THE ADSORPTION OF LINEAR POLY(N-ISOPROPYLACRYLAMIDE) CHAINS ON SURFACTANT-FREE POLYSTYRENE NANOPARTICLES

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Abstract The adsorption of linear poly(N-isopropylacrylamide) (PNIPAM) chains on surfactant-free polystyrene (PS) nanoparticles was used as a model system to study the hydrophobic adsorption of polymer on the surface, because the hydrophobility of PNIPAM can be continuously varied by a small temperature change. The adsorption was investigated by a combination of static and dynamic laser light scattering (LLS) measurements. In static LLS, the absolute excess scattered light intensity led to the amount of PNIPAM adsorbed on the surface. In dynamic LLS, the hydrodynamic thickness of the adsorbed PNIPAM layer was accurately measured. For a given particle concentration, the adsorption increases as the PNIPAM concentration and the incubation temperature increase. The average density of the adsorbed PNIPAM layer is reciprocally proportional to the number of the PNIPAM chains on the surface, revealing a simple scaling of the chain density distribution. The adsorption follows the Langmuir's isotherm. The enthalpy change estimated from the adsorption at 25°C and 30°C is slightly positive, indicating that the adsorption involves the coil-to-globule transition of the chains on the surface.

Keywords Poly(N-isopropylacrylamide), Polystyrene nanoparticles, Surface adsorption of polymers, Light scattering

INTRODUCTION

The adsorption of a linear polymer chain on surface is not only a fundamental theoretical problem but also an important practical issue[1~20]. Narrowly distributed spherical polystyrene (PS) latex particles are often used as a model substrate in the adsorption study, because such a system is directly related to the colloidal stabilization[3, 20]. Moreover, the adsorption of a polymer chain on the particle surface can be used to study hydrophobic interaction. It is generally known that the adsorption increases as the polymer concentration increases, so that the adsorption can be varied by the polymer/surface ratio. Recently, we found that using poly(N-isopropylacrylamide) (PNIPAM) led to a more convenient way to study the adsorption because PNIPAM is an extensively studied thermosensitive polymer[21~25]. At temperatures lower than ~31°C, PNIPAM is hydrophilic and soluble in water. As the temperature increases, it becomes hydrophobic and its chain conformation undergoes a coil-to-globule transition[26~29]. A microcalorimetric study on the coil-to-globule transition of PNIPAM showed that the transition is endothermic[22, 30]. Therefore, for a given PNIPAM/particle solution mixture, we are able to continuously manipulate the adsorption by a very small temperature variations[31]. Our results showed that 1) the "coil-to-globule" transition of the PNIPAM chains on a hydrophobic surface is ~3°C lower than the lower critical solution

temperature (LCST) of individual PNIPAM chains free in water and 2) the shrinkage of the PNIPAM chains on the surface frees more surface for a further adsorption. Therefore, the adsorption and the coil-to-globule transition are mutually promoted.

In this study, a newly developed method of combining static and dynamic laser light scattering was used to quantitatively calculate not only the hydrodynamic thickness of the adsorbed PNIPAM layer, but also the average amount of the PNIPAM chains adsorbed on each particle, so that we were able to determine the average chain density on the particle surface and the enthalpy change of the adsorption.

EXPERIMENTAL

Sample Preparation

Narrowly distributed surfactant-free PS nanoparticles with a nominal average radius of ~22 nm and a polydispersity index of ~1.03 were purchased from Seradyn. The synthesis of PNIPAM has been detailed before[32]. A higher molar mass PNIPAM fraction (M_w = 8.44 × 10^5 g/mol) was used. The adsorption was achieved by stirring a solution mixture of the nanoparticles and PNIPAM for 24 h at constant temperature, with the nanoparticle concentration kept at 2.4×10^{-5} g/mL. Each solution mixture was clarified using a 0.5 μm millipore filter prior to laser light scattering experiments. The sample preparation, including the mixing and clarification, was done strictly at 25 °C or lower.

