

A Simple Scaling of the Density Profile of Long Linear Polymer Chains Adsorbed on Hydrophobic Surface

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The adsorption of a linear polymer chain on a surface has long been studied both in theory and in practice.^{1–10} Narrowly distributed spherical polystyrene latex particles are often used as a model substrate in the adsorption study because they are directly related to the stabilization of colloids in dispersion.^{3,10} It is generally known that the adsorption increases as the polymer concentration increases, so that the adsorption can be controlled by varying the polymer/surface ratio. On the other hand, poly(*N*-isopropylacrylamide) (PNIPAM) has been extensively studied as a thermosensitive polymer.^{11,12} At temperatures lower than ~ 32 °C, PNIPAM is hydrophilic and soluble in water. As the temperature increases, it becomes hydrophobic, undergoing the coil-to-globule transition.^{13,14} Therefore, for a given PNIPAM/particle solution mixture, we are able to continuously manipulate the amount of the adsorption simply by a small temperature variation and study the chain conformation on the surface. In this study, a combination of static and dynamic laser light scattering (LLS) was used to quantitatively calculate not only the hydrodynamic thickness of the adsorbed polymer layer but also the number of polymer chains adsorbed on each particle, so that we were able to study the density distribution of the chains adsorbed on the surface.

Narrowly distributed surfactant-free polystyrene particles with a nominal average radius of ~ 22 nm and a polydispersity index of ~ 1.03 was from Seradyn. PNIPAM was synthesized and fractionated in our laboratory.¹⁴ The PNIPAM fraction used had a weight average molar mass (M_w) of 8.44×10^5 g/mol, a polydisperse index (M_w/M_n) of ~ 1.5 , and an average hydrodynamic radius ($\langle R_h \rangle$) of ca. 30 nm. The adsorption was achieved by stirring a solution mixture of the particles and PNIPAM for 24 h at three different temperatures (25, 30, and 35 °C),¹⁵ where the particle concentration was kept at 2.4×10^{-5} g/mL. The solution mixture was clarified by a 0.5 μ m Millipore filter prior to laser light scattering experiments. The LLS instrumentation was detailed before.¹⁵ The specific refractive index increment (dn/dc) was determined by a novel and precise differential refractometer.¹⁶ In static LLS, considering the nanoparticles adsorbed with polymer chains as a diblock “copolymer”, we were able to calculate the amount (W_{polymer}) of polymer chains adsorbed on the particle surface from the angular dependence of the absolute excess time-averaged scattered intensity $R_v(\theta)$, known as the Rayleigh ratio. In this study, the mixture was so diluted that the extrapolation of $R_v(\theta)$ to infinite

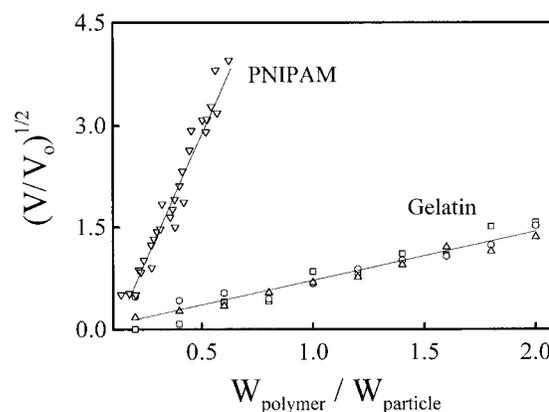


Figure 1. Plot of the square root relative hydrodynamic volume $(V/V_0)^{1/2}$ vs the relative weight ($W_{\text{polymer}}/W_{\text{particle}}$), where V_0 and V , respectively, are the hydrodynamic volumes of the particle and the polymer layer adsorbed on the particle and W_{particle} and W_{polymer} , respectively, are the total weights of the particles and the polymer chains adsorbed on the particles. For PNIPAM/latex, the initial bare latex particles have an average hydrodynamic radius ($\langle R_h \rangle$) of 22 nm, and for gelatin/ β -carotin, $\langle R_h \rangle$, respectively, are 26 nm (Δ), 35 nm (\square), and 61 nm (\circ).

dilution was not necessary. It should be stated that the light scattered from the nanoparticles was ~ 400 times stronger than that from individual PNIPAM chains free in water, so that the light scattered by water and individual unadsorbed polymer chains can 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 lead to the average line-width $\langle \Gamma \rangle$.¹⁷ For a diffusive relaxation, $\langle \Gamma \rangle_{C \rightarrow 0, q \rightarrow 0}$ is proportional to the average translational diffusion coefficient $\langle D \rangle$ which can be further related to the average hydrodynamic radius $\langle R_h \rangle$ by the Stokes–Einstein equation: $\langle R_h \rangle = k_B T / 6\pi\eta \langle D \rangle$, where k_B , η , and T are the Boltzmann constant, solvent viscosity, and the absolute temperature, respectively. The hydrodynamic volume (V) of the polymer layer adsorbed on the particle surface can be deduced from the hydrodynamic radius difference (ΔR_h) between the particle after and before the adsorption; namely, $V = V_0 f(\Delta R_h / \langle R_h \rangle_0)$, where $V_0 = (4/3)\pi \langle R_h \rangle_0^3$ and $f(\Delta R_h / \langle R_h \rangle_0) = 3(\Delta R_h / \langle R_h \rangle_0) + 3(\Delta R_h / \langle R_h \rangle_0)^2 + (\Delta R_h / \langle R_h \rangle_0)^3$ with $\langle R_h \rangle_0$ being the hydrodynamic radius of the particles before the adsorption. Using small nanoparticles enabled us to determine ΔR_h with an accuracy better than $\pm 2\%$.

