Poly(*N*-isopropylacrylamide) Films at the Air–Water Interface

Masami Kawaguchi,* Wataru Saito, and Tadaya Kato

Department of Chemistry for Materials, Faculty of Engineering, Mie University, 1515 Kamihama, Tsu, Mie 514, Japan

Received April 7, 1994; Revised Manuscript Received July 7, 1994®

ABSTRACT: Poly(*N*-isopropylacrylamide) (poly(NIPAM)) film spread at the air–water interface from its aqueous solution has been investigated by surface pressure and ellipsometric measurements at two temperatures (16.0 and 31.3 °C). The surface pressure steeply increased at low real spread concentration of poly(NIPAM), and it more gradually attained a plateau one at high temperature. The plateau surface pressure at 16.0 °C was lower than that at 31.3 °C. The amount of polymer adsorbed at the air–water interface was determined by ellipsometry, and its plateau adsorbed amount at 31.3 °C was twice as large as that at 16.0 °C, whereas the thickness of the adsorbed layer at 16.0 °C was larger than that at 31.3 °C. Such an adsorption behavior at the air–water interface was strongly related to the transition of poly(NIPAM) from a hydrophilic to a hydrophobic structure in bulk solution. Moreover, it was found that some portions of the spread polymer were desorbed from the interface and the magnitude of the adsorbed amount was similar to that on the silica surfaces.

Introduction

Poly(*N*-isopropylacrylamide) (poly(NIPAM)) has the lower critical solution temperature (LCST) at which a macromolecular transition from a hydrophilic to a hydrophobic structure occurs. Experimentally, this lies at ca. 32 °C in aqueous solution.[1] By focusing such a transition, physical properties of poly(NIPAM) have been deeply investigated in many forms including single chains, gels, membranes, coatings, and fibers.[2] The temperature dependence of structural changes in poly(NIPAM) has been more widely understood, and their applications to biological and industrial fields have been performed.[3] Though it can be expected that the transition induced by changes in temperature should strongly influence the interfacial properties of poly(NIPAM) in an aqueous solution as well as a spread film state, the properties have not been well understood.

We studied the adsorption of poly(NIPAM) on hydrophilic and hydrophobic silica surfaces from its aqueous solution as a function of temperature.[4] It was found that the amount of poly(NIPAM) adsorbed at the hydrophobic silica surface more steeply increased than that for the hydrophilic one with an increase in temperature. It was concluded that the adsorption behavior was related with a disrupting water cage surrounding the isopropyl groups, followed by an increase in the hydrophobic interaction between the isopropyl groups and the hydrophobic parts of the surfaces. Thus, such structural changes by an increase in temperature should result in increasing the surface activity of the aqueous solution of poly(NIPAM), leading to a progressive increase in the amount of poly(NIPAM) adsorbed at the air–water interface and to a lowering of the surface tension. Some results on the surface properties of the solution were reported in terms of the surface tension measurements, and the surface tension at 31 °C was 47.8 mN/m.[5] The hydrophobic portion, i.e., the isopropyl group, should play a role in the absorption site at the air–water interface, and poly(NIPAM) forms a stable monolayer film at the interface. However, there is no comprehensive study on poly(NIPAM) films spread at the air–water interface. In this paper, in order to explore the temperature effect of the interfacial properties of poly(NIPAM) films spread at the air–water interface from its aqueous solution, we used both techniques of surface pressure and ellipsometric measurements. We expect that an application of ellipsometry to the polymer spread at the air–water interface allows us to discuss the surface activity and adsorbability of poly(NIPAM) in comparison with its adsorption behavior at the solid surfaces and to confirm whether the polymer films spread at the air–water interface are stable or not.

Experimental Section

Materials. A poly(NIPAM) sample was prepared by radical polymerization of freshly crystallized *N*-isopropylacrylamide in a benzene solution using azobis(isobutyronitrile) as an initiator at 49 °C. The resulting polymer was diluted with acetone, purified by dropwise precipitation in a large amount of benzene, dried under vacuum, and finally freeze dried from its aqueous solution. The molecular weight of poly(NIPAM) was determined from the intrinsic viscosity measurements in water at 20 °C.[6] The molecular weight distribution of poly(NIPAM) was determined from a calibration curve of standard polystyrene samples, using a GPC system of two TSK gel GMH columns, a Toyo Soda RI-8 refractometer, and a Nippon Denshi Science U-228 chart recorded. The fluent used was a 10 mM LiBr–DMF solution.