Laser Light Scattering

The LLS instrumentation has been reported before[31]. The specific refractive index increment (dn/dC) was determined by using a novel and precise differential refractometer[33]. In static LLS, the angular dependence of the absolute excess time-averaged scattered intensity $R_{vv}(\theta)$, known as the Rayleigh ratio, 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:

$$\frac{K C(dn/dC)^2}{R_{vv}(q)} \cong \frac{1}{M_w}(1 + \frac{1}{3} < R_g^2 >_z q^2) \tag{1}$$

where $K = 4\pi^2 n^2/(N_{Av} \lambda_0^4)$ and $q = (4\pi n/\lambda_0)\sin(\theta/2)$ with N_{Av}, n and λ_0 being the Avogadro' constant, the solvent refractive index and the laser wavelength in vacuum, respectively; and $<R_g^2>_z^{1/2}$ (or simply $<R_g>$) is the z-average root-mean-square radius of gyration. In this study, the mixture was so diluted that the extrapolation of $[R_{vv}(\theta)]_{C\to 0}$ was not necessary. It should also be noted that the light scattered from the nanoparticles ($C = 2.4 \times 10^{-5}$ g/mL) was ~400 times stronger than that from individual PNIPAM chains free in water (even for $C \sim 10^{-4}$ g/mL), i.e., the light scattered by water and individual unadsorbed PNIPAM chains can be neglected. In dynamic LLS, the cumulant analysis or the Laplace inversion of the measured intensity-intensity time correlation function $G^{(2)}(\tau, \theta)$ in the self-beating mode can lead to the average line-width $<\Gamma>$[34, 37]. 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, η, and T are the Boltzmann constant, solvent viscosity, and absolute temperature, respectively.

RESULTS AND DISCUSSION

Figure 1 shows that for each given polymer/particle ratio, the adsorption increases as the incubation temperature increases, due to the increase of the average hydrodynamic radius of the nanoparticles adsorbed with PNIPAM. It should be noted that each data point in Fig. 1 was obtained by heating the solution mixture to a desired temperature and incubating it at that temperature for 3 days before cooling it back to 25 °C for the LLS measurements. Also note that no

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interparticle aggregation at higher temperatures was observed. Our results showed that the adsorption approached a constant when the incubation temperature was close to 35℃ (at which the PNIPAM chain was already fully collapsed[28]). Table 1 summarizes all the dynamic LLS results. The adsorption varies with the polymer/particle ratio and also the incubation temperature. Utilizing this property, we were able to vary the amount of PNIPAM adsorbed on PS particles by changing the temperature and composition of the mixture.
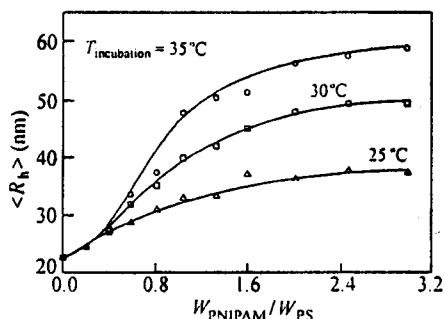

Fig. 1 Incubation temperature ($T_{incubation}$) and relative polymer concentration (W_{PNIPAM}/W_{PS}) dependence of the average hydrodynamic radius ($<R_h>$) of surfactant-free polystyrene (PS) nanoparticles adsorbed with PNIPAM

Table 1. Dynamic LLS results of different PNIPAM/PS mixtures after incubating them at different temperatures*

Fleet weight ratio PNIPAM/PS	Incubation temperature		
	25℃	30℃	35℃
0.202	24.5	24.4	24.4
0.410	27.3	27.0	27.6
0.595	28.6	31.7	33.5
0.820	30.8	35.0	37.3
1.05	32.8	39.8	47.8
1.34	33.2	42.0	50.5
1.61	37.0	45.1	51.4
2.02	36.2	48.0	56.4
2.48	37.7	49.5	57.7
2.99	37.3	49.6	59.0

* The measurement temperature was 25℃

In static LLS, by considering the particle adsorbed with PNIPAM as a polymeric core-shell "micelle" made of diblock "copolymer" chains, we were able to use a simple weight additive method to calculate dn/dC[38], i.e.

