Polymer Bulletin 54, 427–433 (2005)
DOI 10.1007/s00289-005-0387-0

Polymer Bulletin

Fabricating Water-Insoluble Polyelectrolyte into Multilayers with Layer-by-layer Self-assembly

Xinlin Tuo (✉), Di Chen, Hao Cheng, Xiaogong Wang

Department of Chemical Engineering, School of Materials Science and Engineering, Tsinghua University, Beijing, P. R. China, 100084
Email: tuoxl@mail.tsinghua.edu.cn

Received: 17 February 2005 / Revised version: 20 April 2005 / Accepted: 11 May 2005

Summary

A water insoluble azo-containing polyelectrolyte (PEAPB6P-AC) was successfully fabricated into multilayer films based on the layer-by-layer adsorption technique by using N, N-dimethylformamide (DMF) as the assembling media. The multilayer growth and structure were studied with UV-vis spectroscopy, and the multilayer surface were imaged with Atomic Force Microscopy and compared with that fabricated in water. The results show that assembling PEAPB6P-AC in DMF can effectively eliminate the hydrophobic aggregation of the azo units and consequently results in a much smoother multilayer surface than that fabricated in water. This improvement to the layer-by-layer adsorption technique, which can avoid some major difficulties faced when assembling hydrophobic polyelectrolytes in aqueous solutions, seems to be a versatile way to fabricate high quality multilayer films when using the hydrophobic even water-insoluble polyelectrolytes as assembling units.

Introduction

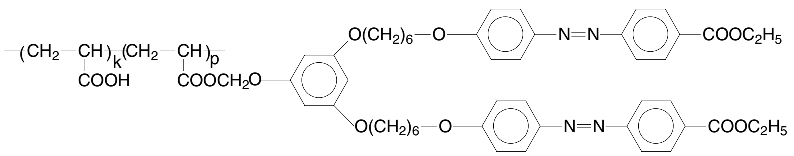
Electrostatic layer-by-layer self-assembly has been extensively studied for the practical applications and academic advance in recent years [1,2]. In a typical process, two oppositely charged polyelectrolytes dissolved in aqueous media are alternately deposited on a support surface based on the electrostatic attraction. Through the repeated adsorption cycles, high-quality multilayer films with controllable thickness can be obtained. This method has been successfully utilized to manipulate a wide variety of electrostatic multilayer films of water-soluble polyelectrolytes with diverse polymeric architectures and functional groups, including commercial-available polyelectrolytes, conjugated polymers, nonlinear optical polymers, poly(phenylene vinylene) precursor polymers among others as described in many reviews [3-7].

However, using aqueous solutions as assembling media has also faced some limitations in the fabrication of polyelectrolyte multilayers. Many polyelectrolytes, especially those incorporated with hydrophobic functional groups or segments are difficultly or cannot be dissolved in water. Although these polyelectrolytes can be fabricated into multilayers by dispersing them in aqueous media, however, the hydrophobic effect may force the polyelectrolyte molecules to undergo intermolecular association and intramolecular aggregation. The association and aggregation can occur both in the dispersing media and on the interfaces. In this case, the adsorption on the substrates is no longer a molecular-level electrostatic attraction process, which usually produce multilayer films with diverse inner structure and rough surfaces.

We report here a modified approach to fabricate hydrophobic even water-insoluble polyelectrolyte multilayer films by using anhydrous polar organic solvents as deposition media. In this study, an azo containing polyelectrolyte was employed as the investigation candidate. The selection is due to the considerations that azo chromophores can be used as a sensitive molecular "probe" to identify local environment and azo polyelectrolyte multilayers are promising for various photonic applications [8-12]. The azo polyelectrolye as the polyanion was dissolved in anhydrous N, N-dimethylformamide (DMF). Commercially available poly(diallyl-dimethylammonium chloride) dissolved in water was used as the polycation. It was observed that through sequential deposition of the oppositely charged polyelectrolytes on the substrate, high quality multilayer films were obtained.