Water purified by a Millipore Q-TM system was used. Pure grade quality benzene and acetone were used after distillation.

Surface Pressure Measurements. A Teflon trough with 29 × 10 × 1 cm^3 was filled with deionized water, and the working temperatures of the water in the trough were controlled within 16.0 ± 0.2 and 31.3 ± 0.2 °C by circulating thermostated water. Thr trough was placed on a stage. The stage and trough were covered by a Plexiglas box to prevent dust particles. After the water surface was cleaned by aspiration, the sandblasted platinum plate (24 × 10 × 0.1 mm^3) was attached to a Chan 2000 electrobalance, and the trough was slowly moved up using the stage until the edge of the plate touched the water surface. The electrobalance was connected to an Advantest TR 6849 digital voltmeter capable of 0.001-mV readings. The sensitivity of the surface pressure was 0.02 mN/m.[7]

Poly(NIPAM) films were spread on the water surface in the trough by delivering aqueous poly(NIPAM) solutions ((1.0–2.0) × 10^{-3} g/mL) with a Hamilton microsyringe. Surface concentrations of poly(NIPAM) were adjusted by changing the amount of the spread solution; namely, the successive addition method was used. Unless the surface pressure did not remain 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. An instrument for ellipsometry was used as in the previous paper.[7,8] Ellipsometry gives the phase difference (Δ) and the azimuth (ψ) of the amplitude ratio for light polarized parallel and normal to the plane of incidence. The changes in

---

® Abstract published in *Advance ACS Abstracts,* August 15, 1994.

0024-9297/94/2227-5882$04.50/0

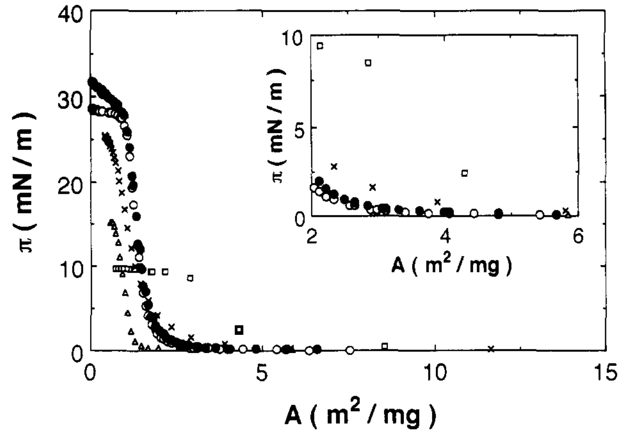

Figure 1. Surface pressure (π)-area (*A*) isotherms of poly(NIPAM) at 16.0 °C (○), poly(NIPAM) at 31.3 °C (●), PEO at 25 °C (□), PVAc at 25 °C (×), and PMMA at 25 °C). The inset shows the expanded π-*A* isotherms for the respective polymers.

Δ and ψ between the clean water and the water surface covered with poly(NIPAM) were expressed as $\delta\Delta = (\bar{\Delta} - \Delta)$ and $\delta\psi = (\bar{\psi} - \psi)$, respectively: $\bar{\Delta}$ and $\bar{\psi}$ for the pure water and Δ and ψ for the water surface covered with poly(NIPAM). The incident angle was 70.6°. We calculated the thickness and the refractive index of the poly(NIPAM) film spread at the air-water interface from the experimental data of Δ and ψ using a FACOM M760/6 computer system with a modified version of McCrackin's program.[9]

For calculation of the amounts of poly(NIPAM) adsorbed at the air-water interface from the thickness and the refractive index of the poly(NIPAM) film layer, the refractive index increments of aqueous poly(NIPAM) solutions (0.3-1.2) × 10^{-3} g/mL) at 16.0 and 31.3 °C were determined using an Ohtsuka Denshi DRM-1022 refractometer.

