Spreading Solvent and Temperature Effects on Interfacial Properties of Poly(*N*-isopropylacrylamide) Films at the Air−Water Interface

Wataru Saito,† Masami Kawaguchi,*,† Tadaya Kato,† and Toyoko Imae‡

Department of Chemistry for Materials, Faculty of Engineering, Mie University,
1515 Kamihama, Tsu, Mie 514, Japan, and Department of Chemistry, Faculty of Science,
Nagoya University, Chikusa-ku, Nagoya, Aichi 464-01, Japan

Poly(*N*-isopropylacrylamide) (poly(NIPAM)) film spread at the air−water interface from its chloroform solution has been investigated by surface pressure and ellipsometric measurements at two temperatures (16.0 and 31.3 °C) by a comparison of poly(NIPAM) spread from water. At the same surface area the surface pressure for chloroform-spread polymer was larger than that for water-spread polymer. The amount of polymer deposited at the air−water interface was determined by ellipsometry, and the plateau-deposited amount for chloroform-spread polymer was larger than that for water-spread polymer at the respective temperatures. The layer thickness determined by ellipsometry was almost constant in the collapse region at the respective temperatures, and its magnitude was larger than that for water-spread polymer. By raising the temperature from 16.0 and 31.3 °C, the amount of poly(NIPAM) deposited at the air−water interface increased, whereas the layer thickness was not varied. For lowering the temperature from 31.3 to 16.0 °C, the deposited amount decreased, and it was in agreement with that spread from chloroform at 16.0 °C, while the layer thickness increased.

Introduction

In a previous paper,[1] we reported that poly(*N*-isopropylacrylamide) (poly(NIPAM)) at the air−water interface spread from its aqueous solution has formed a stable condensed-type monolayer. Ellipsometry indicated that the amount of the polymer deposited at the air−water interface was less than the real spread amount. The loss of polymer from the surface should be attributed to the fact that poly(NIPAM) is a water-soluble polymer and water was used as a spreading solvent. It can be expected that more poly(NIPAM) would be deposited at the air−water interface if a less water-miscible solvent was used as a spreading solvent.

It is known that different morphologies and various orientations of the film-forming molecules at the air−water could be induced by changing the spreading solvent, and some interesting studies have been reported for polymers[2−5] and low molecular weight substance monolayers.[6−13]

Ringard-Lefebvre and Baszkin[5] found that poly(D,L-lactic acid) monolayers spread at the air−water interface from water-miscible solvents, such as acetone and tet-rahydrofuran, showed lower surface pressures than those spread from less water-miscible solvents, such as chloroform, dichloromethane, and ethyl acetate, due to the difference in the orientation of the hydrophobic methyl groups in the polymer.

In this paper, we use chloroform as the spreading solvent for poly(NIPAM) and explore the interfacial behavior of poly(NIPAM) films at the air−water interface by changing the spreading temperature or by changing the temperature after spreading with the surface pressure and ellipsometric measurements. Furthermore, the results will be discussed with those for water-spread poly(NIPAM).[1]

Experimental Section

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

The spreading solvent used to prepare poly(NIPAM) films at the air−water interface was spectrograde chloroform, and we used it without further purification.

Surface Pressure Measurements. The surface pressure measurement apparatus was the same as described in detail before.[1,14,15] A Teflon trough was filled with deionized water with the temperature controlled within 16.0 ± 0.2 and 31.3 ± 0.2 °C, as described previously.[1] Poly(NIPAM) films were spread on the water surface with the area of 290 cm³ in the trough by applying the method of "successive additions" of chloroform poly-(NIPAM) solutions $(1.18-5.28 \times 10^{-3}$ g/mL) with a Hamilton microsyringe to adjust the surface concentration. The successive addition method avoids effects from impurities concomitantly compressed.

