containing a large amount of azo chromophores can hardly be dissolved in water. Consequently, aqueous media are usually not available for ELBL self-assembly. Moreover, azo chromophores tend to exist in the H-aggregation form in aqueous media, which can significantly decrease the photo-isomerization efficiency of azobenzene chromophore [14–17]. In general, the decrease of isomerization efficiency is unfavorable for many optical applications. Therefore, finding proper media is pivotal for the ELBL self-assembly of azo polyelectrolytes and other water-insoluble polyelectrolytes.

In this work, *N*,*N*-dimethylformamide (DMF)/H_2O mixtures were used as the assembling media of azobenzene-containing polyanions. Commercially available poly (diallyldimethylammonium chloride)(PDAC) dissolved in water was used as the polycation. Selection of DMF/H_2O mixtures is based on the following reasons: (1) DMF is a good solvent for most of the azo polymers, and the carboxylic acid groups can be partially ionized in DMF; (2) it is consequently reasonable to monitor the structure and properties of the resulted multilayers by adjusting the ratio of DMF to water. Research was focused on the effect of the ratios of DMF to water in the mixtures on the multilayer growth, structure and surface morphology of the multilayers. Results show that DMF/H2O mixtures are ideal media for the

---

Translated from *Acta Polymerica Sinica*, 2005, (4) (in Chinese)

Tuo Xinlin, Chen Di, Wang Xiaogong (✉)
Department of Chemical Engineering, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China
E-mail: wxg-dce@mail.tsinghua.edu.cn

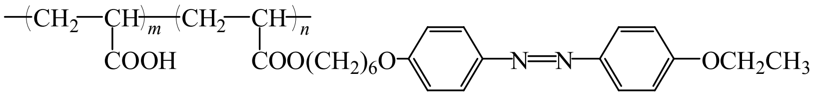

Fig. 1 Chemical structure of PEAPH

ELBL self-assembly of the azobenzene-containing polyanions and PDAC. The ratio of DMF to water in the mixture has significant influence on the multilayer structure and surface morphology.

2 Experimental

The chemical structure of the azo polyelectrolyte PEAPH is shown in Fig. 1. The synthesis and characterization of PEAPH have been given elsewhere [18]. PEAPH is a copolymer of acrylic acid and azobenzene-containing acrylate. The degree of functionization (DF) of PEAPH is 37%. Owing to the high azo chromophore content, PEAPH cannot be dissolved in aqueous media even in a basic condition. On the other hand, PEAPH can be well dissolved in polar organic solvents such as DMF.

PEAPH solution for ELBL assembly was prepared as follows: 5 mg PEAPH was dissolved in 2 mL DMF and the solution was added into 20 mL DMF/H_2O mixtures in drops under ultrasonication. PDAC (MW 20000–35000, 20% solution, Aldrich) was used as polycation and diluted to a concentration of 0.1 mmol/L (repeated unit) with Milli-Q water (resistivity >18MΩ·cm). Hydrophilic quartz and silica slides were prepared by sonication in a 98% H_2SO4/30%H_2O_2 solution (piranha solution) for 1h and in a $H_2O/H_2O_2/NH_4OH$ (5:1:1, v/v/v) solution for another 1 h, followed by a thorough rinse and then dried with an air stream. The multilayer films were fabricated on the pretreated quartz and silica slides by alternately dipping the substrates in the aqueous solution of PDAC and the DMF/H_2O mixture of PEAPH. Each monolayer grew for 10 min before washing with an excess of Milli-Q water and then dried with air stream. UV-vis absorption spectra were measured after each deposition cycle to characterize the PEAPH/PDAC multilayer growth. Atomic force microscopy (AFM, Nanoscope IIIa, Digital Instruments Corp., Tapping mode) was used to characterize the multilayer surface.