Results and Discussion

Surface Pressure. Figure 1 shows surface pressure-area (π-*A*) isotherms of poly(NIPAM) with a molecular weight of 5.97 × 10^5 and a molecular weight distribution of 3.23. The surface area is an apparent area equal to the inverse of the surface concentration (Γ) defined by the real spread amounts of the polymer per unit area. Since poly(NIPAM) is a water-soluble polymer, partial desorption of the spread polymer from the air-water interface probably occurs. This will be made clear by using ellipsometry described below.

In Figure 1, the π-*A* isotherms of poly(ethylene oxide) (PEO), poly(vinyl acetate) (PVAc), and poly(methyl methacrylate) (PMMA) are also displayed. These isotherms were cited from the previous data.[10] Generally, π-*A* isotherms of polymer monolayers were classified mainly into two categories based on the shape of the π-*A* isotherm as advanced by Crisp.[11] One is an expanded type π-*A* isotherm: π is detectable at fairly large surface areas, gradually increases with decreasing area, and finally reaches a plateau value. This type of π-*A* isotherm is usually observed for polymers having a relatively strong hydrophilic property. On the other hand, there is a condensed type of π-*A* isotherm: π is first observed at a smaller surface area than the expanded π-*A* isotherm and shows a steep increase, and then the monolayer shows collpase. The condensed type of π-*A* isotherm in general is observed for polymers having small hydrophilicity and bulky side chains.

Therefore, PEO and PVAc belong to the expanded monolayer, while PMMA falls within the condensed monolayer. As seen from the inset in Figure 1, for larger surface areas than 3 m²/mg the surface pressure of poly(NIPAM) is very small and its surface pressure behavior is similar to that of PMMA; thus, poly(NIPAM) can be classified by the condensed monolayer. The temperature dependence of the surface pressure of poly(NIPAM) was clearly observed at much lower surface area, and the plateau surface pressure at 31.3 °C is higher than that at 16.0 °C. The surface area dependence of surface pressure at lower surface area can be demonstrated more clearly in a plot of the surface pressure versus a surface concentration (Γ) as displayed in Figure 2. The difference in the plateau surface pressures between the two temperatures should be related to the magnitude of the amount of polymer adsorbed at the air-water interface. Ellipsometric measurements described below show that the amount of polymer adsorbed at the air-water interface increases with an increase in temperature because of the temperature dependence of the structural changes of poly(NIPAM).

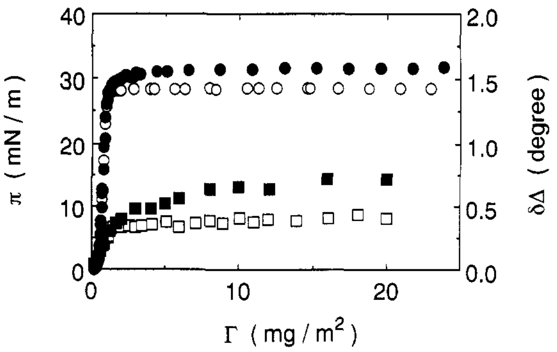

Figure 2. Surface pressure (π) and δΔ as a function of the real spread amount of poly(NIPAM) (Γ); (○) π at 16.0 °C, (●) π at 31.3 °C, (□) δΔ at 16.0 °C, and (■) δΔ at 31.3 °C.

The resulting surface pressure-area isotherms were similar to those obtained from a chloroform solution of poly(NIPAM).[12] We believe that poly(NIPAM) forms as a stable film even if water is used as a spreading solvent. Moreover, the plateau surface pressure at the respective temperatures are also in agreement with those obtained from the surface tension measurements of aqueous poly(NIPAM) solutions.[12]

Ellipsometry. Ellipsometry is a technique for in situ measurements, yielding simultaneous estimates of both the thickness and refractive index of adsorbed layers at various interfaces.[13,14] In particular, it is widely accepted that the technique gives accurately the amount of substances adsorbed at an interface, and the layer thickness should give some structural information of the polymer chains adsorbed at the interface. Therefore, we studied poly(NIPAM) film layers spread at the air-water interface using ellipsometry in order to prove what parts of the real spread amounts of poly(NIPAM) are adsorbed at the air-water interface and what structural changes of the adsorbed polymer are observed at 16.0 and 31.3 °C.

