Notes

Alternate Adsorption of Polymers on a Gold Surface through the Charge-Transfer Interaction

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Introduction

Construction of supramolecular architecture is essential for the functionalization of organic materials, and various studies related to it have been performed.[1] The fabrication of layered structures using intermolecular interactions between polymers is one of the most extensively studied subjects in this field.[2−21]

Previously, we reported that layer-by-layer deposited polymer film could be fabricated by simply dipping a substrate into the solutions of polymers through the charge-transfer (CT) interaction between the electron-donating and the electron-accepting groups attached to side chains of the polymers.[21] Because the CT interaction is the driving force of adsorption, organic solvents can be used for preparation of the film, thus making it possible for a variety of hydrophobic functional groups to be incorporated into the film.

In this paper, we investigated surface morphology and formation kinetics of the layer-by-layer deposited film on a gold surface by atomic force microscopy (AFM) and surface plasmon (SP) measurements. Both techniques can probe the minute changes near the surface and, therefore, give further insight into the adsorption behavior at the early stage of adsorption, which is crucial for determining the overall quality of the films obtained.

Experimental Section

Materials. Figure 1 shows the chemical structures of the compounds used in this study. These polymers, poly[2-(9-carbazolyl)ethyl methacrylate] (PCzEMA, $M_n = 37\,000$) and poly[2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate] (PDNBMA, $M_n = 20\,000$), have electron-donating carbazolyl groups and electron-accepting 3,5-dinitrobenzoyl groups, respectively, in the side chains. These polymers were synthesized as reported.[22,23] All of the solvents used were of spectrophotometric grade. The glass slides (BK-7 or LaSF9) on which gold was vapor-deposited under a pressure of 2×10^{-6} Torr were used for the preparation of the film.

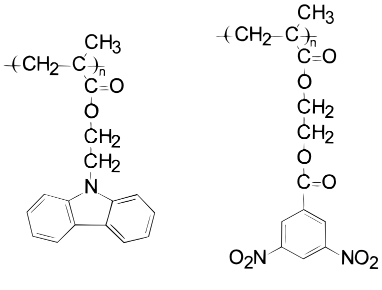

Figure 1. Chemical structures of the polymers used in this study.

Preparation of Layer-by-Layer Deposited Films. Layer-by-layer films were prepared according to the following procedure. First, the substrate was immersed in the solution of PCzEMA in 1,2-dichloroethane (DCE) for 5 min. After being rinsed in DCE for 5 min and dried in air for 5 min, the substrate was immersed in the solution of PDNBMA in DCE, then rinsed in DCE, and dried in air for 5 min each. The multilayered film was prepared by repeating this cycle. The concentration of the solutions was 1.0×10^{-4} mol unit L^{-1}, and the procedure described above was performed at room temperature under the relative humidity of ca. 20%.

Atomic Force Microscopy (AFM). The surface morphology of the layer-by-layer deposited film was observed in air with an atomic force microscope (Shimadzu SPM-9500) in the "contact" mode at room temperature. The "trace" scan (from left to right) and the "retrace" scan (from right to left) yielded the same profile, indicating that the surface was not deformed by the scan. All of the images were observed with a scan rate of 10 μm s^{-1} over a 2×2 μm^2 area, and several areas were observed for each sample.

Surface Plasmon Measurement. The thickness of ultrathin organic films on a metal surface can be determined by surface plasmon measurements,[24] with a precision on the order of angstroms by using the Fresnel equation. For the in situ SP measurement, the angle scan of 20° was made within 4 s at a given time. The concentration of the polymers in DCE was 1.0×10^{-4} mol unit L^{-1} except for that in Figure 7.