Experimental

The chemical structure of the azo polyelectrolyte (PEAPB6P-AC) used in this study is given as



The synthetic details of the polymer have been described elsewhere [13]. PEAPB6P-AC is an acrylic acid based polymer with branched side-chains containing azo chromophores. The degree of functionization (DF) of the polyelectrolyte is 21.5%, i.e. nearly 21.5% of the carboxyl groups were substituted by the branched azo side-chains. In this study, the molecular weight of PEAPB6P-AC was measured by GPC utilizing a Waters Model 515 pump and a Model 2410 differential refractometer with 3 styragel columns HT2, HT3 and HT4 connected in a serial fashion. THF was used as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards with dispersity of 1.08−1.12 obtained from Waters were employed to calibrate the instrument. The molecular weight ($\overline{Mn}$) of the PEAPB6P-AC sample is 13,000 with a polydispersity index of 2.2. Due to the high chromophoric content, PEAPB6P-AC cannot be dissolved in aqueous media even in basic condition. On the other hand, PEAPB6P-AC can be well dissolved in polar organic solvents such as N, N-dimethylformamide (DMF).

Multilayer fabrication

Hydrophilic quartz and silica slides were prepared by sonicating the substrates in 98% H_2SO_4/30% H_2O_2 solution (piranha solution) for 1h, and sonicating in a $H_2O/H_2O_2/NH_4OH$ (5:1:1) solution for another 1 h, followed with a thorough rinse and then dried with an air stream. PEAPB6P-AC was dissolved in anhydrous DMF (0.1mg/mL) and used as anionic dipping solution. Poly(diallyldimethylammonium chloride) (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). The multilayer films were fabricated on the pretreated quartz and silica slides by alternate dipping of the substrates in the aqueous solution of PDAC and the DMF solution of PEAPB6P-AC. Each monolayer grew for 10 min before washed with an excess of Milli-Q water or anhydrous DMF, which was the same as the deposition media, and dried with air stream. UV-vis absorption spectra were measured after each dipping cycle to characterize PEAPB6P-AC/PDAC multilayer growth.

Characterization

UV-vis spectra of the azo polyelectrolyte in solutions and self-assembled multilayers were recorded on a Perking-Elmer Lambda Bio-40 spectrometer. Thickness of the multilayer films on silicon wafers was determined by using an optical ellipsometer (SE400, Sentech Instruments) with a He-Ne laser (632.8 nm) at an incident angle of 70°. The surface images of the multilayers were monitored using AFM (Nanoscope IIIa, tapping mode). For photo-isomerization study, a high-intensity 365 nm UV lamp equipped with 5-inch diameter filter (Cole-Parmer L-97600-05 long wave UV lamp, L-09819-23 filter) was used as the ultraviolet light source. The intensity of the lamp was 20 mw/cm^2 where the samples were placed 20 inch away from the lamp.

Results and discussion

Figure 1 gives the UV-vis absorption spectra of the PEAPB6P-AC/PDAC multilayers varying with the number of bilayers. The maximum UV absorption peak (λ_{max}) at 348 nm is attributed to the π-π* electronic transition of the conjugated trans-azobenzenes. Fig. 2 gives the dependence of the maximum absorbance and the ellipsometry multilayer thickness on the number of deposition cycles. The linear increases of the absorbance and thickness reveal a layer-by-layer uniform assembly of PEAPB6P-AC and PDAC, and soundly suggest that the interaction between PDAC and PEAPB6P-AC is strong enough to overcome the desorption effect of DMF on the adsorbed multilayers. It was observed that by this method, the thickness of PEAPB6P-AC/PDAC multilayer films could grow linearly up to tens of bilayers.