The droplets were delivered to touch the water surface; namely, the distance between the drops and the water surface was as small as possible. They were distributed randomly over the entire trough surface, and the solvent was allowed to evaporate for at least 30 min before the experiment was started. Unless the surface pressure did not remain constant over 10 min, we regarded it as an equilibrium surface pressure. The equilibrium value was not changed if longer time periods than 30 min were passed. It took half a day to obtain the full surface pressure

† Mie University.

‡ Nagoya University.

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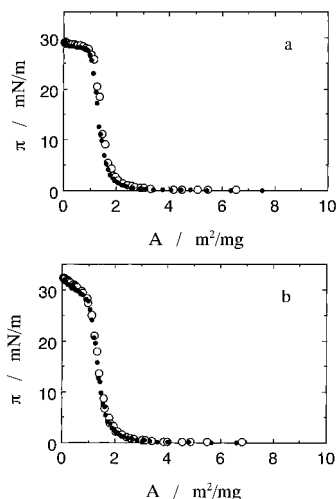(15) Kawaguchi, M.; Tohyama, M.; Mutoh, Y.; Takahashi, A. *Langmuir* **1988,** *4,* 407.

Figure 1. Surface pressure (π)—area *(A)* isotherms of poly-(NIPAM) at 16.0 °C (a) and at 31.3 °C (b) spread from chloroform (○) and water (●).

isotherms. The experimental errors in the surface pressure were less than 0.1 mN/m.

Ellipsometry. The ellipsometry setup has been described in detail elsewhere.[1,14,15] From ellipsometric measurements, two independent parameters were obtained: the azimuth (ψ) of the amplitude ratio for the reflected components parallel and normal to the plane of incidence and the phase difference (Δ) between them. The experimental errors in the values of Δ and ψ were less than 0.03 and 0.02°, respectively. This leads to 10% errors for the layer thickness *(t)* and the refractive index (n_f). The values of t and n_f of the poly(NIPAM) film spread at the air—water interface were calculated using a FACOM M760/6 computer system with a modified version of McCrackin's program[16] by assuming a homogeneous layer.

The refractive index increments (dn/dc) of aqueous poly-(NIPAM) solutions ($0.3-1.2 \times 10^{-3}$ g/mL) at 16.0 and 31.3 °C were determined using an Ohtsuka Denshi DRM-1022 refractometer to calculate the amount of (A_d) of poly(NIPAM) deposited at the air—water interface using the following equation:

$$A_d = t(n_f - n_0)/(\mathrm{d}n/\mathrm{d}c) \qquad (1)$$

where n_0 is the refractive index of the solvent.

At some surface concentrations, ellipsometric measurements were performed by raising the temperature from 16.0 to 31.3 °C or lowering the temperature from 31.3 to 16.0 °C after spreading poly(NIPAM). The ellipsometric data were collected 5 h after changing the temperature.

Results and Discussion

Surface Pressures at 16.0 °C. Figure 1a shows surface pressure—surface area (π—A) isotherms of poly-(NIPAM) together with the π—A isotherm of poly(NIPAM) spread from water.[1] The surface area is an apparent area equal to the inverse of the surface concentration (Γ) defined by the real spread amounts of poly(NIPAM) per unit area. As described in the previous paper,[1] the poly(NIPAM) falls within the condensed monolayer, since the surface pressure of the poly(NIPAM) is very small at larger surface areas. The surface pressure of poly(NIPAM) spread from chloroform is slightly higher than that spread from water in the entire surface area range. By employing chloroform as the spreading solvent, it causes less poly(NIPAM) loss in the water subphase, leading to the large amount of polymer deposited at the air—water interface, and then the high surface pressure is obtained. This will be discussed by taking into account the ellipsometry data described below.
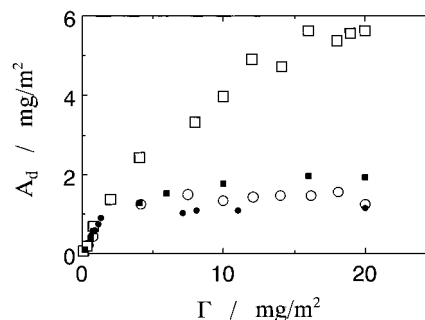
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Figure 2. Ellipsometric adsorbed amount (A_d) of poly(NIPAM) as a function of the real spread amount of poly(NIPAM) (Γ): (○) at 16.0 °C from chloroform; (□) at 31.3 °C from chloroform; (●) at 16.0 °C from water; (■) at 31.3 °C from water.

