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Swelling and Shrinking of Poly(*N*-Isopropylacrylamide) Chains Adsorbed on the Surface of Polystyrene Nanoparticles

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ABSTRACT

As a thermally sensitive polymer, poly(*N*-isopropylacrylamide) (PNIPAM) is hydrophilic at temperatures below its lower critical solution temperature (LCST, ~32°C), but undergoes a coil-to-globule transition in water at higher temperatures. The adsorption of PNIPAM on polystyrene (PS) nanoparticles resulted in a core-shell nanostructure. In the first heating-and-cooling cycle there existed a hysteresis in terms of the thickness of the adsorbed PNIPAM layer; this could be attributed to additional binding of the adsorbed PNIPAM chains to the surface. Moreover, the surface shifted the coil-to-globule transition to a lower temperature and made the transition less sharp. The temperature dependence of the ratio of the radius of gyration to the hydrodynamic radius ($\langle R_g\rangle/\langle R_h\rangle$) revealed that the PNIPAM shell is highly swollen, and the density of the shell in the collapsed state approached that of the PS core.

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INTRODUCTION

Poly(*N*-isopropylacrylamide) (PNIPAM) is an extensively studied, thermally sensitive polymer [1 and references therein]. At temperatures higher than its lower critical solution temperature (LCST, ∼32°C), a PNIPAM chain becomes hydrophobic and insoluble in water. It has been shown that a single polymer chain can collapse from an extended coil to a uniform globule [2–4]. The solution properties of individual PNIPAM chains and its related gels have attracted much attention in the last decade because of their potential applications.

Zhu and Napper [5,6] studied the coil-to-globule transition of linear PNIPAM chains grafted on the surface of large polystyrene (PS) latex particles (240–280 nm) and found hysteresis in terms of the particle size in the heating-and-cooling cycle. The hysteresis was attributed to chain knotting. They also found a difference between the phase transitions of the PNIPAM chains grafted on an electrostatically stabilized surface and those grafted on a sterically stabilized one. Our previous study showed that nearly no knotting existed inside a single PNIPAM chain [2], but there was an additional adsorption of PNIPAM chains on the particle when the solution temperature increased [7]. The hysteresis should be attributed to the adsorption of the grafted chains on the particle surface.

We realize that, in our previous study, the shrinking of the PNIPAM chains on the particle surface was mixed with additional adsorption of the PNIPAM chains free in the dispersion, which complicated the study of the coil-to-globule transition of adsorbed chains on the surface. In the present study, we removed all the nonadsorbed chains after the adsorption, so that the interference of the additional adsorption was eliminated. In this way, we were able to study the true swelling and shrinking of the PNIPAM chains adsorbed on the particle surface. It provides us a model system for investigating the adsorption and desorption of polymer chains on the surface, as well as the conformation of the polymer chains on the surface.

EXPERIMENTAL

Materials

A narrowly distributed, surfactant-free PS latex dispersion (hydrodynamic radius $\langle R_h \rangle \sim 22$ nm, denoted PS22) and four PNIPAM samples ($M_w \sim 7.0 \times 10^3$, 8.6×10^4, 8.4×10^5, and 6.0×10^6 g/mol, respectively denoted as PN1, PN2, PN3, and PN4) were used. Small nanoparticles were used so that the adsorption could result in a relatively larger change in their hydrodynamic size and the thickness of the adsorbed polymer layer could be measured accurately. The synthesis and fractionation of PNIPAM were detailed previously [8]. The hydrodynamic radii of the PNIPAM chains in water at 25°C were about 3, 10, 34, and 110 nm, respectively. The adsorption of the PNIPAM chains onto the particle surface reached equilibrium within minutes after mixing the PNIPAM solution with the nanoparticle dispersion. Double-distilled deionized water was used as the dispersion medium. The nonadsorbed PNIPAM chains were removed by several cycles of ultracentrifugation and decantation of the supernatant at 33,000 rpm and 10°C. The dispersions were clarified by using a 0.5-μm filter to remove dust.