Figure 1 shows that $V/V_0 [= f(\Delta R_h / \langle R_h \rangle_0)]$ increases as $W_{\text{polymer}}/W_{\text{particle}}$ increases, where V_0 is a constant for a given particle size and the straight line shows V/V_0 is proportional to $(W_{\text{polymer}}/W_{\text{particle}})^{2.0+0.1}$. It is noted that W_{polymer} is proportional to the average number ($n_{\text{chain}} = N_{\text{chain}}/N_{\text{particle}}$) of the chains adsorbed on each particle because N_{chain} , the total number of the adsorbed chains, is proportional to W_{polymer} and N_{particle} , the total number of the particles, is a constant for a given particle concentration. Also note that the volume per adsorbed chain (v_{chain}) is proportional to V/n_{chain} . Since $V \propto n_{\text{chain}}^2$, then $v_{\text{chain}} \propto n_{\text{chain}}$. Further, we studied a complete different system; namely, the adsorption of the gelatin chains on three different sizes of β -carotin particles. It was striking to found the same result, i.e., $V/V_0 \propto (W_{\text{polymer}}/W_{\text{particle}})^{2.0+0.1}$ or $v_{\text{chain}} \propto n_{\text{chain}}$, also shown in

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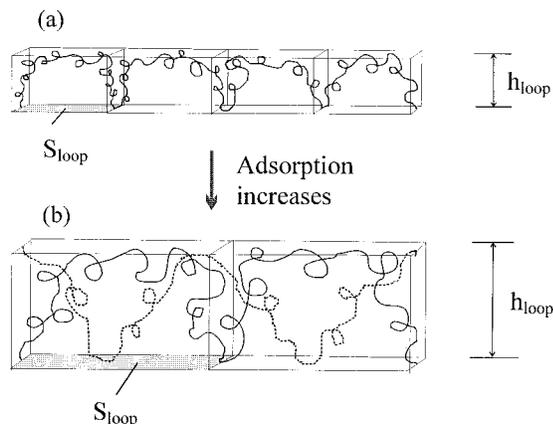


Figure 2. (a) Schematic of a polymer chain adsorbed on a given surface, where S_{loop} and h_{loop} respectively are the average surface area and height of each loop. (b) Schematic of how S_{loop} and h_{loop} change when the number of the chains adsorbed on the surface doubles.

Figure 1. The fact that two complete different systems displayed the same scaling between v_{chain} and n_{chain} tells us that there exists a common physics behind the adsorption of long linear polymer chains on a hydrophobic surface.

Qualitatively, for each adsorbing site (which could involve a small segment of the chain), 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 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. Experimentally, we tested the desorption by measuring the nanoparticles adsorbed with PNIPAM at 4 °C at which water is a very good solvent for PNIPAM. What we found is that the desorption is slow and the extent of the desorption is very low.

If more polymer 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 shown in Figure 2. This leads to the stretching of the “loop” and the increase of v_{chain} . Assuming that each chain on the surface forms n_{loop} loops, and on average, each loop has a hydrodynamic volume of v_{loop} , we have $v_{\text{chain}} \propto v_{\text{loop}} n_{\text{loop}}$. Further, it is reasonable to assume that the total number of the adsorbing sites available on each particle is a constant; i.e., $n_{\text{loop}} n_{\text{chain}}$ is a constant or $n_{\text{loop}} \propto n_{\text{chain}}^{-1}$. As shown in Figure 2, v_{loop} is proportional to its occupied surface (S_{loop}) and its extension from the surface (h_{loop}), i.e., $v_{\text{loop}} \propto S_{\text{loop}} h_{\text{loop}}$, where both S_{loop} and h_{loop} are proportional to n_{chain} so that $v_{\text{loop}} \propto n_{\text{polymer}}^2$. This very simple qualitative picture justifies $v_{\text{chain}} \propto n_{\text{chain}}$, the exact same scaling observed in our experiments. Note that the above qualitative discussion is independent of a particular polymer/particle system. Also note that we have assumed the chain conformation in the loop is independent of the loop size, which should be true when the loop size is sufficiently large.

This scaling leads to the following important conclusion. Considering that on a unit area (the x - y plane), the density profile ($\rho(z)$) of the adsorbed chains is a function of the distance (z) away from the surface, we have $\int_0^\infty \rho(z) dz = W_{\text{polymer}} \propto n_{\text{chain}}$. Assuming that $\rho(z)$ can be scaled by a characteristic length (ξ), we have $\xi \int_0^\infty \rho(z/\xi) d(z/\xi)$. The observed scaling, $v_{\text{chain}} \propto n_{\text{chain}}$, suggests that $\xi \propto n_{\text{chain}}$ and $\rho(z/\xi)$ is an invariant. On the other hand, Auroy et al.¹⁸ reported that for grafted polymer layers at the solid-liquid interface, the hydrodynamic volume of a chain grafted on the surface is proportional to the chain length. In comparison with the loops schematically shown in Figure 2, we can view each loop as two grafted chains with their free ends tied together. It has been known that a linear chain and a ring chain have the same scaling between the chain size and the molar mass; i.e., they have the same exponent.¹⁹ The scaling description of a flat polymer layer on the surface has been predicted by both Aubouy, et al.²⁰ and Joanny et al.²¹

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