It is noteworthy that we can not give the direct evidence that PEAPB6P-AC/PDAC multilayer assembly is based on the electrostatic attraction just because of the

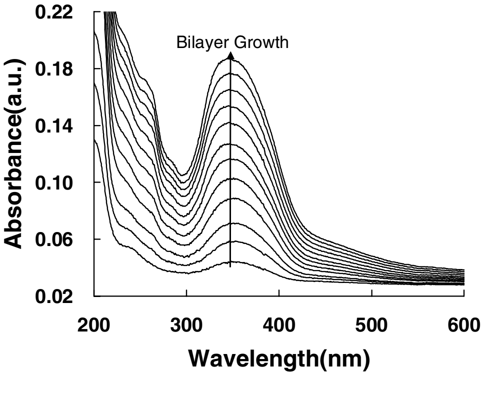


Figure 1. The UV-vis absorption spectra of PEAPB6P-AC/PDAC multilayers versus the number of bilayers. From bottom to top the number of bilayers is from 1 to 12.

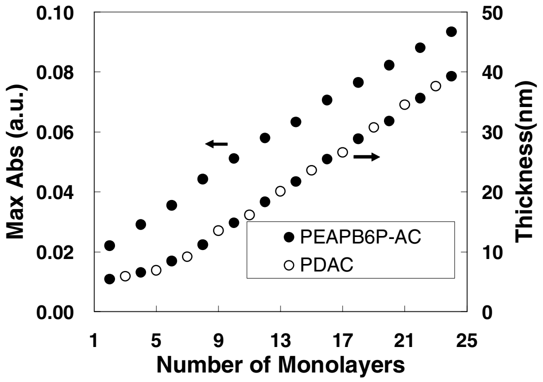


Figure 2. The maximum absorbance and the thickness of the multilayers versus the number of layers.

complicated structure of PEAPB6P-AC, which make it impossible to track the ionization of the –COOH in multilayers with FTIR spectroscopy. However, some experimental results can partly demonstrate that the PEAPB6P-AC growth in DMF is based on the electrostatic attraction instead of other interaction. First, not all organic solvents for PEAPB6P-AC can be used as the dipping media for PEAPB6P-AC/PDAC multilayer assembly. For example, PEAPB6P-AC can be well dissolved in tetrahydrofuran (THF), but alternate deposition in the PDAC solution and the THF solution of PEAPB6P-AC by the same procedure mentioned above could not produce a linearly growing multilayer. Obviously, the carboxyl acid groups in PEAPB6P-AC can be ionized in DMF while can not in THF, which induces the difference between the assembling in DMF and THF. Second, the PEAPB6P-AC/PDAC multilayers is stable in DMF and desorption of multilayers was not observed in several hours.

To study the absorption dynamics of PEAPB6P-AC, the dipping process of PEAPB6P-AC on the PDAC layer was measured with UV-vis spectroscopy. A quartz slide covered with the first PDAC layer was immersed in the DMF solution of PEAPB6P-AC for different dipping interval, then washed with DMF and dried with air stream. Fig. 3 shows the growth of the maximum absorbance versus the dipping time.

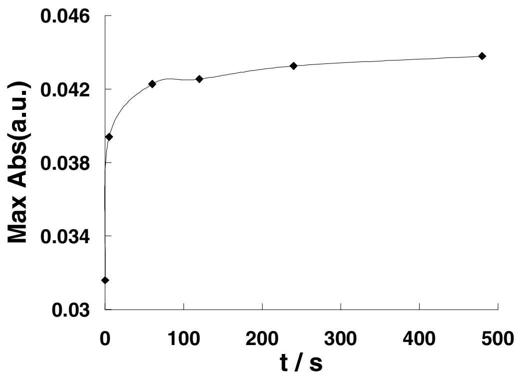


Figure 3. The maximum absorbance of the PEAPB6P-AC layer on the first assembled PDAC layer versus the immersion time.

