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Layer-by-Layer Deposited Multilayer Assemblies of Ionene-Type Polyelectrolytes Based on the Spin-Coating Method

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Introduction. During the past several years, the electrostatic self-assembly (ESA) technique has been devoted to realization of a variety of multilayer heterostructures on a solid substrate,[6] especially ultrathin films and coatings of polymers. This technique was developed on the basis of a solution-dipping method. A good reason for a rapid increase of using the technique in surface modification is its striking simplicity. However, one disadvantage of the technique is a rather long time required to assemble a monomolecular film that lasts in general between 1 min and 1 h depending on adsorbing systems, typically 10−20 min. This is due to a two-step adsorption process: polymer chains are anchored to the surface by some segments (a fast initial step) and then relax to pack densely (a slower second step), as indicated by several studies.[7]

We are seeking for an alternative method to reduce the assembly time of a monomolecular film. One plausible method would be the use of a spin-coating method. In this respect, we have investigated the effect of spinning on the assembling of a monomolecular film of polyelectrolytes on a solid substrate. The structure of the spin-coated multilayer assemblies, i.e., surface roughness and domain feature revealed by AFM and X-ray diffraction, was compared with that of a film prepared by a solution-dipping method. It turned out that the surfaces of spin-coated films are much smoother than those of solution-dipped films.

Experimental Section. a. Materials. Poly(allylamine hydrochloride) (M_w = 8000−11 000) PAH and ι-carrageenan CAG, obtained from Aldrich, were used as received. The synthesis and the detailed characterization of the poly(((4,4′-bis(6-dimethylammonio)hexyl)oxy)azobenzene bromide) PAZ-6 is described in the forthcoming literature.[8]

b. Preparation of Multilayer Assemblies. Two different solid substrates, i.e., fused silica slides and silicium wafers, were employed in this work. Initially, cleaned solid substrates were precoated with five bilayers of PAH and CAG in order to increase the charge density of the surface, as described previously;[8] the concentrations of PAH and CAG in H_2O were 1 unit mM (pH 4.0) and 2 unit mM (pH 6.3), respectively. A PAZ-6 polyionene solution (0.1 unit mM) was prepared in a mixture of DMSO/H_2O (1/1) and a CAG solution (2 unit mM) in H_2O. The preparation of multilayer assemblies based on the solution-dipping method was achieved using well established procedures by dipping alternately in cationic and then in anionic solution (each time dipped for 20 min); the substrate was rinsed three times with water (each time for 1 min) between these two steps, as already described in the forthcoming literature.[8] A similar procedure was adopted when assembling the multilayers by a spin-coating method. In this case, however, the polymer/solvent solution (ca. 0.5 mL) was poured onto a substrate, and then the substrate was spun at a speed of 5000 revolutions per minute (rpm) for 20 s. Subsequently, 1 mL of deionized water was put on the substrate, and then the substrate was spun again at 5000 rpm for 20 s. The washing steps were repeated three times. The amount of polymer material deposited at each step was estimated from its absorption spectrum taken with a Perkin-Elmer UV/vis spectrophotometer (Lambda 40).

