

Grafting Density Induced Stretching and Collapse of Tethered Poly(ethylene oxide) Chains on a Thermally Sensitive Microgel

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Received March 5, 2001; Revised Manuscript Received June 5, 2001

ABSTRACT: Poly(ethylene oxide) (PEO) chains have been grafted onto a thermally sensitive poly(*N*-isopropylacrylamide) (PNIPAM) spherical microgel to form a novel quasi-planar polymer brush. The shrinking of the microgel at temperatures higher than 32 °C dramatically reduces its surface area, providing a convenient way to vary the grafting density. At the initial stage of the shrinking, we observed an expected steric repulsion-driven chain stretching, in which the hydrodynamic volume of the grafted PEO chains is incompressible, contrary to previously reported results. A further increase of the grafting density to $\sim 150 \text{ nm}^2$ per PEO chain led to an unexpected collapse of the stretched chains, which could be attributed to the long-predicted *n*-clustering attraction among densely packed brush chains. The stretching and collapse of the grafted chain in the heating-and-cooling cycle was fully reversible, and there was no hysteresis.

Introduction

Polymer brushes represent a special kind of chain conformation at the interface in which one end of the chain is grafted on surface. Recently, polymer brushes have attracted much attention due to their technological implications, such as the adsorption of polymers on the surface,¹ the alignment of diblock polymers at the interface of polymer blends or in Langmuir membranes,² and photocontrolled gating.³ The steric repulsion between densely grafted polymer chains forces them to adopt an extended conformation to avoid chain overlapping. In principle, polymer brushes can be formed via selective physisorption or covalent binding. The physisorption is normally less stable and results in a lower grafting density. In comparison, the covalent binding is stronger and can be achieved by either grafting from or grafting onto a surface.

To graft narrowly distributed polymer chains from a surface, the surface should be treated that it can initiate anionic,⁴ cationic,⁵ or living free radical polymerization.⁶ Despite numerous attempts, the success of grafting from a surface using living polymerization is still limited because it is rather difficult to uniformly modify a surface with initiators, especially in an aqueous system. Moreover, the number of resultant chains is much less than that expected on the basis of the number of initiators.⁵ On the other hand, such grafting requires that each chain has to be prepared with one functionalized anchoring end. This approach normally leads to an even lower grafting density because of the steric hindrance between the chain grafted on surface and the chain free in solution. Up to now, the preparation of densely grafted polymer brushes is still a challenge, and it has certainly hindered the experimental study of polymer brushes.

On the other hand, the experimental difficulties have not slowed down the development of theory in the study of polymer brushes. The theoretical studies have mainly focused on two following aspects: the chain segment

distribution⁷ and the local domains.⁸ The analytical derivation,⁷ the self-consistent-field calculation,⁹ and molecular dynamic simulations¹⁰ have shown that the chain density profile is parabolic rather than a “steplike” one predicted earlier.¹¹ Auroy and co-workers^{12,13} investigated the chain length and density dependence of polymer brush thickness (height). The study of local domains of polymer brushes mainly focuses on the pattern formation on surface or between two approaching polymer brushes.^{14,15}

To prepare dense polymer brushes, instead of a traditional way of grafting more polymer chains on a given surface, we have recently adopted an opposite approach, namely, reducing the area of a surface on which a fixed number of polymer chains are grafted. In this novel approach, linear poly(ethylene oxide) (PEO) chains were grafted on a spherical poly(*N*-isopropylacrylamide) (PNIPAM) microgel. PNIPAM is thermally sensitive. It dissolves in water at room temperature but becomes insoluble when the temperature is higher than 32 °C.¹⁶ Therefore, the microgel made of PNIPAM shrinks as the temperature increases and so does its surface area. Using this novel kind of polymer brushes, we were able to change the grafting density by a simple temperature variation.

Experimental Section

Sample Preparation. *N*-Isopropylacrylamide (NIPAM) was recrystallized three times in the mixture of *n*-hexane and benzene. Narrowly distributed monohydroxyl ($M_w = 5000$, 42 000) or styrene-terminated poly(ethylene oxide) ($M_w = 14\ 500$) purchased from Polymer Source, Inc., were used as received. Potassium persulfate (KPS) was recrystallized in water. Three polymer brushes with different chain lengths were prepared. Hereafter, they are denoted as PB5000, PB14500, and PB42000, respectively. The details are as follows.