$$(\frac{dn}{dC})_{PS+PNIPAM} = \chi_{PNIPAM}(\frac{dn}{dC})_{PNIPAM} + (1 - \chi_{PNIPAM})(\frac{dn}{dC})_{PS} \qquad (2)$$

where $\chi_{PNIPAM} = \gamma W_{PNIPAM}/(\gamma W_{PNIPAM} + W_{PS})$ with W_{PS} and W_{PNIPAM} being the macroscopic weights of the particles and PNIPAM, respectively; and γ being the fraction of the PNIPAM chains adsorbed on the particles. Therefore, the weight concentration (C) of the particles adsorbed with PNIPAM is $(W_{PS} + \gamma W_{PNIPAM})/V$, or written as, $(1 + \gamma W_{PNIPAM}/W_{PS})C_{PS}$, where $C_{PS} = W_{PS}/V$ is the initial bare particle concentration before the adsorption. The measured specific refractive index increments of the PNIPAM chains and the particles in water are 0.167 and 0.256 mL/g, respectively. A combination of Eqs. (1) and (2) leads to

$$(M_w)_{PS+PNIPAM} = \frac{[R_{vv}(\theta)]_{PS+PNIPAM}}{K\,[(dn/dC)_{PS+PNIPAM}^2]C_{PS+PNIPAM}} \tag{3}$$

where $[R_{vv}(q)]_{PS+PNIPAM}$ and $(M_w)_{PS+PNIPAM} = (1 + \gamma W_{PNIPAM}/W_{PS})(M_w)_{PS}$ are the Rayleigh ratio and the weight average molar mass of the particles adsorbed with PNIPAM, respectively, and $(M_w)_{PS}$ [$= R_{vv}(q)]_{PS}/[(K'(dn/dC)^2_{PS}C_{PS}]$ is the weight average molar mass of the PS particles without any adsorption. Eq. (3) can be rearranged as

$$\gamma\frac{W_{PNIPM}}{W_{PS}} = \frac{(dn/dC)_{PS}}{(dn/dC)_{PNIPAM}}\left\{\left(\frac{[R_{vv}(\theta)]_{PS+PNIAPPAM}}{[R_{vv}(\theta)]_{PS}}\right)^{1/2} - 1\right\} \tag{4}$$

where $[R_{vv}(\theta)]_{PS}$ is a constant for a given C_{PS}, dn/dC can be independently measured, and W_{PNIPAM}/W_{PS} is known from the sample preparation, so that γ can be determined from $[R_{vv}(\theta)]_{PS+PNIPAM}$ measured in static LLS. It should be noted that $\gamma W_{PNIPAM}/W_{PS}$ represents the weight ratio of the adsorbed PNIPAM chains to the particles. In dynamic LLS, the hydrodynamic volume (V) of the PNIPAM layer adsorbed on the particle surface is related to the hydrodynamic radius difference (ΔR_h) between the nanoparticle after and before the adsorption by:

$$V = (4/3)\,\pi\,[(<R_h>_0 + \Delta R_h)^3 - <R_h>_0^3] = (4/3)\,\pi\,<R_h>_0^3 f(\Delta R_h/<R_h>_0) \tag{5}$$

where $f(\Delta R_h/R_{h,0}) = 3(\Delta R_h/<R_h>_0) + 3(\Delta R_h/<R_h>_0)^2 + (\Delta R_h/<R_h>_0)^3$. It can be seen that using small nanoparticels enabled us to accurately determine ΔR_h and V.

Figure 2 shows that V increases as $\gamma W_{PNIPAM}/W_{PS}$ increases, where the line represents the least square fitting of V (nm^3) $= 1.7 \times 10^6$ $(\gamma W_{PNIPAM}/W_{PS})^{2.0\pm0.1}$. It is noted that for a given particle concentration, the average number (n_{chain}) of the adsorbed chains per particle is proportional to γW_{PNIPAM} and the average chain density $<\rho>$ of the PNIPAM layer equals $\gamma W_{PNIPAM}/V$. Therefore, $<\rho> \propto (\gamma W_{PNIPAM})^{-1} \propto n_{chain}^{-1}$.
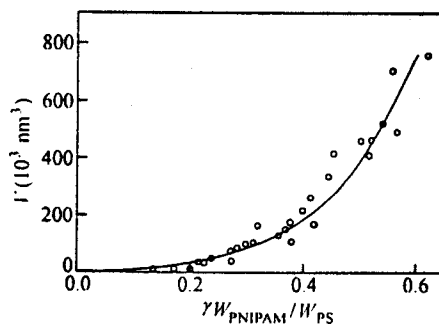