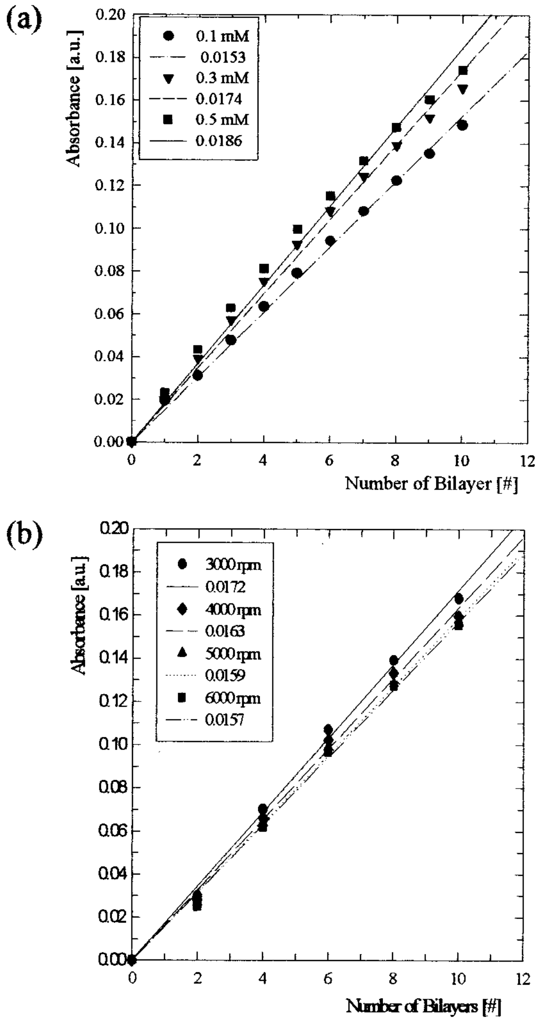

Figure 1. Plot of the UV/vis absorbance vs number of deposition cycles in dependence of the concentration of polymer/solvent solution (a) and the spin speed (b).

c. Characterization. AFM images were obtained in air at room temperature by using a Digital Instruments model Nanoscope IIIa scanning probe microscope. Using a 125 μm long Si cantilever (Nanoprobe, Digital Instru-

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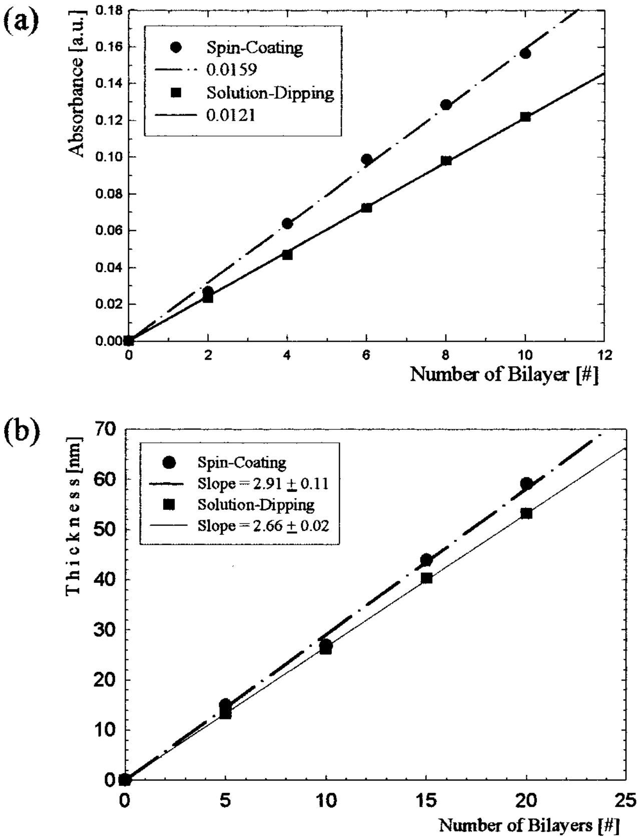

Figure 2. Plot of the absorbance (a) and the ellipsometric thickness (b) vs the number of deposition cycles of PAZ-6/CAG bilayer on the precoating five-bilayer film of PAH/CAG that were prepared by spin-coating and solution-dipping techniques.

ments), topographic images were recorded in tapping mode at a scan rate of 2−5 Hz. The film thickness was determined by using an optical ellipsometer (Rudolph/Auto EL). The measurement was performed with the 632.8 nm line of a He/Ne laser incident upon the sample at 70°. As usual, the refractive index of the polyelectrolyte film was assumed to be 1.54. At least five different sampling points were considered in obtaining an average thickness value. The ellipsometric thickness values were compared with those obtained from X-ray reflectivity measurement using a Cu Kα (λ = 1.54 Å) beam originating from a narrow line source of a 18 kW Rigaku Ru-300 rotating anode generator.