Similar with most polyelectrolyte assembly in aqueous solutions, PEAPB6P-AC adsorbed from the DMF solution on the PDAC layer is a diffusion-controlled process [14,15]. The maximum absorbance of PEAPB6P-AC increases very rapidly at the beginning and gradually reaches equilibrium in about 5 minutes. Similar results were obtained for the adsorption dynamic process of PEAPB6P-AC on the PDAC layers at the top of the PEAPB6P-AC/PDAC multilayers. In this study, the proper dipping time for PEAPB6P-AC was selected to be 10 min, which is the same as the dipping time for the assembly in aqueous media reported by most literature.

To study the multilayer structure, azo chromophore was used as probe and detected with UV-vis spectroscopy. It is known that for the multilayers containing azo chrmophores the absorption bands in UV-vis spectroscopy are mainly attributed to the azo chromophores and significantly depends on the state of azo chromophore. It has been well documented that those transitions that are blue-shifted and thus appear at shorter wavelengths than molecular absorption band (M-band) correspond to face-to-face dye aggregation and are named as hypsochromic bands or H-bands[16,17]. This spectroscopic character can be used to distinguish 'isolated' chromophores from H-aggregates both in the solutions and multilayers. The λ_{max} of PEAPB6P-AC in anhydrous DMF was observed to be 360 nm, which corresponds to the 'isolated' azobenzene chromophores. When the azo chromophores of PEAPB6P-AC existed in a highly H-aggregated state, the λ_{max} of PEAPB6P-AC blue-shifted to 325 nm [13]. For the PEAPB6P-AC/PDAC multilayer films, the maximum absorbance appeared at 348 nm as shown in figure 1, which indicates partial H-aggregation induced when the PEAPB6P-AC chains were transferred from the dipping media to the multilayers. The washing process during the assembly has obvious influence on the existing state of the azobenzenes. When the multilayer films were washed with water (or dipped in the PDAC aqueous solution), the λ_{max} was blue-shifted to 335 nm. On the other side, when the multilayer films were washed with DMF (or dipped in the PEAPB6P-AC/DMF solution), the λ_{max} was red-shifted to 348 nm. When the multilayer films were immersed in DMF for a long period (for example 12 h), the λ_{max} was further red-shifted to 353 nm. These results strongly demonstrate that the dipping media have significant effect on the state of azo chromophores in the multilayer films. Assembly with anhydrous DMF as dipping media can effectively decrease the hydrophobic aggregation of azobenzene chromophores in the multilayer films.

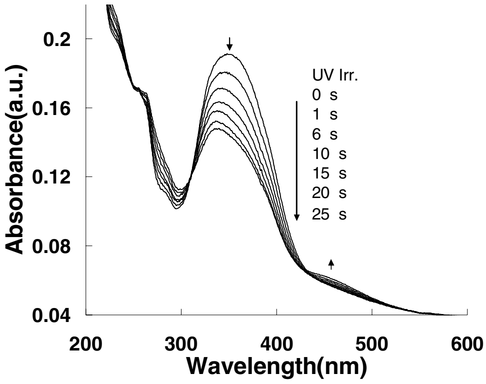


Figure 4. The absorption spectra of the multilayers varying with the irradiation time of 365nm UV light. The irradiation time is given in the figure.

Figure 4 gives the UV-vis absorption spectra of the multilayers varying with the UV irradiation time. Upon irradiation of the 365 nm light, the maximum absorbance of the multilayers decreased and the λ_{max} blue-shifted gradually. In less than one minute, the isomerization reaches the photostationary state. Two isosbestic points appeared at 310 nm and 430 nm indicates that the spectrum variation is predominated by a single photochemical isomerization process. This result shows that most of the azobenzenes in the multilayers exist in isolated state. A lot of studies have demonstrated that H-aggregation of azobenzene chromophores can significantly suppress the photo-induced trans to cis isomerization of azobenzenes so that the elimination of the H-aggregate of azobenzenes is favorable in most of the optical applications [18,19].
The multilayer surface morphology is studied with atomic force microscopy (AFM). Figure 5 give the AFM surface of the multilayers assembled on quartz slide with PEAPB6P-AC as the outmost layer. In this image we can see that the multilayer surface is rather smooth, which is significantly different with that of the multilayers fabricated in PEAPB6P-AC aqueous dispersions[13]. The smooth surface is believed to be another contribution of the elimination of the hydrophobic aggregates. In aqueous solution, the hydrophobic aggregation of azobenzene chromophores both in dipping solutions and on the multilayer surfaces makes the PEAPB6P-AC molecules to agglomerate, which produces a rough multilayer surface. On the contrary, PEAPB6P-AC in DMF exists in isolated state and can be fabricated into multilayers in molecular level, which results in the smooth surface.