To prepare PB5000, PEO macromonomers were first converted to acrylic terminated chains. PEO macromonomers were dissolved in anhydrous tetrahydrofuran. Excess amount of acryloyl chloride was added dropwise to convert the chain end to an acrylic terminated one. Triethylamine was added to remove HCl produced. The resultant salt was removed by

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filtration. The macromonomers were recovered by pouring the reaction mixture into acetone. Further purification of the macromonomers was achieved by three-cycle precipitation in the chloroform/ether mixture. Spherical PNIPAM microgels grafted with the macromonomers were prepared in water by dispersion polymerization, and their size distribution was narrow.¹⁷

Into a 100 mL three-neck flask equipped with a reflux condenser, a thermometer, and a nitrogen-bubbling tube were added 0.3 g of PEO macromonomer, 0.5 g of NIPAM, 0.007 g of *N,N*-methylenebis(acrylamide) (BIS), and 50 mL of deionized water. The solution was magnetically stirred and bubbled with nitrogen for half an hour to remove oxygen before adding 0.03 g of KPS dissolved in 5 mL of deionized water to initiate the polymerization. The final concentration of the dispersion was determined by gravimetry. ¹H NMR showed that the weight fraction of PEO was ~7% for PB5000. On average, each microgel was grafted with 370 PEO chains, and the grafting density was 320 nm² per PEO chain at 25 °C. PB14500 was prepared by the same method except that the styrene-terminated PEO (*M_w* = 14 500) was directly used.

PB42000 was prepared by a different method. Monohydroxyl PEO (*M_w* = 42 000) was used to initiate the polymerization of NIPAM in water with Ce(IV) as oxidant.¹⁸ Into a 100 mL double-neck flask equipped with a reflux condenser, a thermometer, and a nitrogen-bubbling tube were added 0.3 g of the PEO macromonomer, 0.44 g of NIPAM, 0.008 g of BIS, and 50 mL of deionized water. The solution was magnetically stirred and bubbled with nitrogen for half an hour to remove oxygen before adding 0.2 mL of Ce(NH₄)₂(NO₃)₆ solution (0.1 M) to initiate the polymerization. It is rather difficult to remove all unreacted PEO chains and un-cross-linked diblock PEO–PNIPAM chains. However, the remaining trace amount of them has no interference with the laser light-scattering study because they scatter much less than the microgels. In other words, we do not “see” them in the light scattering.

Laser Light Scattering. A modified commercial light scattering spectrometer (ALV/SP-125) equipped with an ALV-5000 multitau digital time correlator was used. In static LLS, we were able to obtain both the weight-average molar mass (*M_w*) and the *z*-average root-mean-square radius of gyration ($\langle R_g^2 \rangle_z^{1/2}$ (or written as $\langle R_g \rangle$) of the scattering objects in an extremely dilute solution from the scattering vector *q* (angular) dependence of the excess absolute scattering intensity, known as the Rayleigh ratio *R_v*(*q*). In dynamic LLS, the cumulant analysis of the measured intensity–intensity time correlation function $G^{(2)}(t)$ of narrowly distributed scattering objects is sufficient for an accurate determination of the average line width $\langle \Gamma \rangle$. For a diffusive relaxation, $\langle \Gamma \rangle$ can be related to the average translational diffusive coefficient ($\langle D \rangle$) by $\langle D \rangle = \langle \Gamma \rangle / q^2$ (*q* → 0, *c* → 0) and further to the average hydrodynamic radius ($\langle R_h \rangle$) by $\langle R_h \rangle = k_B T / (6\pi\eta\langle D \rangle)$ where *k_B*, η , and *T* are the Boltzmann constant, the solvent viscosity, and the absolute temperature, respectively. The details of the LLS instrumentation and theory can be found elsewhere.^{19,20}

Results and Discussion

Figure 1 shows that in the heating-and-cooling cycle the shrinking-and-swelling of the microgels grafted with the PEO chains is completely reversible. It indicates that there was no hysteresis in the process. This is apparently inconsistent with a previous prediction for the grafted PEO chains²¹ and also different from the hysteresis observed in the same process of a single ultralong PNIPAM chain in water.²² In the case of a single PNIPAM chain, the hysteresis was attributed to the intrachain hydrogen bonding formed in the collapsed state. In this study, such an intrachain association of PEO is unlikely existed. On the other hand, the collapse of a long chain has a much higher entropy penalty than the shrinking of a microgel. The fact that no hysteresis was observed for the grafted PEO chains can also be attributed to the short chain length.

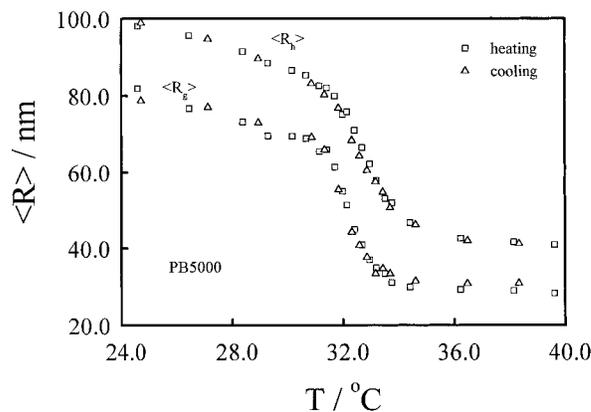


Figure 1. Typical temperature dependence of average hydrodynamic radius of PNIPAM microgels grafted with linear PEO chains in the heating-and-cooling cycle, where the dispersion concentration is $\sim 1.0 \times 10^{-5}$ g/mL.