Results and Discussion. At first, we examined the dependences of the concentration of a polymer/solvent solution and the spin speed of the substrate on the adsorption behavior of polyelectrolytes on a charged substrate. In Figure 1, successive deposition of CAG/PAZ-6 layers is confirmed by UV/vis measurement. Again, a linear increase in absorbance indicates the regular proceeding of the deposition process. It was found that the amount of polymer adsorbed per bilayer grew with increasing the concentration of PAZ-6 from 0.1 to 0.5 unit mM (Figure 1a). When increasing the spin speed between 3000 and 5000 rpm, the adsorbed amount of the polymer was decreased with using a fixed concentration of PAZ-6 solution (0.1 mM), as usually observed in the spin-coating technique (Figure 1b). We have also to mention that the thickness could be controlled with changing ionic strength and pH of the polymer solution (data not shown).

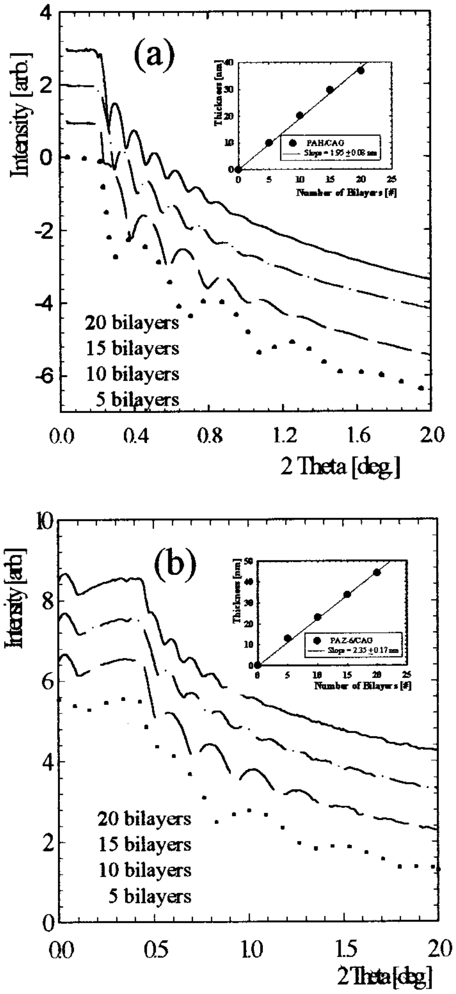

Figure 3. Buildup of a SCESA multilayer film composed of PAH/CAG (a) and PAZ-6/CAG bilayers (b) monitored by small-angle X-ray scattering (plot of the thickness vs the number of deposition cycles of each bilayer in inset of the figures).

For a comparative study, PAZ-6/CAG multilayers were assembled using spin-casting as well as solution-dipping methods. Preparation conditions such as concentration and solvent were the same for both methods except that the spin speed was exclusively chosen to be 5000 rpm for all samples when using a spin-casting method. Figure 2 a shows the maximum $\pi\pi^*$ absorbance of PAZ-6 at 360 and 363 nm as a function of the number of bilayers for both the spin-coated and solution-dipped multilayers, respectively. A linear fit of data yields an average increase of the optical density of 0.0121 for the spin-coated film which is slightly higher than that of the solution-dipped film (0.0091). In accordance of the UV/vis absorbance, the ellipsometric thickness of bilayers increased also linearly with the number of PAZ-6/CAG bilayers, as can be seen in Figure 2b. From the slopes, the growth step per bilayer is estimated to be 2.9 and 2.7 nm, respectively, for the spin-coated and the solution-dipped films. Here, it should be also noted that the difference of the thickness is not significant in a spin-coated 20 bilayers film of PAZ-6/CAG, when measured ellipsometrically at eight points chosen arbitrarily cross the substrate via the center (32.6, 33.4, 33.2, 33.2, 35.5, 33.4, 33.1, and 32.9 Å).