Figure 2 shows the δΔ values at two temperatures as a function of surface concentration together with the surface pressures. The δΔ value is a useful quantity to judge whether the real spread substances at the air-water interface remain or are partially desorbed from the interface. The δΔ value initially increases with an increase in the surface concentration and gradully approaches a plateau value at the respective temperatures though the values of δΔ are somewhat scattered at a higher surface concentration range. The plateau value of δΔ at 31.3 °C is larger than that at 16.0 °C, indicating a larger amount of poly(NIPAM) adsorbed at the air-water interface for higher temperature. Although the spread amount of poly(NIPAM) is increased, an appearance of the plateau value of δΔ manifests that some spread poly(NIPAM) chains are desorbed from the air-water interface. Similar results were obtained for the PEO film.[8] Since PEO is a water-

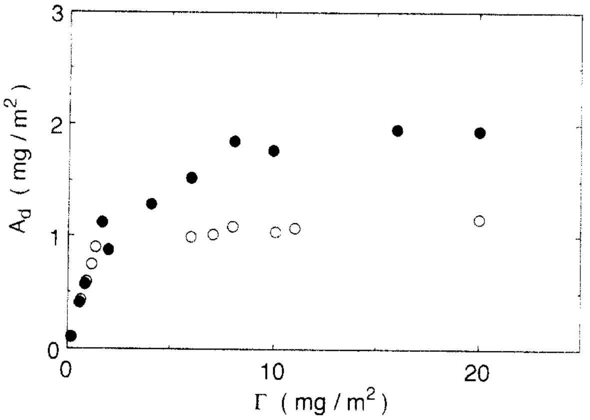

Figure 3. Ellipsometric adsorbed amount of poly(NIPAM) at 16.0 °C (○) and at 31.3 °C (●) as a function of the real spread amount of poly(NIPAM).

soluble polymer, PEO so desorbed dissolves in the water phase. Desorption of poly(NIPAM) from the air-water interface will be discussed later by taking into account the amounts of the polymer adsorbed at the air-water interface. Moreover, the surface concentration dependence of $\delta\Delta$ is quietly similar to that of the surface pressure, irrespective of temperature.

The other ellipsometric quantity of $\delta\psi$, on the other hand, is less sensitive to the value of $\delta\Delta$, and $\delta\psi$ is smaller than 0.1° in the entire surface concentration range. We calculated the thickness (t) and the refractive index (n_f) of the poly(NIPAM) layer adsorbed at the air-water interface. In calculation, the poly(NIPAM) layer was assumed to be a homogeneous one since the polymer is a water-soluble polymer. However, the small $\delta\psi$ value happens to lead to some scattering in the calculated thickness and the refractive index.

Since the refractive index of the adsorbed layer is related to the polymer concentration in the layer, it is possible to calculate the average polymer concentration (C_f) in the polymer layer by using the following relation, which is useful for adsorption of polymers at the interfaces.[13,14]

$$C_f = (n_f - n_0)/(\partial n/\partial c) \qquad (1)$$

where n_0 is the refractive index of the solvent and $\partial n/\partial c$ is the refractive index increment. The values of $\partial n/\partial c$ were determined to be 0.175 and 0.170 mL/g at 16.0 and 31.3 °C, respectively, from the refractometer. Therefore, the amount (A_d) of poly(NIPAM) adsorbed at unit area of the air-water interface can be obtained from the product of C_f and t. Figure 3 shows plots of the calculated A_d values as a function of Γ, and the plateau value of A_d at higher Γ is 1 order of magnitude less than the real amount of polymer spread at the air-water interface. This fact indicates that the large portions of the spread amount of poly(MIPAM) dissolve into the bulk solution. The plateau value of A_d is 16.0 °C attains at lower surface concentration than that at 31.3 °C, and a similar concentration dependence is observed for the $\delta\Delta$ as shown in Figure 2. Moreover, the plateau value of A_d at 16.0 °C is half that at 31.3 °C.

It is important to discuss what process is responsible for the formation of the poly(NIPAM) layer at 31.3 °C, which is near the LCST. Two processes, such as polymer self-aggregation and adsorption will be considered; however, we observed no precipitation and no decrease in the scattered light intensity for the bulk solution of poly(NIPAM) at 31.3 °C. Similar results have been reported by Kubota et al.[15] Moreover, any flocculates at the air-water interface were not detected by eye observation, and no changes in the reflected light intensity at the interface were observed. Thus, the polymer layer would be formed by an adsorption process accompanied with polymer self-aggregation.