Laser Light Scattering

The laser light scattering (LLS) instrumentation was detailed previously [4]. The specific refractive index increment (dn/dC) was determined using a novel and precise differential refractometer [9]. In static LLS, the angular dependence of the absolute excess time-averaged scattered intensity, known as the Rayleigh ratio $R_{vv}(\theta)$, was measured. For a very dilute solution at a relatively small scattering angle θ, the weight-average molar mass M_w is related to $R_{vv}(\theta)$ by [10]

$$\frac{KC}{R_{vv}(q)} \cong \frac{1}{M_w}\left(1+\frac{1}{3}<R_g^2>_z q^2\right) \tag{1}$$

where $K = 4\pi^2 n^2 (dn/dC)^2/(N_A \lambda_0^4)$ and $q = (4\pi n/\lambda_o)\sin(\theta/2)$ with N_A, n, and λ_o being the Avogadro constant, solvent refractive index, and wavelength of the laser light in vacuum, respectively, and $<R_g^2>_z^{1/2}$ (or written as $<R_g>$) is the z-average root-mean-square radius of gyration. In this study, the mixture was so diluted that the concentration correction was not necessary. Note that the light scattered from each nanoparticle was at least about 400 times stronger than that from water and individual PNIPAM chains free in water, so that the light scattered by water and individual nonadsorbed PNIPAM chains could be neglected.

In dynamic LLS, the cumulant analysis of the measured intensity-intensity time correlation function $G^{(2)}(\tau,\theta)$ in the self-beating mode leads to the average line width $<\Gamma>$ [11,12]. For a diffusive relaxation, $<\Gamma>_{C\to 0, q\to 0}$ is proportional to the average translational diffusion coefficient $<D>$ by $<\Gamma> = <D>q^2$; and $<D>$ can be further converted to the hydrodynamic radius $<R_h>$ by the Stokes-Einstein equation $<R_h> = k_B T/6\pi\eta<D>$, where k_B, T, and η are the Boltzmann constant, absolute temperature, and solvent viscosity, respectively.

RESULTS AND DISCUSSION

Figure 1 shows that the adsorption density σ, the adsorbed polymer mass per unit surface area, sharply increases in the low range of the macroscopic weight ratio $W_{\mathrm{PNIPAM}}/W_{\mathrm{PS}}$ before reaching the plateau ($\sigma_{\max} \sim 0.8$ mg/m^2), indicating strong adsorption. Note that the ratios of $W_{\mathrm{PNIPAM}}/W_{\mathrm{PS}}$ at which σ reaches the plateaus are nearly identical, but the thickness of the adsorbed PNIPAM layer $\Delta<R_h>$ is quite different for different chain lengths. This suggests that the maximum adsorption is limited by the total available surface area S, independent of the polymer chain length, which agrees well with theoretical calculations for the adsorption of polymer chains in a good solvent [13]. On the other hand, at the maximum adsorption, we have $\sigma = (W_{\mathrm{PNIPAM}})_{ad}/S$ and $S = s \cdot N = s \cdot [N_A (W_{\mathrm{PNIPAM}})_{ad}/M]$, where $s\,(\propto <R_g^2>$ or $<R_h>^2)$ is the average surface area occupied per PNIPAM chain, N is the number of adsorbed chains, $(W_{\mathrm{PNIPAM}})_{ad}$ is the weight of the chains adsorbed on the particle surface, and M is the molar mass of the PNIPAM chain. The fact that $\sigma_{\max}$ is nearly a constant leads to $M \propto s$, or further, $M \propto <R_g^2>$ or $<R_h>^2$, indicating that the surface makes the adsorbed PNIPAM chain behave as a coil chain in the Θ-state. Note that $\Delta<R_h>_{\max}$ is

