Surface Pressure, Ellipsometric, and Atomic Force Microscopic Study of Poly(*N*-isopropylacrylamide) Film at the Air–Water Interface

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Introduction

In a previous paper,[1] we reported that poly(*N*-isopropylacrylamide) (poly(NIPAM)) formed a stable monolayer at the air–water interface when spread from its aqueous solution. Since poly(NIPAM) is a water-soluble polymer, some of the actual amount of poly(NIPAM) spread is desorbed from the air–water interface, and the amount of poly(NIPAM) adsorbed at the air–water interface is dependent on temperature. The layer thickness determined from ellipsometry is often useful to obtain structural information about the polymer spread at the air–water interface.

On the other hand, it is interesting to understand how changes in the conformation when the polymer chains spread at the air–water interface are transferred on the solid surface as the Langmuir–Blodgett (LB) film. In this note, we report the surface properties of poly(NIPAM) films spread at the air–water interface using ellipsometric and surface pressure measurements and atomic force microscopy (AFM) images of the one-layer LB film of poly(NIPAM). We chose chloroform as a spreading solvent, since it is expected that more poly(NIPAM) will adsorbs at the air–water interface because of a less water-miscible solvent.

Experimental Section

Materials. The poly(NIPAM) sample used was the same as in a previous paper.[1] Its molecular weight and molecular weight distribution were 5.97×10^5 and 3.23, respectively.

We used spectrograde chloroform to prepare poly(NIPAM) film at the air–water interface without further purification.

Surface Pressure Measurements. The apparatus used for surface pressure measurement was the same as described in detail before.[1–3] A Teflon trough was filled with deionized water, and the working temperature was controlled within 31.3 ± 0.2 °C by circulating thermostated water.[1] Poly(NIPAM) films were spread on the water surface with an area of 290 cm² in the trough by applying the method of "successive additions" of chloroform poly(NIPAM) solutions ($1.06–5.28 \times 10^{-3}$ g/mL) with a Hamilton microsyringe. When the surface pressure remained constant over 10 min, we regarded it as an equilibrium surface pressure. The experimental errors in the surface pressure were less than 0.1 mN/m.

Ellipsometry. The ellipsometry setup has been described in detail elsewhere.[1–3] Ellipsometric measurements were performed at 31.3 °C. From the two ellipsometric parameters, i.e., the phase difference (Δ) and the azimuth (ψ) of the amplitude ratio for light polarized parallel and normal to the plane of incidence, we calculated both the layer thickness (t) and the refractive index (n_f) of the poly(NIPAM) film spread
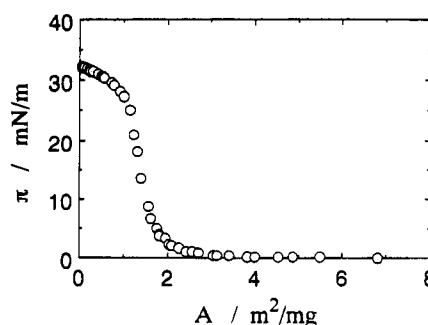
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Figure 1. Surface pressure–surface area (π–A) isotherm of poly(NIPAM) spread at the air–water interface at 31.3 °C.

at the air–water interface using a FACOM M760/6 computer system with a modified version of McCrackin's program.[4]

Langmuir–Blodgett Film Preparation. The one-layer Langmuir–Blodgett (LB) films were prepared with normal dipping using an NL-LB140S-MWC trough (Nippon Laser & Electronics Lab, Nagoya, Japan). The solid substrates for LB deposition were freshly cleaved micas. Transfers of poly(NIPAM) films were performed at constant surface pressures of 0.08, 21.0, and 32.1 mN/m. A deposition speed of 1.0 cm/min resulted in transfer ratios of ca. 0.8. The substrate temperature was kept constant at 31 ± 0.5 °C.

Atomic Force Microscopy. Atomic force microscopy (AFM) experiments were performed with a Nanoscope III AFM equipped with microfabricated silicon cantilevers (Digital Instruments, Santa Barbara, CA). All AFM images of poly(NIPAM) films were taken under the tapping mode at ambient temperature in air.