Surface Pressures at 31.3 °C. Figure 1b shows π—A isotherms of poly(NIPAM). The dependence of the surface pressure on temperature was clearly observed at much lower surface area, where the poly(NIPAM) monolayer can be considered to represent a so-called collapse state, its surface pressure attained a collapsed value, and the collapse surface pressure is higher than that at 16.0 °C. This dependence is the same as that for water-spread poly(NIPAM).[1] The higher surface pressure should be related to the larger amount of polymer deposited at the air—water interface. The ellipsometric and atomic force microscopy (AFM) measurements described below could show that the amount of polymer deposited at the air—water interface increases with an increase in temperature.

Ellipsometry at 16.0 °C. Ellipsometry is often a useful method to investigate adsorption behavior, since it gives simultaneously the thickness and refractive index of layers formed at various interfaces by the Drude equation.[17] Moreover, it is widely accepted that ellipsometry yields accurately the amount of substances adsorbed at an interface and it also provides some information on the structural changes in the polymer layer adsorbed at the interface in terms of the layer thickness.[18,19] Therefore, ellipsometric measurements of poly(NIPAM) film layers spread at the air—water interface have been performed to prove what parts of the real spread amounts of poly-(NIPAM) are deposited at the interface and what structural changes of the deposited polymer occur with changing temperature.

From the refractometer, the values of the refractive index increment dn/dc were determined to be 0.219 and 0.213 mL/g at 16.0 and 31.3 °C, respectively. We can calculate the value of A_d from eq 1. The values of t and n_f show an increasing trend with an increase in Γ, and they are somewhat scattered ($7 < t < 17$ nm; $1.354 < n_f < 1.374$) due to the small changes in ψ. In Figure 2, the A_d values are plotted as a function of Γ, together with the values of A_d for the water-spread polymer. The error margins for the value A_d are within 20% at $\Gamma < 1.0$ mg/m², and they are within 10% at $\Gamma > 1.0$ mg/m². The plateau value of A_d for the chloroform-spread polymer is larger than those for the water-spread polymer at both temperatures,[1] which is related to the difference in the spreading solvent. Since chloroform is a less water-miscible solvent, poly(NIPAM) chains spread from chloroform more preferentially stay on the water surface at the initial stage after spreading than those spread from water.

Ellipsometry at 31.3 °C. The values of t are 13 ± 3 nm, the n_f values range over $1.407-1.427$, and the A_d

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(18) Kawaguchi, M.; Takahashi, A. *Adv. Colloid Interface Sci.* **1992**, *37*, 219.
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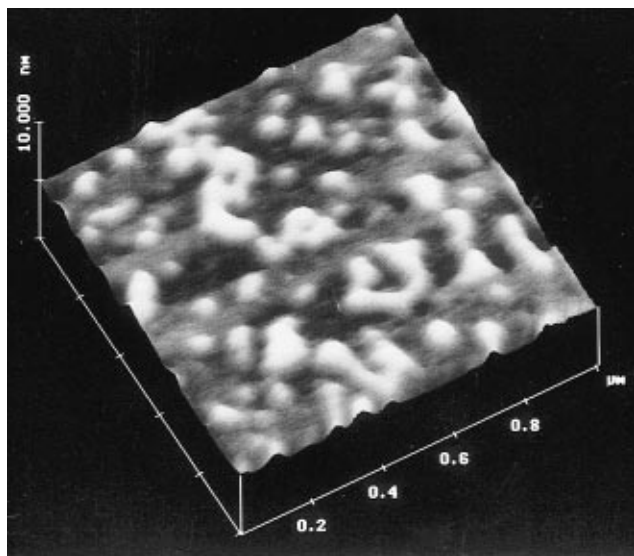**Figure 3.** AFM image of the LB film for poly(NIPAM) prepared from chloroform at 16.0 °C at Γ = 10.4 mg/m^2.