Results and Discussion

Surface Morphology. Figure 2 shows AFM images of the surfaces of (a) a gold-deposited substrate and (b) the eight-layered film on the gold surface. The surface of the gold-deposited substrate was smoothed out by the consecutive adsorption of the polymers. To evaluate the change in the surface morphology, we used a smoothness parameter S_m, which describes the mean distance between an adjacent pair of regions above and below the mean line of height profile. S_m can be described as

$$S_m = \frac{1}{n}\sum_{i=1}^{n} S_{m\,i} \tag{1}$$

in which n and $S_{m\,i}$ are the number of peak−valley pairs on a line drawn in the image and the distance of adjacent points at which the profile intersects the mean line, respectively. Figure 3 shows the dependence of S_m (Figure 3a) and the thickness increment Δd (Figure 3b) on the number of layers. Δd was measured by the SP

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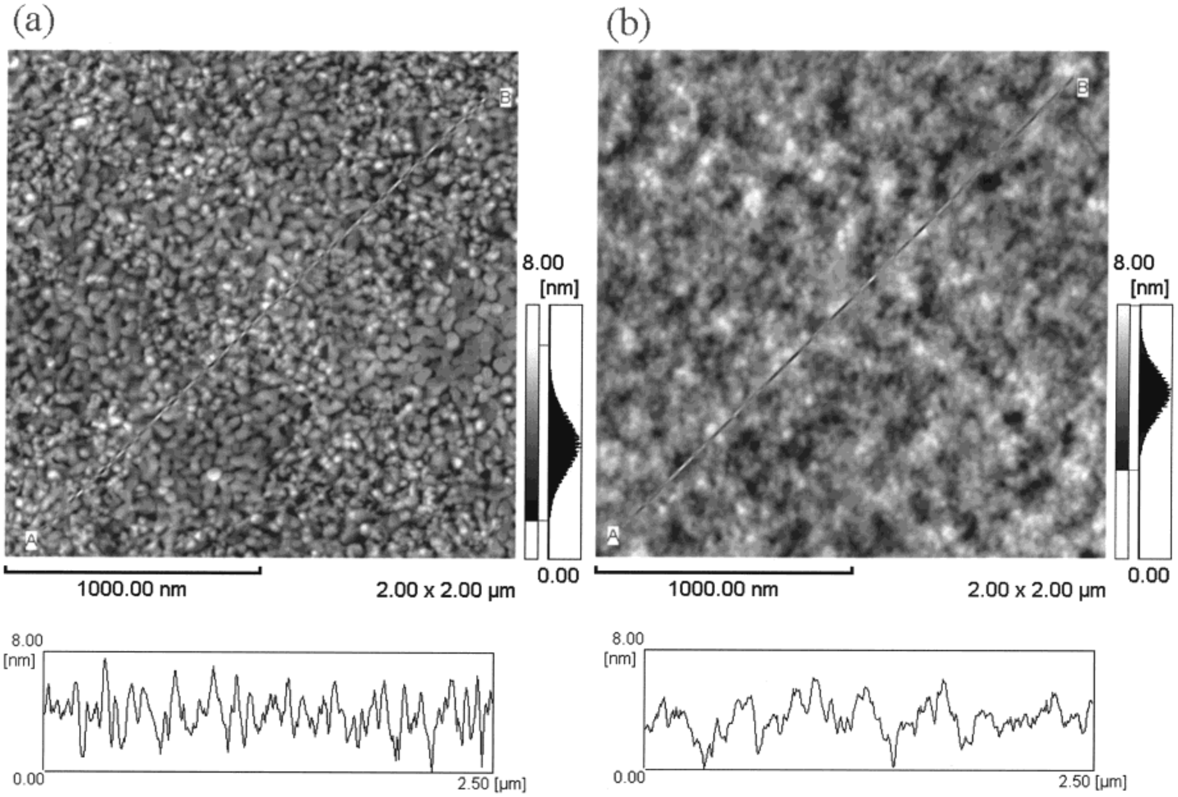

Figure 2. AFM images (2 × 2 μm^2) of the surfaces of (a) a gold-deposited substrate and (b) an eight-layered layer-by-layer deposited film. Cross sections of the topographic images (8 nm in height) are also shown below each figure.