Results and Discussion

Figure 1 shows the surface pressure–surface area (π–A) isotherm of poly(NIPAM) at 31.3 °C and poly(NIPAM) belongs to the condensed monolayer. The surface pressure is first observed at smaller surface area and then it steeply increases with a decrease in surface area. The collapsed surface pressure is ca. 32 mN/m and does not change even with an increase in the spread amount ($\Gamma = 1/A$) of poly(NIPAM), namely, above $\Gamma = 5$ mg/m².

Ellipsometry and AFM were performed at surface pressures of 0.09, 21.0, and 32.1 mN/m, respectively, and the corresponding Γ values are 0.09, 0.82, and 10.4 mg/m². The difference in the spread amount of poly(NIPAM) should influence the polymer layer thickness at the interface. As expected, the average values of the layer thickness and the refractive index of the poly(NIPAM) layer adsorbed at the air–water interface are obtained: 0.65 nm, 1.361 at $\Gamma = 0.09$ mg/m²; 6.9 nm, 1.361 at $\Gamma = 0.82$ mg/m²; and 11.2 nm, 1.414 at $\Gamma = 10.4$ mg/m², respectively. The error margins for the values of t and n_f are within 20% at lower Γ due to small changes in ψ and they are within 10% at the highest Γ. From the values of t and n_f, it can be expected to form a thicker and denser layer with an increase in Γ. In particular, the larger layer thickness than 10 nm at $\Gamma = 10.4$ mg/m² suggests that some portions of the adsorbed poly(NIPAM) chains dangle into the water phase with the formation of large loops due to a water-soluble polymer. The loops are one type of subchains in the description of conformations of adsorbed polymer chains and they have no contacts with the interface and connect with two trains, which have all their polymer segments in contact with the interface.[5]

Moreover, we can calculate the ellipsometric amount (A_d) of poly(NIPAM) adsorbed at the air–water interface

Figure 2. AFM image of the LB film of poly(NIPAM) prepared at $\pi = 0.08$ mN/m.
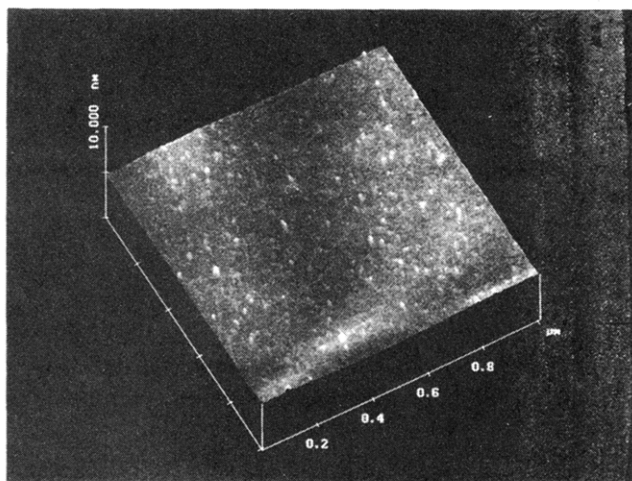

Figure 3. AFM image of the LB film of poly(NIPAM) prepared at $\pi = 21.0$ mN/m.

using the following equation:

$$A_d = t(n_f - n_0)/(dn/dc) \qquad (1)$$

where (dn/dc) is the refractive index increment and n_0 is the refractive index of the solvent. The refractive index increment of the aqueous poly(NIPAM) solution at 31.3 °C was determined to be 0.213 mL/g, and the A_d values obtained from eq 1 were 0.064, 0.68, and 4.0 mg/m^2 at $\Gamma = 0.09$, 0.82, and 10.4 mg/m^2, respectively. The A_d value at $\Gamma = 10.4$ mg/m^2 is somewhat less than the threshold of the plateau amount of the poly(NIPAM) adsorbed at the air–water interface.[6] The magnitude of A_d is twice as large as that for water spread poly-(NIPAM)[1] since chloroform is a less water-miscible solvent than water. At lower surface concentrations, the A_d value seems to be in agreement with the Γ value taking into account the experimental reproducibility. At the highest Γ the value of A_d, however, is less than the actual amount of poly(NIPAM) spread at the air–water interface. This means that some of the spread poly-(NIPAM) is desorbed from the air–water interface and dissolves into the subphase water.