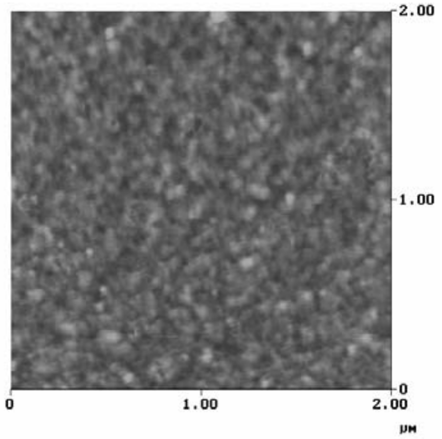


Figure 5. The AFM surface morphology of the PEAPB6P-AC/PDAC multilayers with 12 bilayers.

From the results, it can be reasonably concluded that the hydrophobic polyelectrolyte PEAPB6P-AC dissolved in DMF can be self-assembled into multilayer films through the layer-by-layer deposition process, which has eliminated the difficulties such as poor solubility and hydrophobic aggregation in aqueous media. This improvement is promising for fabricating high quality multilayer films of the hydrophobic and even water-insoluble polyelectrolytes.

Acknowledgements. Financial support from NSFC (project No.59925309 and 50303008) is gratefully acknowledged.

References

1. Decher G, Hong JD (1991) Makromol. Chem. Macromol. Symp. 46:321
2. Decher G, Hong JD (1991) Ber. Bunsenges. Phys. Chem. 95:1430
3. Knoll W (1996) Current Opin. Colloid & Interface Sci. 1:137
4. Decher G (1997) Science 277:1232
5. Decher G, Eckle M, Schmitt J, Struth B (1998) Current Opin. Colloid & Interface Sci. 3:32
6. Hammond PT (2000) Current Opin. Colloid & Interface Sci. 4:430
7. Schönhoff M (2003) Current Opin. Colloid & Interface Sci. 8:86
8. Lenahan KM, Wang YX, Liu YJ, Claus RO, Heflin JR, Marciu D, Figura C (1998) Adv. Mater. 10:853
9. Heflin JR, Figura C, Marciu D, Liu Y, Claus RO (1999) Appl. Phys. Lett. 74:495
10. Wang XG, Balasubramanian S, Li L, Jiang XL, Sandman DJ, Rubner MF, Kumar J, Tripathy SK (1997) Macromol. Rapid Commu. 18:451
11. Lvov Y, Yamada S, Kunitake T (1997) Thin Solid Films 300:107
12. Delcorte A, Bertrand P, Wischerhoff E, Laschewsky A. (1997) Langmuir 135:125
13. Cheng H, Tuo XL, Wang GJ, Wang XG (2001) Macromol. Chem. & Phys. 202:3530
14. Ferreira M, Rubner MF (1995) Macromolecules 287:107
15. Raposo M, Pontes RS, Mattoso LH, Oliveira ON (1997) Macromolecules 30:6095
16. Ariga K, Lvov Y, Kunitake T (1997) J. Am. Chem. Soc. 119:2224
17. Laschewsky A, Wischerhoff E (1997) Macromolecules 30:8304
18. Song X, Perlstein J, Whitten DG (1997) J. Am. Chem. Soc. 119:9144
19. Weener JW, Meijer EW (2000) Adv. Mater. 12:741