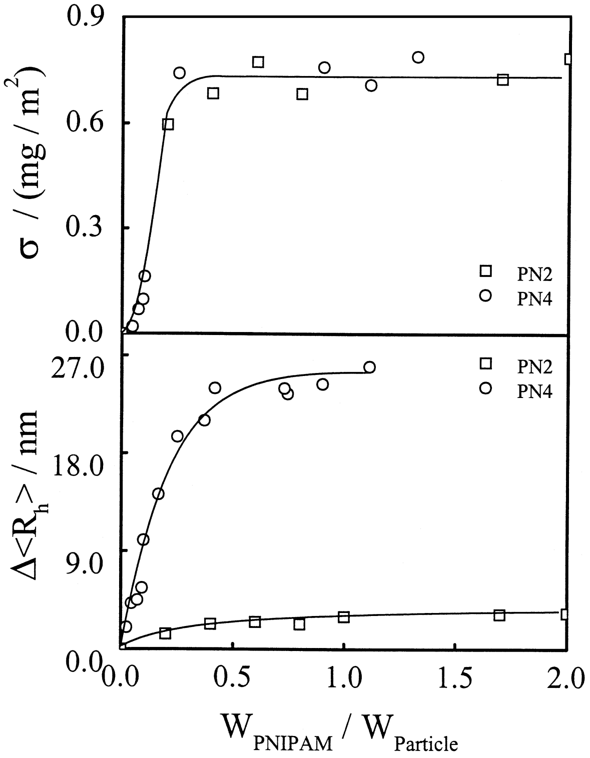

FIG. 1. Adsorption isotherms in the mixtures of two different kinds of PNIPAM chains and polystyrene nanoparticles (PS22) for which the PS22 concentration was kept at 1.2×10^{-5} g/mL; $T = 25$°C; σ is the adsorption density, defined as the adsorbed polymer mass per unit surface area; W_{PNIPAM} and W_{PS} are macroscopic weights of PNIPAM and polystyrene nanoparticles, respectively; and $\Delta\langle R_h\rangle = \langle R_h\rangle - \langle R_h\rangle_0$ with $\langle R_h\rangle$ and $\langle R_h\rangle_0$ being the hydrodynamic radii of the nanoparticles with and without the adsorbed PNIPAM chains, respectively.

still smaller than the hydrodynamic diameter ($2\langle R_h\rangle_{\mathrm{PNIPAM}}$) of the PNIPAM chains free in water because the adsorption prevents the chain expansion. It should be stated that, if the shortest chains (PN1) were used, no adsorption was obtained.

Figure 2 shows that when the adsorption is low, the thickness of the adsorbed layer $\Delta\langle R_h\rangle$ only decreases slightly as the temperature increases in the range 25°C–35°C, but there is no change in σ. The constant σ indicates that there is no additional adsorption at a higher temperature, which is expected because free PNIPAM chains have already been removed. The nearly constant $\Delta\langle R_h\rangle$ contradicts what we knew for the PNIPAM chains free in water; namely, the PNIPAM chain undergoes a coil-to-globule transition, and its size could shrink as much as about 8 times when the solution temperature increases from 25°C to 35°C [2]. Figure 2 indicates that the PNIPAM chains lie flat on the particle surface if only a few chains are adsorbed on the surface.

Figure 3 shows that, after the first heating-and-cooling cycle, $\Delta\langle R_h\rangle$ becomes smaller for high adsorption. It should be stated that there was no change in the scattered intensity during the heating-and-cooling cycle, that is, there was no adsorption or desorp-