Fig. 2 Adsorption dependence of the hydrodynamic volume (V) of the PNIPAM layer adsorbed on the nanoparticles

Figure 3 shows that $<\rho>$ decreases as γW_{PNIPAM} increases. The inset shows $<\rho> \propto n_{chain}^{-1}$. The decrease of $<\rho>$ with increasing n_{chain} indicates the stretching of the PNIPAM chains on the surface, which is very similar to the adsorption of gelatin on the β-carotin particles[39]. The fact that two different systems, PNIPAM on the polystyrene particles and gelatin on the β-carotin particles, have the same behavior indicates that there exists a common physics behind the adsorption. Qualitatively, when the adsorption is low, each chain covers a large area and lays on the surface, or in other words, the adsorption attracts the chain onto the surface, so that $<\rho>$ is close to the density of a crumpled PNIPAM chain[28]. For each adsorbing site (could involves a number of chain segments), there exists a dynamic equilibrium between the adsorption and desorption. However, the complete desorption of a long polymer chain from the surface requires not only a

simultaneously releasing of all the adsorbing sites, but also the fast diffusion of the polymer chain away from the surface. Therefore, it is rather difficult for an adsorbed long chain to become free again after its adsorption on the surface.
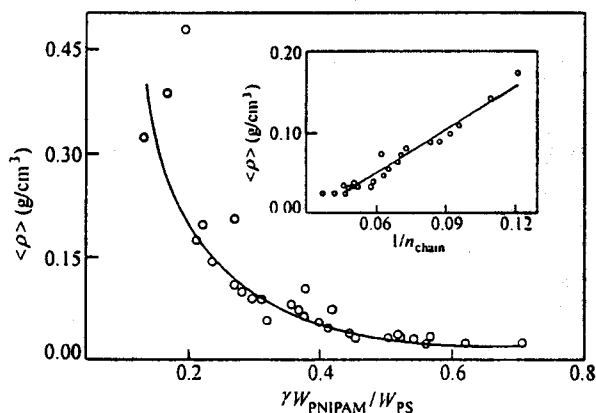

Fig. 3 Adsorption dependence of the average chain density ($<\rho>$) of the PNIPAM layer adsorbed on the nanoparticles

Figure 4 shows that $<R_h>$ is nearly independent of time after lowering the temperature of the mixture from its incubation temperature (35°C) to room temperature at which water is a good solvent for PNIPAM. Figure 4 indicates no obvious desorption. If more chains are added, the adsorbing site released by one chain can be occupied by another chain, so that the average number of the adsorbing sites per chain decreases and the average chain length between two neighboring adsorbing sites, i.e. the loop length, increases, as schematically shown in Fig. 5. $<\rho>$ decreases as the "loop" stretches. It is noted that the hydrodynamic volume (V) of the adsorbed PNIPAM layer is proportional to both the average hydrodynamic volume (V_{chain}) of one chain adsorbed on the surface and the average number (n_{chain}) of the chains per particle, i.e. $V \propto V_{chain}n_{chain}$. According to its definition, $<\rho> \propto n_{chain}/V$, or $<\rho> \propto v_{chain}^{-1}$. Therefore, $V_{hain} \propto n_{chain}$.
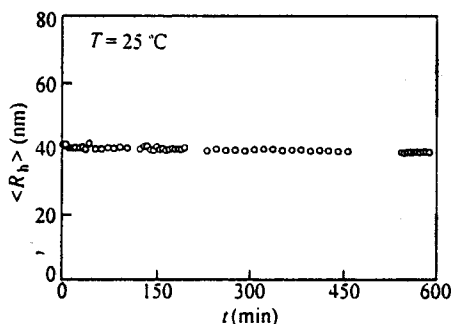

Fig. 4 Desorption kinetics of the PNIPAM chains the particle surface, reflecting from the change of the hydrodynamic radius of the particles adsorbed with PNIPAM