3 Results and discussion

3.1 PEAPH/PDAC multilayer fabrication

The stable attraction between opposite-charged poly-electrolytes is a basic requirement for the polyelectrolyte multilayer growth based on ELBL assembly. In the case of PEAPH/PDAC multilayer fabrication, when the multilayer with PDAC as the outmost layer is dipped into the PEAPH/DMF/H_2O mixture, the carboxyl acid groups in PEAPH chains will be electrostatically attracted by the ammonium groups in PDAC chains. This attraction interaction can attach PEAPH chains to the PDAC layer. However, the effect of DMF on PEAPH chains can also dissolve the PEAPH chains into solution. Therefore, PEAPH/PDAC multilayer growth is more complicated in DMF/H_2O mixture than that in water. Experimentally, a series of DMF/H_2O mixtures with different ratios were utilized as the PEAPH assembling media, and UV-vis absorption spectra were detected to investigate the PEAPH/PDAC multilayer growth. Figure 2 shows the PEAPH/PDAC multilayer growth in the case of a high content of DMF in the mixture (DMF/H_2O=9/1, v/v), the linear growth indicates the uniform attraction between PEAPH and PDAC, which also demonstrates that the attraction is strong enough to stabilize the PEAPH chains on the surface of PDAC layers even in a high DMF content mixture.

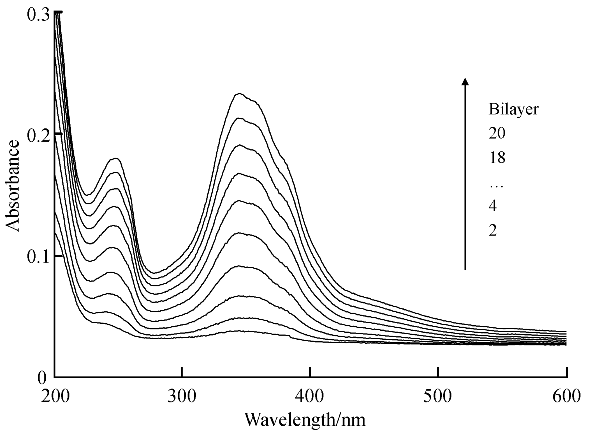

Fig. 2 UV-Vis spectra of PEAPH/PDAC multilayers varying with the number of bilayers

It is noteworthy that in this ELBL assembling process, PEAPH was dissolved in the DMF/H_2O mixture while PDAC-in water, so that much attention should be paid to the influence of the solvent variation on the multilayer growth. Figure 3 shows the relationship of PEAPH and PDAC layer growth with the number of monolayers. It can be seen in this figure that no polyelectrolyte desorption occurs when multilayer grows either in PEAPH/DMF/H_2O mixture or in the aqueous PDAC solution. The deposition of PDAC on PEAPH layer does not bring obvious change to the UV-Vis absorption spectra, which indicates that the PEAPH layer on the surface is stable in the following deposition in the PDAC solution.

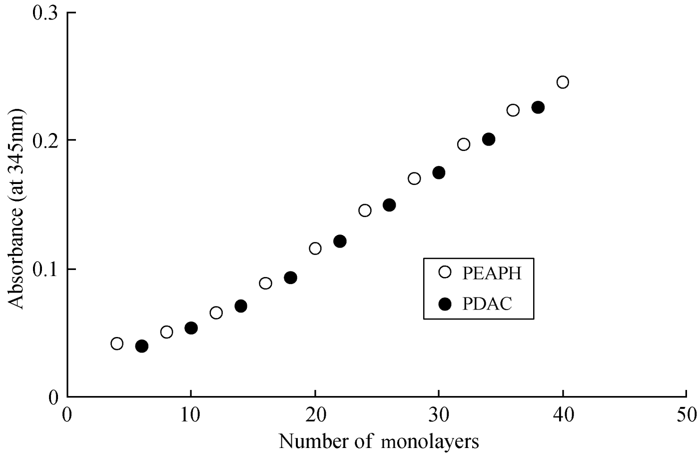

Fig. 3 The maximum absorbance of PEAPH/PDAC multilayers versus the number of monolayers. In this figure, (○) represents the maximum absorption intensity of the multilayers after dipping in the PEAPH solution, while (●) represents that after dipping in the PDAC solution

