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Notes

Adsorption of Poly(*N*-isopropylacrylamide) on Silica Surfaces

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Introduction

Physical properties of poly(*N*-isopropylacrylamide), poly(NIPAM), have been deeply investigated in many forms including single chains, macroscopic gels, microgels, latexes, thin films, membranes, coatings, and fibers.[1] Particularly, in an aqueous solution of poly(NIPAM) it 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.[2]

It can be expected that such a hydrophilic–hydrophobic transition should strongly influence the adsorption behavior of poly(NIPAM) on solid surfaces from its aqueous solution. Thus, it is interesting to investigate its temperature dependence. In this note, in order to deduce what interaction between poly(NIPAM) and the solid surfaces dominates poly(NIPAM) adsorption, we measured the amounts of poly(NIPAM) adsorbed on the hydrophilic and hydrophobic silica surfaces as a function of temperature.

Experimental Section

Materials. A poly(NIPAM) sample was prepared by radical polymerization of freshly distilled *N*-isopropylacrylamide in benzene solution using AIBN as an initiator at 50 °C. The resulting polymer was diluted by acetone, purified by dropwise precipitation of the solution in a large amount of *n*-hexane, and dried under vacuum. The molecular weight of poly(NIPAM) was determined to be 980 × 10^3 in water at 20 °C from intrinsic viscosity measurements.[3] The molecular weight distribution of poly(NIPAM) was determined to be 2.54 from a calibration curve of standard polystyrene samples, using a Toyo Soda HLC-802A gel permeation chromatography (GPC) instrument. The eluent used was tetrahydrofuran (THF).

Two silicas were used: Aerosil 130 (hydrophilic silica) with a surface area of 130 ± 25 m^2/g, particle diameter of 16 nm, and silanol density of 2.5/nm^2; Aerosil R972 (hydrophobic silica) with a surface area of 110 ± 20 m^2/g, particle diameter of 16 nm, and ca. 70% silanol groups on the silica surfaces modified by dimethyldichlorosilane. The degree of hydrophobicity of the silica surface for Aerosil R972 was analyzed by a reaction with LiAlH$_4$ according to the manufacturer. All of them were dried in a vacuum oven at 200 °C.

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

Adsorption of Poly(NIPAM). The amounts of poly(NIPAM) adsorbed on the respective silicas were determined as follows. A 20-mL aqueous poly(NIPAM) solution with a known concentration was mixed with 0.1 g of silica in a stoppered glass centrifuge tube. The tube was placed in the incubator where it was controlled at a given measuring temperature. After equilibration (1 day) by stirring with a magnetic chip, the supernatant solution was separated to precipitate the silica at 5000 rpm for 20 min using a Kubota 6700 centrifuge by controlling the respective adsorption temperatures in a camber of the centrifuge. The equilibrium concentration, Cp, in the supernatant solution for poly(NIPAM) was determined by a gravimetric method: following the evaporation of the solvent in a defined amount on the supernatant weighed, the residue was dried under vacuum and weighed. To confirm the reproducibility of the experiments, we performed at least two measurements for the same concentrations. The error in the adsorbed amount was less than 10% even if in the neighborhood of the LCST (30 °C).

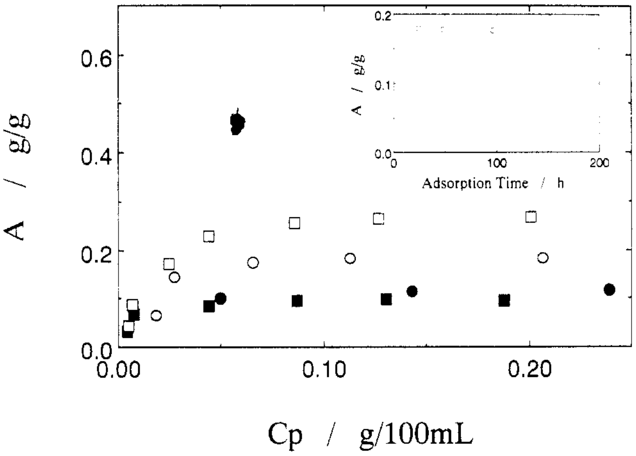

Figure 1. Adsorption isotherms of poly(NIPAM) on (■) Aerosil 130 silica at 19 °C, (●) Aerosil 130 silica at 27 °C, (○) R-972 silica at 27 °C, and (□) R-972 silica at 30 °C. The insert shows the time dependence of the adsorbed amounts of poly(NIPAM) on an R-972 silica surface at 27 °C from the initial concentration of 0.2 g/100 mL.

Results and Discussion

When mixed with water, Aerosil 130 silica was capable of dispersing in water, whereas Aerosil R972 silica could not be dispersed in water even if violently stirred and it floated on the water surface. On the other hand, when an aqueous solution of poly(NIPAM) was mixed with Aerosil R972 silica, the hydrophobic silica powder was gradually dispersed in the poly(NIPAM) solution, attributed to adsorption of poly(NIPAM) on the hydrophobic surface, and finally the mixture was well dispersed within 2 h. Thus, it was found that hydrophobic materials can be well dispersed in aqueous poly(NIPAM) solutions.