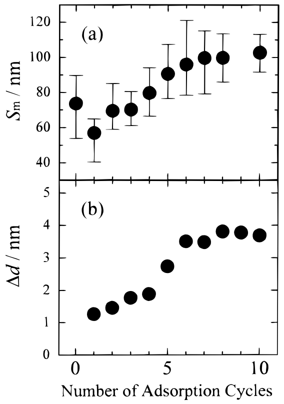

Figure 3. Dependence of (a) S_m and (b) the thickness increment (Δd) on the number of adsorption cycles. The plotted values in part b were evaluated by fitting the SP curves with Fresnel's equation.

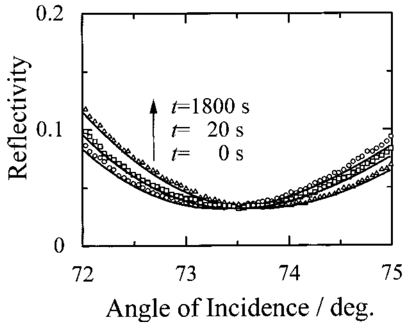

Figure 4. SP curves for the adsorption of PCzEMA on a gold surface and their corresponding theoretical fits. Denoted in the figure are the times at scan; the adsorption starts at t = 0 s. Concentration of the polymers in DCE was 1.0 $\times 10^{-4}$ mol unit L^{-1}.

measurement in air. Both figures show that the measured quantities (S_m and Δd) were leveled off around the sixth layer, indicating that the deposition of six layers made the gold surface into the surface intrinsic to the layer-by-layer deposited film.

In Figure 3b, Δd increased with the increase in the number of layers before saturation. This can be explained as follows. The thickness of the first PCzEMA layer, which is adsorbed onto a gold surface, is so thin (ca. 1 nm) that the layer does not have enough adsorption sites for the next PDNBMA, resulting in a thinner second layer than when saturated. As the number of adsorption cycles increases, the influence of the thinness of the first layer on the thickness increment gradually disappears, and the increment becomes constant around the sixth layer. Decher et al. also reported the nonlinear increase in total thickness of the layer-by-layer films adsorbed from polyelectrolyte solutions, which was observed by neutron reflectometry measurements.[12]

Adsorption Behavior. To investigate the adsorption behavior in the formation of the layer-by-layer deposited films on the gold surface, we performed in situ SP measurements. Figure 4 shows the change in the SP curves for the adsorption of PCzEMA onto a gold surface, along with their corresponding theoretical fits. The resonance curves shifted toward higher angles with the increase in the adsorption time, indicating that the amount of PCzEMA adsorbed on the surface increased with time. After the adsorption of PCzEMA for 30 min, the surface was rinsed in DCE for 30 min. Then, no shift in SP curves was observed. This means that the PCzEMA was strongly bound to the gold surface. The adsorption of PCzEMA onto the gold surface is a specific case, for PDNBMA is not adsorbed onto the gold surface. The adsorption of PCzEMA onto the gold surface is probably due to the interaction between the gold surface

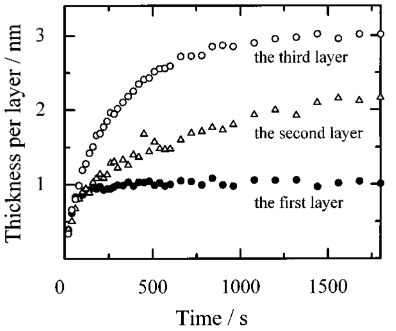

Figure 5. Time evolution of the thickness of each layer. The plotted values were evaluated by fitting the SP curves with Fresnel's equation. The concentration of the polymers in DCE was 1.0×10^{-4} mol unit L^{-1}.

and electron-donating carbazolyl group. The interaction between the gold surface and electron-donating functional groups, such as amino and pyridine groups, has been reported.[25]

The curves further shifted toward higher angles for the following adsorption of PDNBMA onto the PCzEMA surface (adsorption of the second layer) and the adsorption of PCzEMA onto the PDNBMA surface (adsorption of the third layer). No rinse effect was seen for either the second or third layer, indicating that the polymers were irreversibly adsorbed through the charge-transfer interaction between the carbazolyl and 3,5-dinitrobenzoyl groups.