On the other hand, the thicknesses of the adsorbed poly(NIPAM) layer at 16.0 °C are covered in 7-10 nm at the plateau region, whereas at 31.3 °C the plateau layer thicknesses range over 4-5 nm. These thicknesses are larger than those of the PEO film[7,16] and smaller than the diameter of a free chain. The thinner layer thickness and the larger adsorbed amount at 31.3 °C suggest the formation of a more compact layer of poly(NIPAM) at the air-water interface than that at 16.0 °C. This should be related to the thermal behavior in aqueous media of poly(NIPAM), namely, the hydrophilic-hydrophobic structural transition by an increase in temperature. At higher temperature the isopropyl groups exposed by disruption of the water cage play a role in increasing the surface activity, and poly(NIPAM) can easily and much adsorb at the air-water interface.

The magnitudes in the calculated amount of poly(NIPAM) adsorbed at the air-water interface is about twice as large as the adsorbance at the hydrophilic silica surface at respective temperatures, whereas it is similar to the adsorbance at the hydrophobic silica surface. The discrepancy is due to the nature and the curvature of the surface: the hydrophilic silica particles dispersed in water tend to flocculate (aggregrate), and the resulting silica aggregation is regarded as a fractal object with an open structure; the hydrophobic silica particles separated and floated in water are dispersed by adsorption of poly(NIPAM) on their surfaces, whereas the air-water interface is fluctuated thermally to generate the capillary wave with a small amplitude of 0.3-1.0 nm and a wavelength of 100 μm, which is temporal damped by the liquid viscosity.[17]

Conclusions

We first demonstrated the interfacial properties of poly(NIPAM) films spread at the air-water interface from its aqueous solution by use of surface pressure measurements and ellipsometry. An application of ellipsometry to the spread water-soluble polymer film is capable of direct measurement of the amount of polymer adsorbed at the air-water interface and the thickness of the adsorbed layer. It was found that the spread poly(NIPAM) layer is stable and some portions of the real spread amounts of the polymer remain at the air-water interface, and moreover its magnitude is similar to the adsorbed amount of polymer at the silica surfaces. The temperature dependence of the adsorbed amount and the layer thickness is in accord with that of the solution properties.

References and Notes

(1) Fujishige, S.; Kubota, K.; Ando, I. *J. Phys. Chem.* **1989**, *93*, 3311.
(2) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163.
(3) Fujishige, S. *Bull. Res. Inst. Polym. Text.* **1991**, *No. 167*, 1.
(4) Tanahashi, T.; Kawaguchi, M.; Honda, T.; Takahashi, A. *Macromolecules* **1994**, *27*, 606.
(5) Fujishige, S.; Koiwaii, K.; Kubota, K.; Ando, I. *Bull. Res. Inst. Polym. Text.* **1991**, *No. 167*, 47.
(6) Fujishige, S. *Polym. J.* **1987**, *19*, 297.
(7) Nagata, K.; Kawaguchi, M. *Macromolecules* **1990**, *23*, 3957.
(8) Kawaguchi, M.; Tohyama, M.; Mutoh, Y.; Takahashi, A. *Langmuir* **1988**, *4*, 407.
(9) McCrackin, F. L. *NBS Technical Note* **1969**, 479.
(10) Kawaguchi, M.; Nishida, R. *Langmuir* **1990**, *6*, 492.
(11) Crisp, D. J. *J. Colloid Sci.* **1946**, *1*, 49.
(12) Saito, W.; Kawaguchi, M.; Kato, T., unpublished data.
(13) Kawaguchi, M.; Takahashi, A. *Adv. Colloid Interface Sci.* **1992**, *37*, 219.
(14) Kawaguchi, M. *Prog. Polym. Sci.* **1993**, *18*, 341.
(15) Kubota, K.; Fujisige, S.; Ando, I. *J. Phys. Chem.* **1990**, *94*, 5154.
(16) Kawaguchi, M.; Nagata, K. *Langmuir* **1991**, *7*, 1478.
(17) Langevin, G. In *Light Scattering by Liquid Surfaces and Complementary Techniques*; Langevin, G. Ed.; Marcel Dekker: New York, 1992; pp 9-13 and 15-34.