From a kinetics study of the adsorption, 1 day was enough to reach adsorption equilibrium, as shown in the insert in Figure 1. Figure 1 shows typical adsorption isotherms of poly(NIPAM) on Aerosil 130 and R972 silica surfaces at several temperatures. An adsorption isotherm reflecting the wide molecular weight distribution of poly(NIPAM) is the rounded isotherm. Such a polydispersity of the polymer effect on the adsorption isotherm has been frequently observed in many systems.[4,5] It seems that the initial concentration of 0.2 g/100 mL was enough in the plateau region of the adsorption isotherms. Thus, we will discuss in detail the amount of poly(NIPAM) adsorbed on the silica surfaces at an initial polymer concentration of 0.2 g/100 mL as a function of temperature.

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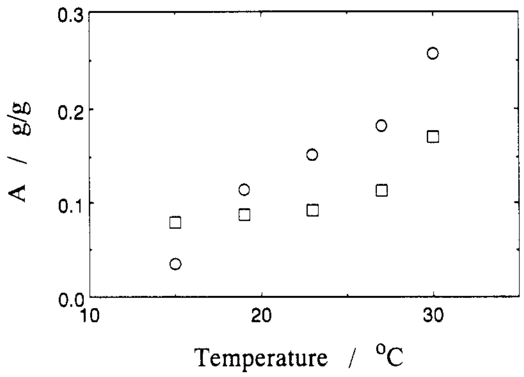

Figure 2. Plots of the amount of poly(NIPAM) on Aerosil 130 (□) and R-972 (○) silica surfaces as a function of temperature.

The temperature dependence of the amounts of poly(NIPAM) adsorbed on two silica surfaces is displayed in Figure 2. We noticed some features. At 15 °C the amount of poly(NIPAM) adsorbed on Aerosil 130 silica is larger than that on the hydrophobic silica surface. At 19 °C the amount of poly(NIPAM) on the hydrophobic silica surface exceeds that on Aerosil 130. Up to 27 °C the amount of poly(NIPAM) adsorbed on the hydrophobic silica surface increases more steeply with an increase in temperature than that on the hydrophilic silica surface. At 30 °C the amounts of poly(NIPAM) adsorbed on two silica surfaces show a rapid increase. Such a complex adsorption phenomena should be strongly correlated with changes in the properties of the aqueous poly(NIPAM) solution with temperature.

The larger amount of poly(NIPAM) adsorbed on the hydrophilic silica surface at 15 °C as opposed to that on the hydrophobic silica surface is attributed to the hydrogen bonding between the carbonyl groups of the poly(NIPAM) chains and the silanol groups on the silica surface. An increase in temperature leads to a gradual disruption of the water cage surrounding the hydrophobic parts, such as isopropyl groups of poly(NIPAM) chains, and larger proportions on the isopropyl groups are exposed. As a result, such exposed isopropyl groups tend to interact with the hydrophobic parts on the silica surfaces, namely siloxane groups of the skeleton structure of the silica and methyl groups of Aerosil R972. For Aerosil R972 silica the effective adsorbing sites interacting with the isopropyl groups are larger than those for Aerosil 130 silica, leading to the larger amount of poly(NIPAM) adsorbed on the hydrophobic silica surface. At 30 °C the steep increase in the amount of poly(NIPAM) on the respective silica surfaces is attributed to an intermolecular association of poly(NIPAM), since the temperature is close to the LCST. Some experimental results on the intermolecular association of poly(NIPAM) have been reported. Fujishige et al. demonstrated that the coil–globule transition and intermolecular aggregation occurred at 30 °C by static and dynamic light scattering measurements.[2,6] Tam et al. also showed that intermolecular aggregation occurred at ca. 28 °C from the viscosity measurements of a poly(NIPAM) solution with a finite concentration as a function of temperature.[7]

References and Notes

(1) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163.
(2) Fujishige, S.; Kubota, K.; Ando, I. *J. Phys. Chem.* **1989**, *93*, 3311.
(3) Fujishige, S. *Polym. J.* **1987**, *19*, 297.
(4) Cohen-Stuart, M. A.; Cosgrove, T.; Vincent, B. *Adv. Colloid Interface Sci.* **1986**, *24*, 143.
(5) Kawaguchi, M. *Adv. Colloid Interface Sci.* **1990**, *32*, 1.
(6) Kubota, K.; Fujishige, S.; Ando, I. *J. Phys. Chem.* **1990**, *94*, 5154.
(7) Tam, K. C.; Wu, X. Y.; Pelton, R. H. *Polymer* **1992**, *33*, 436.