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Hydrogen-bonding-directed layer-by-layer polymer films: Substrate effect on the microporous morphology variation

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Abstract

The layer-by-layer (LbL) films composed of poly(4-vinylpyridine) and poly(acrylic acid) were assembled on four kinds of different substrates and their morphology variation in basic solution was comparatively studied. It was discovered that the morphology variation of the films on hydroxyl-tailored substrates was much faster than on amino-tailored substrates. Similarly, the films on carboxyl-tailored substrates could more easily yield microporous morphology than on amino-tailored substrates. The experiment results indicated that substrates played a critical role in the formation and variation process of the microporous morphology. The attractive interaction between substrates and PVP influenced the reconformation/aggregation of poly(4-vinylpyridine) chains, which led to gradually variational microporous morphology. The stronger attraction between substrates and PVP would result in slower microporous morphology variation. The investigation results in this article not only have provided some helpful experience for controlling microporous films but also have deepened the understanding of the formation mechanism of microporous morphology.

Keywords: Layer-by-layer polymer film; Microporous morphology; Hydrogen bonding; Post-treatment; Substrate effect

1. Introduction

The layer-by-layer (LbL) assembly technique has made great progress since it was introduced by Decher [1]. On one hand, besides electrostatic attraction, diverse other interaction, such as hydrogen bonding [2,3], covalent bonding [4], specific molecular recognition [5] and stereocomplex interaction [6], was also employed as the driving force for LbL assembly, which greatly expanded the application of LbL assembly technique. On the other hand, in order to fabricate functional LbL films, besides directly assembling some functional components, such as nanoparticles, non-linear optical materials, biomacromolecules, capsules and even living cells, into LbL films, many post-treatment methods have been successfully developed, including annealing [7], cross-linking [8], surface patterning [9], electrochemical deposition [10] and acid/basic solution immersion [11,12], etc. Among these methods, solution post-treatment is highlighted because of its simplicity, noticeable effects and reliability.

It has brought many advantages to use hydrogen bonding as the driving force of LbL assembly.

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Hydrogen bonding can form in organic solvent, providing a feasible method for assembling the molecules that cannot dissolve in water into LbL films. It has moderate strength, is sensitive to pH values and can easily be destroyed and re-form, which makes hydrogen-bonding-directed LbL films suit for solution post-treatment. A typical example is the fabrication of microporous films via the basic solution post-treatment of hydrogen-bonding-directed LbL films. Hydrogen-bonding-directed poly(4-vinylpyridine)(PVP)/poly(acrylic acid)(PAA) LbL films can yield microporous morphology after immersion in basic solution, attributing to the reconformation/aggregation of remaining PVP on substrates following the release of PAA from the films [12]. Microporous films have great potential of application in many fields [13]. So it is significant to investigate the factors influencing microporous morphology formation and variation. Because the reconformation/aggregation of PVP occur on the interface of substrates and solvent, it behaves differently from that in solvent only and will inevitably be influenced by substrate environment. Therefore, the investigation on the variation processes and rules of microporous morphology on different substrates is very important and helpful for developing the methods for modulating morphology parameters, regulating appropriate application scopes and clarifying the formation mechanism of microporous films.

In this article, we obtained four kinds of different substrates by chemically modifying their surfaces and prepared PVP/PAA LbL films on these substrates. Next, we comparatively studied the morphology variation of these films in basic solution, analyzed the substrate effect on microporous morphology variation and further discussed the formation mechanism of microporous morphology.

2. Experimental section

2.1. Materials

PVP ($M_w = 60{,}000$) and PAA ($M_w = 2000$) were purchased from Aldrich and their structures are shown in Scheme 1. 3-Aminopropyldimethylmethoxysilane[$CH_3OSi(CH_3)_2(CH_2)_3NH_2$] was obtained from Acros. Cystamine dihydrochloride($NH_2CH_2CH_2S$–$SCH_2CH_2NH_2 \cdot 2HCl$) was purchased from Changzhou Furong Fine Chemicals Company, China. 3-Mercaptopropionic acid ($HSCH_2CH_2COOH$) was obtained from Koch-Light Laboratories Ltd., Coinbrook Bucks, England. Methanol and

Poly(acrylic acid) Poly(4-vinyl pyridine)

Scheme 1. The structures of PAA and PVP.

other chemicals were purchased from Beijing Chemicals Company, China. All chemicals were used without further treatment. Quartz and gold-plated glass plates were obtained from Changchun Institute of Optics & Fine Mechanics and Physics, Chinese Academy of Sciences.

2.2. Methods

UV–vis spectra were recorded on a PerkinElmer Lambda 800 UV–vis spectrometer. Atomic force microscopy (AFM) images were taken with a multimode Nanoscope IIIA (Digital Instrument) under ambient conditions. AFM was operated in the tapping mode with an optical readout using Si cantilevers. X-ray diffraction (XRD) was carried out on a Rigaku X-ray diffractometer (D/max 2500V PC, using Cu KR radiation of a wavelength of 1.5406 Å).

2.3. Preparation of different substrates

We prepared the following four kinds of substrates by chemically modifying quartz and gold-plated glass plates in our experiments.

Quartz plates were cleaned in a mixture of H_2SO_4–H_2O_2 (V:V = 7:3) (Piranha), washed with much pure water and dried with nitrogen gas. As a result, many hydroxyls appeared on the surface of quartz plates. Such substrates are noted as Si–OH for the convenience of further discussion.

If the above substrates were dried at 80 °C, immersed in 3-aminopropyldimethylmethoxysilane solution in dimethylbenzene (V:V = 1:1000) for 12 h [14], and washed with methylbenzene, acetone and chloroform, they would yield an amino-tailored surface. Such substrates are noted as Si–$OSi(CH_3)_2$-$(CH_2)_3NH_2$.

Gold-plated glass plates were rinsed with water, ethanol and chloroform, dried with nitrogen gas and then immersed in 0.01 M 3-mercaptopropionic acid solution in ethanol for 12 h. Because Au and mercapto groups formed Au–S bonds [15], the substrates with a carboxyl-tailored surface were obtained. Such substrates are noted as Au–SCH_2CH_2COOH.