3.2 Influence of the ratio of DMF to H_2O on the multilayer formation

To systemically study the influence of the ratio of DMF to H_2O on the multilayer structure, a series of DMF/H_2O mixtures with DMF/H_2O = 1/20, 1/9, 1/4, 1/2, 1/1, 2/1, 4/1, 9/1 was used for the ELBL self-assembly. The multilayer growth in those DMF/H_2O mixtures is shown in Fig. 4. With the increase of DMF content in the mixture the PEAPH/PDAC multilayer growth rate decreases gradually. However, the linear relationship of absorption with multilayer number is improved especially in the early stage. For instance, in the case of DMF/H_2O=1/20, the multilayer shows an accelerated growth in the deposition of the first several bilayers. On the contrary, the multilayer grows linearly in the case of DMF/H_2O=9/1. It is believed that this difference is due to the different existing states of PEAPH in the DMF/H_2O mixtures. In the case of high water content in mixture azo polyelectrolytes exist in loose entangled states for the hydrophobicity of azobenzenes, which leads to the nonlinear growth at the beginning stage [13,19]. When these structures deposit on the PDAC surface, part of PEAPH chains penetrate into the former layer in order to stabilize in a compact stacking manner, which may result in the increase of PEAPH deposition and UV absorbance in spectra. It is noteworthy that all of the PEAPH/PDAC multilayers can be assembled up to several tens bilayers. These results demonstrate that DMF/H_2O mixtures are the proper media for PEAPH/PDAC multilayer assembly.

The existing states of azobenzene chromophores in multilayers were studied with UV-Vis absorption spectra. Figure 5 gives the spectra of the PEAPH/PDAC multilayers obtained from different DMF/H_2O mixtures. The 350 nm absorption band is attributed to the $\pi \rightarrow \pi^*$ transition of the conjugated electrons of azobenzenes and the 450 nm absorption

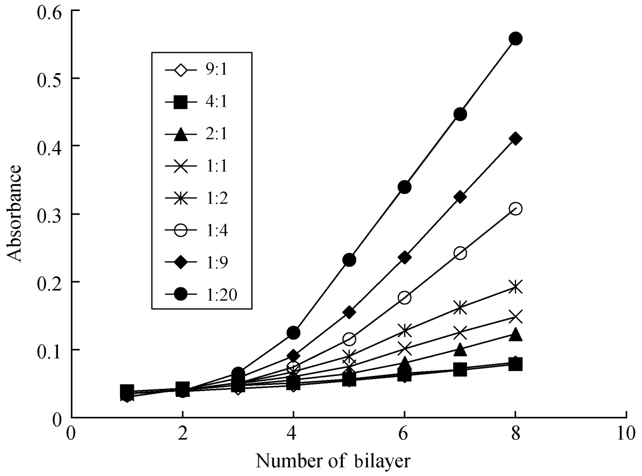

Fig. 4 The maximum absorbance of multilayers versus the bilayer number

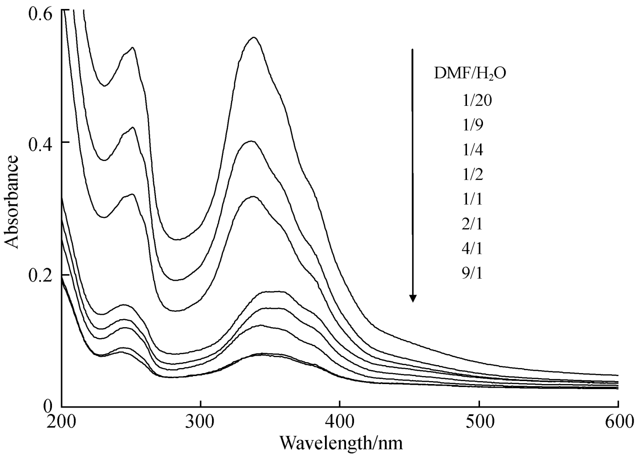

Fig. 5 The UV-Vis absorption spectra of PEAPH/PDAC multilayers fabricated from PEAPH solutions with different DMF/H_2O ratios (all with 16 bilayers)