Figure 5 shows the time evolution of the thickness of each layer obtained by fitting the SP curves with Fresnel's equation. In Figure 5, it is noticed that the curves have two stages, that is, the diffusion-limited adsorption stage ($t < 60$ s) and a stage with the rearrangement of polymer chains ($t > 60$ s).

In the early stage of adsorption, ($t < 60$ s), the adsorption rate was independent of the film surface. This is due to the fact that the adsorption rate in this stage is limited by the diffusion of polymers in solutions. For the diffusion-limited adsorption onto the surface, the adsorption rate can be described as follows.[26]

$$\frac{\partial\Gamma}{\partial t} = C\Phi\sqrt{\frac{D}{\pi t}} = C\sqrt{\frac{D}{\pi t}} \times \frac{\Gamma_f - \Gamma}{\Gamma_f} \qquad (2)$$

where Γ is the amount of polymers adsorbed at the surface, C is the concentration of the polymer in solution, D is the diffusion coefficient, Φ is the fraction of surface available for adsorption, and Γ_f is the final adsorbance value. Equation 2 can be integrated to give Γ as a function of time.

$$\Gamma = \Gamma_f\left[1 - \exp\left(-\frac{2C}{\Gamma_f}\sqrt{\frac{Dt}{\pi}}\right)\right] \qquad (3)$$

Equation 3 can be simplified with the Taylor expansion to give eq 4 when

$$t \ll \frac{\pi\Gamma_f^{\,2}}{4DC^2}$$

$$\Gamma = 2C\sqrt{\frac{Dt}{\pi}} \qquad (4)$$

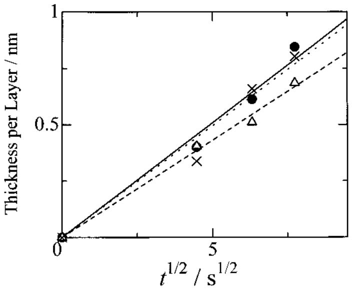

Figure 6. Plots of the layer thickness against $t^{1/2}$ for the first (filled circles, solid line), second (unfilled triangles, broken line), and third layers (cross symbols, dotted line). The lines are the least-squares fits of the data. The concentration of the polymers in DCE was 1.0×10^{-4} mol unit L^{-1}.

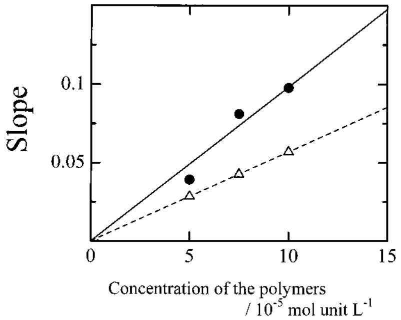

Figure 7. Dependence of the slope ($2C(D/\pi)^{1/2}$) on the concentration of the polymers for the first (filled circles) and second layers (unfilled triangles). The lines are the least-squares fits of the data.

Therefore, Γ would increase linearly with $t^{1/2}$ for the early stage of adsorption. Figure 6 shows the plots of the layer thickness against $t^{1/2}$ and their least-squares fits. In this figure, the layer thickness increases linearly with $t^{1/2}$, suggesting that the adsorption rate in this stage is diffusion-limited.

It is noticed from eq 4 that the slope of the line in Figure 6 equals $2C(D/\pi)^{1/2}$. Thus, the slope should increase linearly with the concentration of the polymers. Figure 7 shows the concentration dependence of the slope and that the slope increased linearly with the concentration. These results show that the adsorption of the polymers up to 60 s is diffusion-limited. The diffusion coefficient of PCzEMA in DCE could be evaluated from eq 4 to be 1.5×10^{-7} cm^2 s^{-1}, assuming that the density of the PCzEMA layer is the same as that of the PCzEMA bulk film (1.23 g cm^{-3}).

In the second stage ($t > 60$ s), the difference was seen in the adsorption behavior of each layer (Figure 5). For the adsorption of the first layer onto the gold surface, the thickness was saturated within the diffusion-limited stage. However, for the adsorption of the second and third layers, the thickness increased further after the diffusion-limited stage. This is probably due to the rearrangement of the polymer chain that results in the increase in the number of available adsorption sites.

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