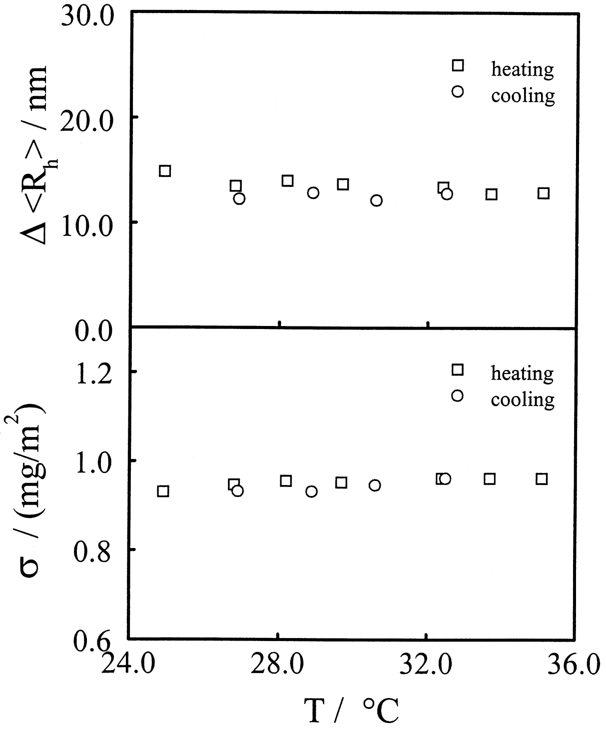

FIG. 2. Temperature dependence of the hydrodynamic thickness of the PNIPAM (PN4) layer (shell) on the polystyrene nanoparticles (PS22) for which the PS22 concentration was 1.2×10^{-5} g/mL and the PN4/PS22 weight ratio was 0.2.

tion. The hyteresis of $\Delta<R_h>$ can be explained as follows. As expected, the adsorbed PNIPAM chains would have more chance to attach to the surface in the collapsed state, resulting in many small chain loops on the surface and a thinner PNIPAM layer. After the first heating-and-cooling cycle, the change of $\Delta<R_h>$ in the following heating-and-cooling cycles was completely reversible.

It should be noted that the coil-to-globule transition of the PNIPAM chains adsorbed on the surface was continuous and smooth, in contrast to that of the PNIPAM chains free in water [2]. This supports a theoretical prediction, namely, that the ternary interaction can lead to a strong repulsion between the chains adsorbed on the surface. This strong repulsion not only shifts the transition toward a lower temperature, but also makes it smooth in comparison with the behavior of a polymer chain free in a three-dimensional space [14]. The smooth transition without the interparticle aggregation at high temperatures also reveals that the adsorption of the PNIPAM chains on originally electrostatically stabilized particles makes the steric stabilization dominant [5]. To our knowledge, it is rare to observe switching from electrostatic to steric stabilization without flocculation.

Figure 4 shows that $<R_g>/<R_h>$ increases as the temperature increases, completely different from that of the PNIPAM chains free in water [2]. The difference can be attrib-

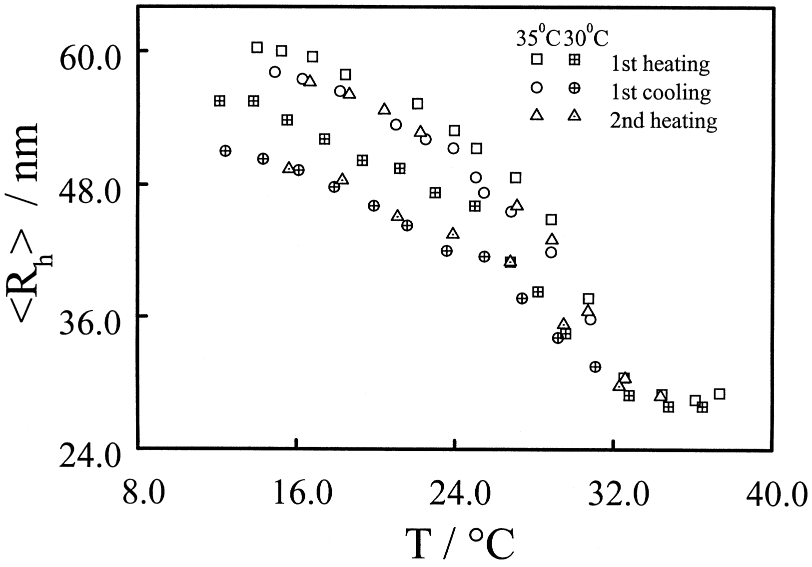

FIG. 3. Temperature dependence of the thickness of the PNIPAM (PN3) layer $\Delta(<R_h>)$ adsorbed on the polystyrene nanoparticle (PS22) surface for which the PS22 concentration was 1.2×10^{-5} g/mL and the PN3/PS22 weight ratio was 2.0.