X-ray reflectivity measurements are employed for estimating the thickness of the multilayer assemblies of PAZ-6/CAG and that of the precoating PAH/CAG

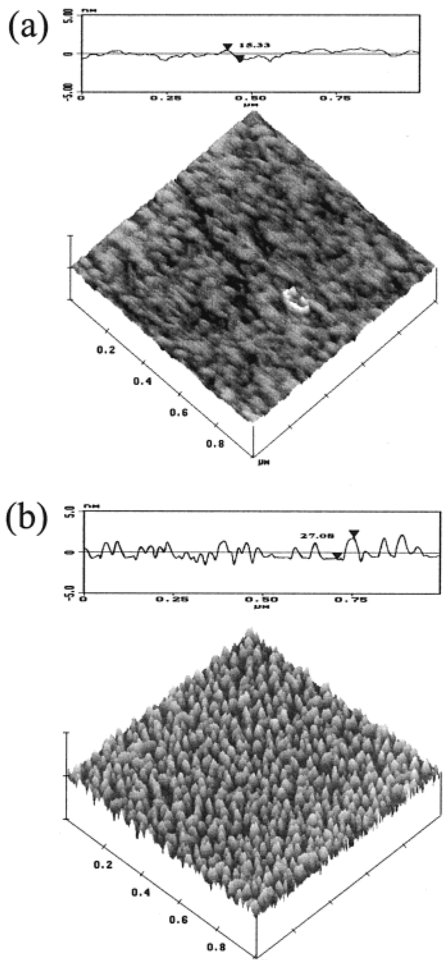

Figure 4. Tapping mode AFM image (1 μm × 1 μm) of the SCESA (a) and the solution-dipped monolayers on mica. Upper parts represent the relative height profiles against the lowest point of the whole two-dimensional image, and lower ones show raw AFM images.

bilayers, as shown in Figure 3. It is remarkable that typical Kiessig fringes[9] are clearly identified for the spin-coated film, while one can hardly observe such fringes for the solution-dipped film of PAZ-6/CAG (Figure 3b). That might be a reliable evidence for the effect of the spinning process on the enhanced local planarization of polymer films. The results of the calculation of the thickness from the fringes according to Bragg's equation were plotted vs the number of the adsorbed layers (Figure 3, inset). An average value of 2.35 ± 0.17 nm per PAZ-6/CAG is consistent with the ellipsometric thickness ($\sim$2.9 nm) with experimental error. Also, Kiessig fringes are observed for the precoating layers of PAH/CAG. The thickness of the layer pair can be estimated to be 1.95 ± 0.08 nm, which is in fact consistent with the values that are known for polyelectrolyte multilayers in the literature.[2]

The AFM images should provide more detailed information on the domain structure and the surface roughness of the polyelectrolyte film. Parts a and b of Figure 4 show the AFM images for the spin-coated and the solution-dipped monolayer of PAZ-6 on mica substrates, respectively. The spin-coated monolayer is obviously much smoother than the solution-dipped monolayer; the solution-dipped monolayer exhibits a uniform granular structure (size 2−4 nm). The rms roughness of the spin-coated monolayer is at best $\sim$3.5 Å, while that of the solution-dipped monolayer is ca. 7.7 Å. From the section analyses, the thickness of the PAZ-6 is also determined to be 2.71 nm, which is consistent with that from the theoretical model calculations.[8]

Conclusion. The SCESA technique is shown to be advantageous over the conventional solution-dipping technique when assembling ultrathin multilayer films based on the ESA method. First, the preparation time per single layer can be reduced drastically, i.e., from 20 min to 20 s. Second, as evidenced from the X-ray reflectivity measurement, the films prepared by a spin-coating method should be much smoother than those prepared by a solution-dipping method.

We have also found it possible to deposit the polycations and polyanions that are normally used to assemble these films such as poly(styrenesulfonate) (PSS), poly(allylamine hydrochloride) (PAH), and poly(acrylic acid) (PAA). Here, it should be noted that further deposition of PSS was not observed in 5 times repeated adsorption steps on PSS surface. In addition, the method could be successfully applied to the buildup of the organic/inorganic multilayer films composed of PAH and CdS nanoparticles carrying negative charges on the surface.[10] All of these observations indicate that most of the solution-dipped multilayer systems of polyelectrolytes can be realized by the SCESA technique. Since the preparation steps can be automated along with an easy access of the quality control, we are sure that the spin-coating electrostatic self-assembly technique will be widely applied in the near future for fabricating new promising polyelectrolyte films.

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