On the other hand, assuming that on average, each chain on the surface forms n_{loop} loops and each loop has a hydrodynamic volume of V_{loop}, we have $V_{chain} \propto V_{loop}n_{loop}$. Further, it is reasonable to assume that the average number of the adsorbing sites available on each particle is a constant, i.e. $n_{loop}n_{chain}$ is a constant or $n_{loop} \propto n_{chain}^{-1}$. As shown in Fig. 5, V_{loop} is proportional to its occupied surface (S_{loop}) and its extension away from the surface (h_{loop}). Both S_{loop} and h_{loop} are proportional to n_{chain}. Therefore, $V_{loop} \propto S_{loop}h_{loop} \propto n_{chain}^2$. Finally, putting everything together leads to $V_{chain} \propto$

n_{chain}, a simple scaling as we observed. It is worth noting that the above discussion is independent of a particular polymer/particle system.

Further, considering that on a unit area (the x-y plane), ρ is a function of the distance (z) away from the surface, we have $\int_0^\infty \rho(z)dz = W_{chain} \propto n_{chain}$, where W_{chain} is the total weight of the chains adsorbed on the surface. If $\rho(z)$ can be scaled by a characteristic length ξ, we will be able to rewrite above equation as $\xi \int_0^\infty \rho(z/\xi)d(z/\xi) \propto n_{chain}$. Note that for a given surface, $\xi \propto V$ and $V \propto n_{chain}$ so that $\int_0^\infty \rho(z/\xi)d(z/\xi)$ is a constant and an invariant, even independent of the shape of $\rho(z)$ as long as it can be scaled by a characteristic length ξ.
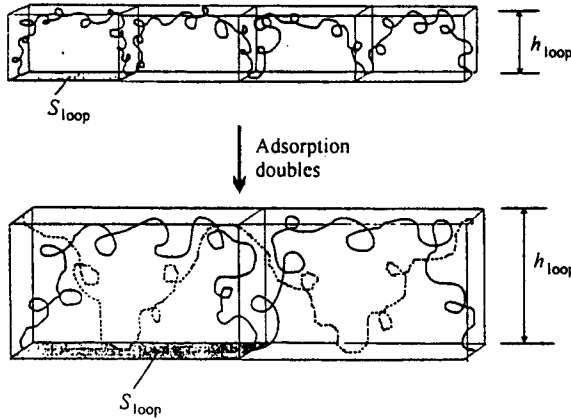

Fig. 5 Schematic of a polymer chain adsorbed on the surface

Figure 6 shows that the adsorption of PNIPAM on the PS nanoparticles follows the Langmuir isotherm for a monolayer physical adsorption. A linear relationship between $W_{PS}/(\gamma W'_{PNIPAM})$ and $[1/(1-\gamma)C_{PNIPAM}]$ was obtained. According to the Langmuir isotherm, the adsorption equilibrium constants estimated from the ratio of the intercept to the slop of each line in Fig. 6 are 1.4 and 2.3, respectively, for the isotherms at 25°C and 30°C. The average enthalpy change in the process of PNIPAM (free) → PNIPAM (adsorbed) between 25 °C and 30 °C can be estimated from the thermodynamic equation:

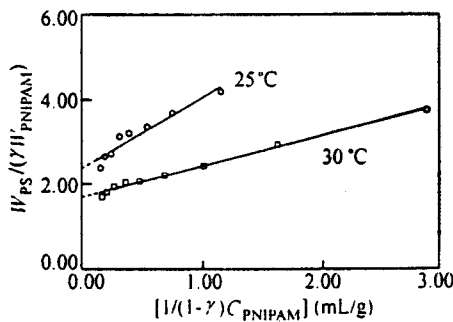$$\ln\frac{K_{T_2}}{K_{T_1}} = \frac{(\Delta H_m)_{ad}(T_2 - T_1)}{RT_1T_2} \qquad (6)$$

Fig. 6 Adsorption isotherms at two temperatures

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Using the values of K at 25°C and 30°C, we found that $(\Delta H_m)_{ad} = 72$ kJ/mol, showing that 1) the average enthalpy change per NIPAM monomer unit is small (~ 17 J/mol); and 2) The positive $(\Delta H_m)_{ad}$ indicates that the adsorption is an entropy controlled endothermic process and the entropy change for the adsorption must be positive, just as we experienced that the adsorption increases as the temperature increases.

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