Figure 4. AFM image of the LB film for poly(NIPAM) prepared from chloroform at 31.3 °C at Γ = 10.4 mg/m^2.

Figure 5. Changing temperature effect on the layer thickness *(t)* of poly(NIPAM) at the air−water interface as a function of Γ: raising the temperature from 16.0 (○) to 31.3 °C (●); lowering the temperature from 31.3 (□) to 16.0 °C (■).

values are shown in Figure 2. The larger value of n_f leads to the large amount of the polymer deposited at the air−water interface. We notice that for the plateau A_d value is three times as large as that for the water-spread polymer at the higher temperature. Since the high temperature is near the lower critical solution temperature (LCST) of poly(NIPAM) in water lying at ca. 32 °C,[20] more polymer spread from chloroform could stay near the surface. This should be related to the thermal behavior of poly(NIPAM) in water, namely hydrophilic−hydrophobic structural transition with increasing temperature. It is generally accepted that the transition is driven by the entropy gained by the release of water molecules which are partially immobilized by the hydrophobic propyl groups. However, the plateau value of A_d at a higher temperature is less than the real amount of the polymer spread at the air−water interface. This indicates that some of the spread polymers dissolve into the water phase and the remaining parts are deposited at the air−water interface.

The plateau thickness is almost independent of temperature, though for the water-spread polymer the layer thickness at 31.3 °C is half as large as that at 16.0 °C.[1] By taking into account the deposited amount and the layer thickness, we can imagine the following interfacial structures of poly(NIPAM) at the air−water interface: at 31.3 °C poly(NIPAM) chains are concentrated near the water surface with stronger chain entanglements, whereas at 16.0 °C they form a less closely packed layer deposited at the interface. Furthermore, such an interfacial structure will be proved by AFM of Langmuir−Blodgett (LB) films transferred on a solid substrate.

AFM Study. A preliminary AFM experiment for poly-(NIPAM) has been performed using a Nanoscope III with microfabricated silicon cantilevers.[21] AFM images of poly-(NIPAM) films transferred on a freshly cleaved mica at Γ = 10.4 mg/m^2 were taken under tapping mode at 25 °C in air. A deposition speed of 1.0 cm/min resulted in transfer ratios of about unity. Figures 3 and 4 show AFM images of poly(NIPAM) spread from chloroform at 16.0 and 31.3 °C, respectively. At 16.0 °C the round-shape grains and clusters connected with the grains are randomly distributed, whereas at 31.3 °C peaked-shape grains are crowded, indicating that the poly(NIPAM) chains are
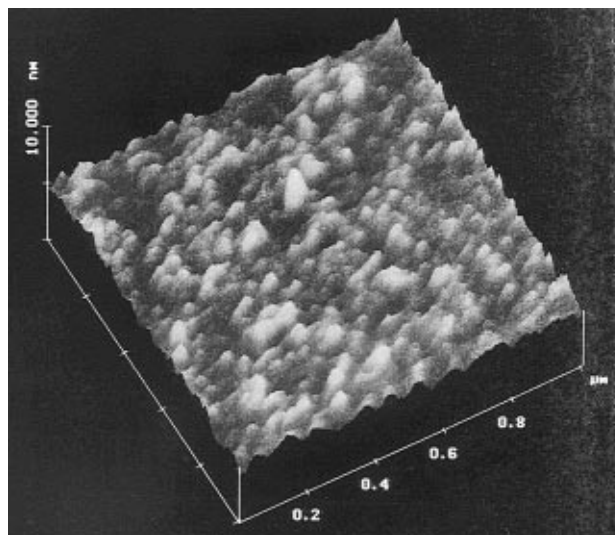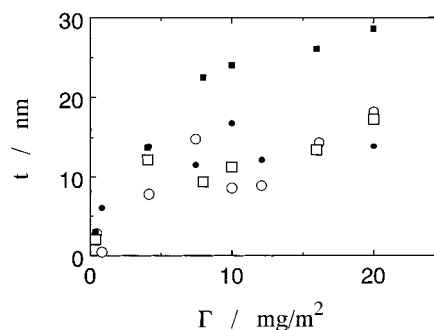
more closely packed structures of the collapsed layer. The peak-to-valley values in the AFM images at 16.0 and 31.3 °C are 1.0 ± 0.2 and 2.0 ± 0.7 nm, respectively. The large peak-to-valley value would show the formation of large loops in the deposited layer, and they should be attributed to a large amount of polymer deposited at the air−water interface.