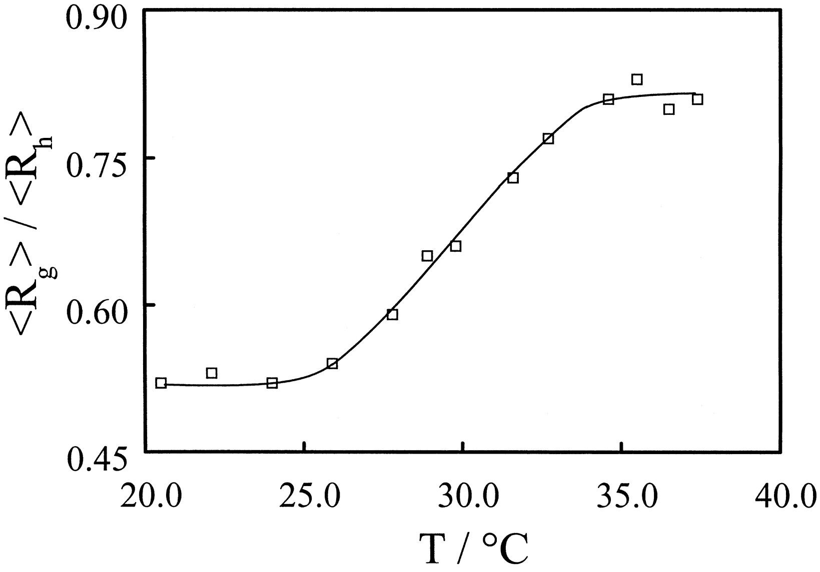

FIG. 4. Temperature dependence of $<R_g>/<R_h>$ for the polystyrene nanoparticles (PS22) adsorbed with the PNIPAM (PN3) chains for which the PS22 concentration was 1.2×10^{-5} g/mL and the PN3/PS22 weight ratio was 2.0.

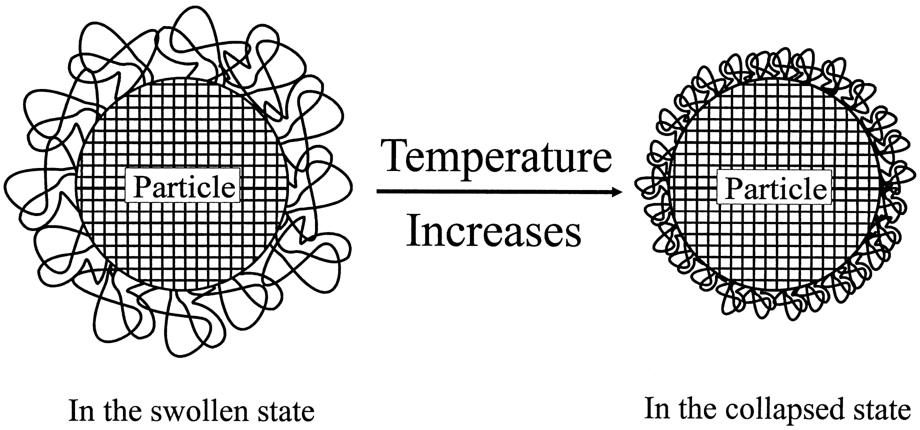

FIG. 5. Schematic of swelling and shrinking of the PNIPAM chains adsorbed on the nanoparticle as the dispersion temperature varied.