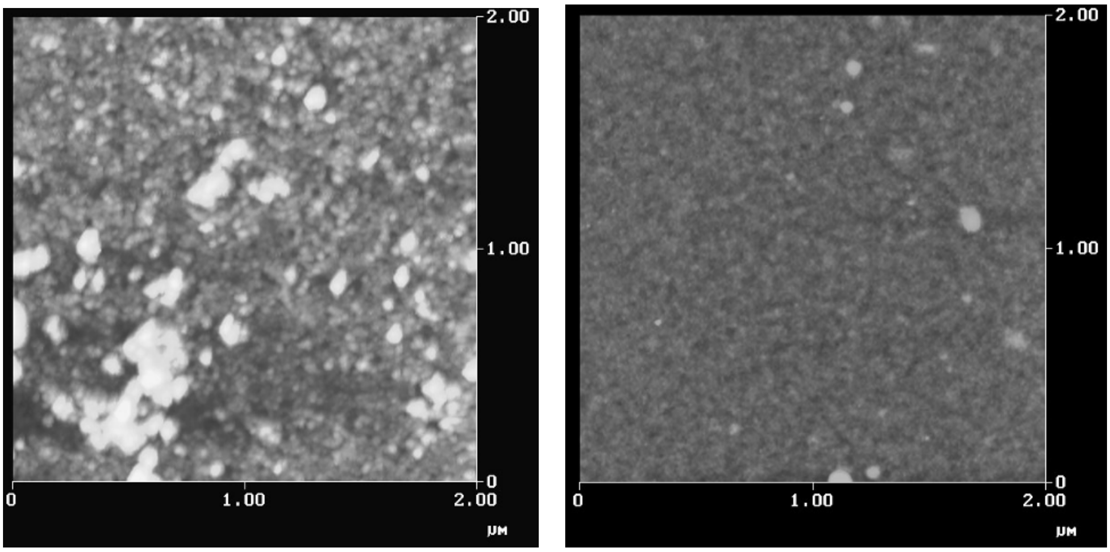

Fig. 6 The AFM surface morphology of the multilayers fabricated from different PEAPH solutions. a) DMF/H2O=1/9, b) DMF/H_2O=9/1 (Both multilayers have 16 bilayers and PEAPH as the outmost layer)

band-to the n→π* transition. The wavelength of the maximum absorbance (λ_{max}) of the PEAPH/PDAC multilayers, obtained from different DMF/H_2O mixtures, obviously differs from each other. The λ_{max} of the PEAPH/PDAC multilayers from DMF/H_2O=1/9 mixture is at 335 nm, while that from DMF/H_2O=9/1 mixture is at 355 nm. The blue-shift of the azobenzene absorption band is the typical characteristics of H-aggregation of azobenzenes. A significant part of azobenzenes in the PEAPH/PDAC multilayers obtained from DMF/H_2O=1/9 mixture exists in the H-aggregation state, while that from DMF/H_2O=9/1 mixture is on the contrary. The difference in spectra also reveals that the existing state of PEAPH chains has been stabilized before being deposited onto the PDAC surface, and the subsequent washing and drying have little influence on the existing state of PEAPH chains. These results also demonstrate that the assembling media have a significant influence on the multilayer structure, and it is an effective method to adjust the multilayer structure by adjusting the assembling media.

Furthermore, the surface morphology of the PEAPH/PDAC multilayers obtained from different DMF/H_2O mixtures obviously differs from each other (Fig. 6). The multilayer prepared from the DMF/H_2O mixture with higher DMF content shows a smoother surface. It can also be attributed to the difference of the PEAPH assembling media. In higher water content mixtures PEAPH chains exist in a more shrunken conformation with intermolecular aggregation. When these chains are deposited on the multilayers, the surface is rough. As shown in Fig. 6a, some particles can be observed on the surface. The difference in the surface morphology demonstrates again that it is a valuable method to control the PEAPH/PDAC multilayer structure by adjusting the ratio of DMF to water.

Acknowledgements This work was supported by the National Natural Science Foundation of China (No. 59925309).