Ellipsometry for Changing the Temperature after Spreading. We examined the effects of raising the temperature from 16.0 to 31.3 °C and lowering the temperature from 31.3 to 16.0 °C on the ellipsometric parameters at various amounts of poly(NIPAM) spread from chloroform. The effects of raising the temperature on the layer thickness and the deposited amount are displayed as a function of the spread amount of poly-(NIPAM) in Figures 5 and 6, respectively. The larger deposited amount at higher temperature permits us to propose a mechanism for readsorbing the polymer from the water phase. Upon heating, coiled poly(NIPAM) chains with loops in the water phase are partially collapsed, since the temperature is near the LCST. Thus, the polymer can be easily adsorbed at the air−water interface for 5 h after changing the temperature, even at a dilute concentration of poly(NIPAM). By assuming that the amounts of poly(NIPAM) nondeposited at the air−water interface dissolve into the water phase, the bulk concentration is calculated to be on the order of 0.1 mg/L. Surface tension measurements of aqueous poly(NIPAM) solutions with concentrations on the order of 0.1 mg/L indicated that equilibrium is attained within several hours

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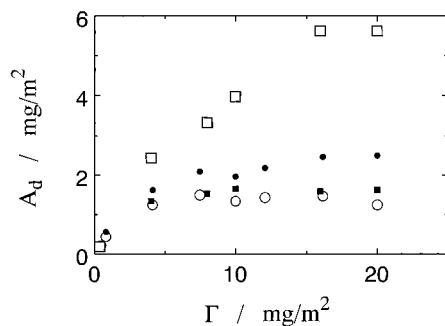
Figure 6. Changing temperature effect on the adsorbed amount (A_d) of poly(NIPAM) at the air−water interface as a function of Γ. The symbols are the same in Figure 5.

at 31.3 °C,[22] whereas the layer thickness does not show any regular trends with increasing temperature.

For lower temperatures, the layer thickness and the deposited amount are shown in Figures 5 and 6, respectively. The deposited amount of poly(NIPAM) was decreased due to desorption of polymer from the air−water interface, and the plateau adsorbed amount was in agreement with that for chloroform spread at 16.0 °C. By contrast, the layer thickness was twice as large as that

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chloroform spread at 31.3 °C. Since poly(NIPAM) chains were more efficiently packed with chain entanglements at the interface at 31.3 °C, such entanglements prevent easy desorption of the polymer chains from the interface, leading to the larger t and lower n_f to maintain the similar deposited amount to that at 16.0 °C. More than 12 h after cooling, both t and n_f show no changes.

Conclusions

The influence of temperature on the interfacial behavior of poly(NIPAM) films spread at the air−water interface from chloroform solution has been compared with that for water-spread polymer using surface pressure and ellipsometric measurements. Since chloroform is a less water-miscible solvent, more poly(NIPAM) can deposit at the air−water interface, leading to the larger amount and the higher layer thickness of polymer deposited at the air−water interface than those for the water-spread polymer.[1]

The effects of raising and lowering the temperature on the deposited amount and layer thickness are also interesting. In particular, upon cooling, the layer thickness is increased to twice as much as that at 31.3 °C, regardless of the similarly deposited amount to that spread from chloroform at 16.0 °C.