uted to the "core-shell" structure of the particle with longer polymer chains adsorbed. Note that the size of the core is independent of temperature; $<R_g>$ is related to the mass distribution in space; and the core has much more mass than the PNIPAM shell. In the swollen state, the PNIPAM shell has a much lower density than the core, resulting in a smaller $<R_g>$ in comparison with a uniform sphere with the same $<R_h>$. This is why $<R_g>/<R_h>$ is smaller than 0.774, a value predicated for a uniform nondraining sphere. As the temperature increases, the shrinking of the shell leads to a decrease of $<R_h>$ much faster than $<R_g>$ so that $<R_g>/<R_h>$ increases. It is interesting to find that, in the collapsed state (i.e., $T > \sim 32°\text{C}$), $<R_g>/<R_h>$ approaches about 0.8, indicating that the shell and the core have a similar density (~1 g/cm^3), much higher than the density (~0.3–0.4 g/cm^3) of individual collapsed PNIPAM chains free in water [15,16], which further illustrates that the surface enhances the collapse of the adsorbed polymer chains. The transition is schematically shown in Fig. 5.

CONCLUSIONS

We found that the maximum adsorption of PNIPAM chains on PS nanoparticles was independent of the chain length, but was determined by the total available surface area. The surface area occupied per adsorbed chain at 25°C was proportional to the molar mass of the chain, which leads to $M \propto R^2$, indicating that the PNIPAM chains adsorbed on the surface are in the Θ-state even though water is a good solvent for nonadsorbed chains under the same condition. There exists a hysteresis in the first heating-and-cooling cycle because more segments of the adsorbed polymer chain have more chance to attach themselves to the surface in the collapsed state. The coil-to-globule transition of the PNIPAM chains on the surface is smoother than that of free chains in water, and the surface shifts the transition temperature lower. Moreover, the temperature dependence of $<R_g>/<R_h>$ reveals that the adsorbed chains are stretched in the swollen state and are able to collapse into a state with a density similar to that of the nanoparticle core, indicating that the surface can enhance the polymer chain collapse.

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REFERENCES

1. H. G. Schild, *Progr. Polym. Sci.*, *17*, 163 (1993).
2. C. Wu and S. Zhou, *Phys. Rev. Lett.*, *77,* 3053 (1996).
3. M. Nakata and T. Nakagawa, *Phys. Rev. E.*, *56,* 3338 (1997).
4. K. Kubota, S. Fujishige, and I. Ando, *J. Phys. Chem.*, *94*, 5154 (1990).
5. P. W. Zhu and D. H. Napper, *J. Colloid Interface Sci.*, *168,* 380 (1994).
6. P. W. Zhu and D. H. Napper, *J. Colloid Interface Sci.*, *164,* 489 (1994).
7. J. Gao and C. Wu, *Macromolecules*, *30*, 6873 (1997).
8. S. Zhou, S. Y. Fan, S. T. F. Au-yeung, and C. Wu, *Polymer*, *36*, 1341 (1995).
9. C. Wu and K. Q. Xia, *Rev. Sci. Instrum.*, *65*, 587 (1994).
10. B. H. Zimm, *J. Chem. Phys.*, *16*, 1099 (1948).
11. B. Chu, *Laser Light Scattering*, 2nd ed., Academic, New York, 1991.
12. B. Berne and R. Pecora, *Dynamic Light Scattering*, Plenum, New York, 1976.
13. G. J. Fleer, M. A. Cohen Stuart, J. M. H. M. Scgeutjens, T. Cosgrove, and B. Vincent, *Polymers at Interfaces*, Chapman and Hall, London, 1993, p. 265.
14. E. B. Zhulina, O. V. Borisov, V. A. Pryamitsyn, and T. M. Birshtein, *Macromolecules*, *24*, 140 (1991).
15. C. Wu and S. Zhou, *Macromolecules*, *28*, 5388 (1995).
16. C. Wu and S. Zhou, *Macromolecules*, *28*, 8381 (1995).

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