References

1. Ikeda T., Tsutsumi O., Optical switching and image storage by means of azobenzene liquid-crystal films. Science, 1995, 268: 1873–1875
2. Natansohn A., Rochon P., Gosselin J., Xie S., Azo polymers for reversible optical storage. 1. Poly[4'-[[2-(acryloyloxy)ethyl]-ethylamino]-4-nitrozaobenzene. Macromolecules, 1992, 25: 2268–2273
3. Natansohn A., Xie S., Rochon P., Azo polymers for reversible optical storage. 2. Poly[4'-[[2-(acryloyloxy)ethyl]ethylamino]-2-chloro-4-nitrozaobenzene. Macromolecules, 1992, 25: 5531–5532
4. Rochon P., Bissonnette D., Natansohn A., Xie S., Azo polymers for reversible optical storage. 3. Effect of film thickness on net phase retardation and writing speed. Appl Opt, 1993, 32: 7277–7280
5. Wang X. G., Balasubramanian S., Li L., Jiang X. L., Sandman D. J., Rubner M. F., Kumar J., Tripathy S. K., Self-assembled second order nonlinear optical multilayer azo polymer. Macromol Rapid Commun, 1997, 18: 451–459
6. Ariga K., Lvov Y., Kunitake T., Assembling alternate dye-polyion molecular films by electrostatic layer-by-layer adsorption. J. Am. Chem. Soc., 1997, 119: 2224–2231
7. Decher G., Hong J. D., Schmitt J., Buildup of ultrathin multilayer films by a self-assembly process: III. Consecutively alternating adsorption of anionic and cationic polyelectrolyte on charged surfaces. Thin Solid Films, 1992, 210/211: 831–835
8. Decher G., Fuzzy nanoassemblies toward layered polymeric multicomposites. Science, 1997, 277: 1232–1237
9. Cheung J. H., Fou A. F., Rubner M. F., Molecular self-assembly of conducting polymers. Thin Solid Films, 1994, 244: 985–989
10. Fou A. C., Onitsuka O., Ferreira M., Rubner M. F., Fabrication and properties of light-emitting diodes based on self-assembled multilayers of poly(phenylene vinylene). J. Appl. Phys., 1996, 79: 7501–7509

11. Ferreira M., Rubner M. F., Molecular-level processing of conjugated polymers. 1. Layer -by- layer manipulation of conjugated polyions. Macromolecules, 1995, 28: 7107–7114
12. Tuo X. L., Chen Z., Wu L. F., Wang X. G., Liu D. S., Self-assembly of photo-responsive azo polyelectrolytes. Chem. J. Chin. Univ., 2001, 22: 329–333
13. Tuo X. L., Cheng H., Chen Z., Wang X. G., Studies on growth and architecture of self-assembled multilayers fabricated from side chain azo polyelectrolytes. Chem. J. Chin. Univ., 2001, 22: 1581–1586
14. Cheng H., Tuo X. L., Wang G. J., Wang X. G., A Novel Polyelectrolyte with Branched Azo Side Chains: Synthesis, Characterization and Self-Assembled Nano- structures. Macromol. Chem. Phys., 2001, 202: 3530–3535
15. Tuo X. L., Wang X. G., Liu D. S., Aggregation and micelle-like nano-structure of two azo polyelectrolytes. Acta Polym. Sin., 2002, (4):462–466
16. Cheng H., Tuo X. L., Gao W. W., Wang X. G., Synthesis and properties of a novel side-chain azo polyelectrolyte. Acta Polym. Sin., 2002, (1):96–101
17. Tuo X. L., Wu L. F., Wang X. G., Aggregation and photo- responsive behavior of azo polyelectrolytes in aqueous media. Chem. J. Chin. Univ. , 2002, 23: 1805–1808
18. Wu L. F., Tuo X. L., Cheng H., Chen Z., Wang X .G., Synthesis, photoresponsive behavior and self-assembly of poly(acrylic acid) based azo polyelectrolytes. Macromolecules, 2001, 34: 8005–8013
19. Laschewsky A., Wischerhoff E., Kauranen M., Persoons A., Polyelectrolyte multilayer assemblies containing nonlinear optical dyes. Macromolecules, 1997, 30: 8304–8309