Figures 2–4 show AFM images of poly(NIPAM) at surface pressures of 0.08, 21.0, and 32.1 mN/m, respectively. The scale of the Z axis in each image is 10 nm with 5 nm/div. The respective AFM images were almost the same without any damage through scanning was done repeatedly and the reproducibility of the images was good. When the AFM was operated in the contact mode, however, it was found that some portions of the LB films were taken off. No clear periodic structure could be seen from a Fourier transform of the images, indicating that the surface is somewhat disordered.

We can notice some features in the respective AFM images. At the lowest surface concentration, the AFM image looks smooth without any peaks on a scan area of $1.0 \times 1.0 \ \mu m^2$ and it is less than 0.2 nm peak-to-valley, suggesting a nearly flat film formed on the mica surface. In the corresponding area, since there is no
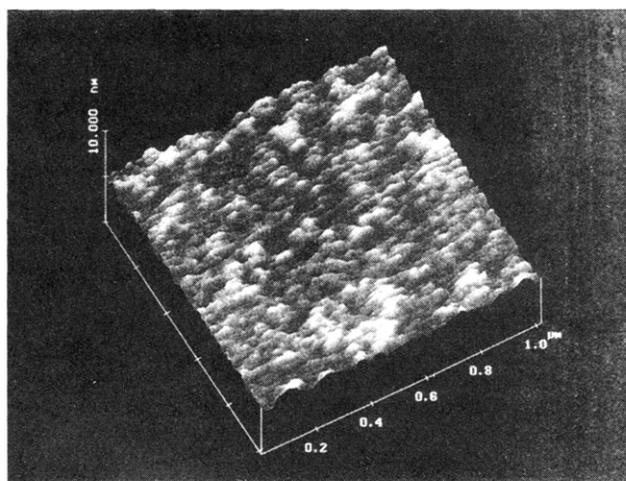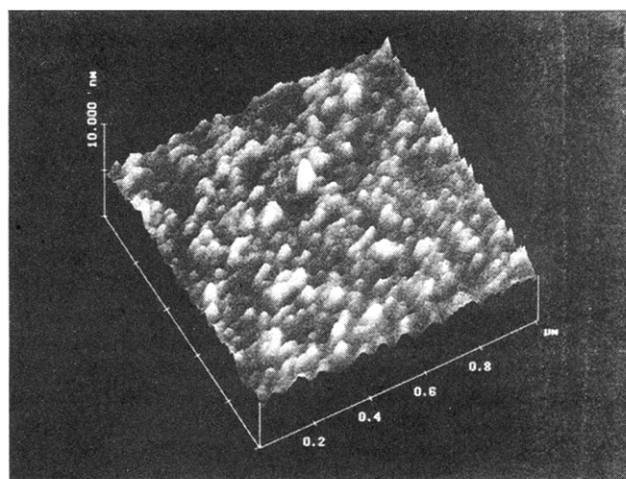

Figure 4. AFM image of the LB film of poly(NIPAM) prepared at $\pi = 32.1$ mN/m.

image of mica substrate with its characteristic hexagonal lattice spacing at an image size 5×5 nm^2, we believe that the substrates are covered by poly(NIPAM). The peak-to-valley values are 1.3 ± 0.4 and 2.0 ± 0.7 nm for the AFM images at $\Gamma = 0.82$ and 10.4 mg/m^2, respectively. An increase in the peak-to-valley value should be attributed to the formation of longer loops, which lead to a larger amount of poly(NIPAM) adsorbed at the air–water interface.

References and Notes

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MA946388Y