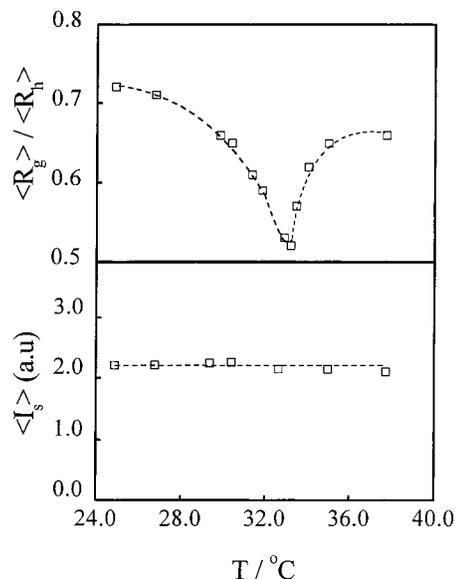


Figure 2. Typical temperature dependence of the ratio of average radius of gyration to average hydrodynamic radius ($\langle R_g \rangle / \langle R_h \rangle$) and the average scattering density ($\langle I_s \rangle$) of PNIPAM microgels grafted with linear PEO chains.

Figure 2 shows a typical change of $\langle R_g \rangle / \langle R_h \rangle$ with increasing dispersion temperature. As the temperature increases, the PNIPAM core shrinks and the grafting density increases. As expected, due to the steric repulsion, the grafted PEO chains stretch, i.e., the thickness of the PEO shell (h_{brush}) increases, as the grafting density increases. In this way, the PNIPAM core becomes denser, but the PEO shell swells. Note that the core has ~90% of mass so that the shrinking of the core has a more profound effect on $\langle R_g \rangle$, while the stretching of the grafted PEO chains in the shell slows down the decrease of $\langle R_h \rangle$, according to their own definitions. This explains the decreases of $\langle R_g \rangle / \langle R_h \rangle$ in the temperature range 23–33 °C. To our surprise, $\langle R_g \rangle / \langle R_h \rangle$ starts to increase when the temperature is higher than ~33 °C and approaches 0.71 at ~40 °C. As shown in Figure 1, when $T > \sim 37$ °C, the decrease of $\langle R_g \rangle$ nearly stops, but $\langle R_h \rangle$ still decreases. Therefore, the increase of $\langle R_g \rangle / \langle R_h \rangle$ could be attributed to the collapse of the PEO shell. This can be effectively and better viewed from the change of the PEO shell thickness.

Figure 3 shows the grafting density dependence of the average thickness of the PEO shell ($\langle h \rangle_{\text{brush}}$), i.e., the

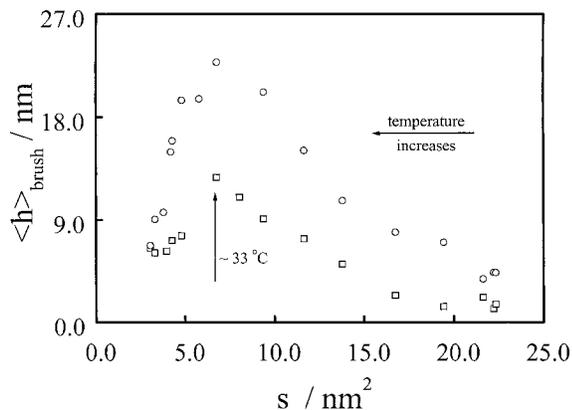


Figure 3. Dependence of the average PEO brush height ($\langle h \rangle_{\text{brush}}$) on the surface area per grafted chain (s), where $\langle h \rangle_{\text{brush}}$ was calculated by two different methods. The squares represent $\langle h \rangle_{\text{brush}}$ from the difference between the average radii of the PNIPAM microgels with and without the grafted PEO chains and the circles from the ratio of $\langle R_g \rangle / \langle R_h \rangle$ (see text for details).

average height of the grafted PEO chains, where $\langle h \rangle_{\text{brush}}$ was obtained by two completely different methods. One is from the difference between the average radii of the microgels with and without the grafted PEO chains, i.e., $\langle h \rangle_{\text{brush}} = \langle R_h \rangle_{\text{microgel+PEO}} - \langle R_h \rangle_{\text{microgel}}$. The other is indirectly from $\langle R_g \rangle / \langle R_h \rangle$, which involves a combination of static and dynamic LLS results. The principle of the second method is outlined as follows. The microgel grafted with the PEO chains can be considered as a core-shell nanostructure, in which the masses of the core (M_c) and the shell (M_s) are

$$M_c = \frac{4}{3}\pi\rho_c R_c^3 \quad \text{and} \quad M_s = \frac{4}{3}\pi\rho_s (R^3 - R_c^3) \quad (1)$$

where R_c and R are the radii of the core and the microgel grafted with PEO; ρ_c and ρ_s are the densities of the core and the shell, respectively. Note that for the first approximation we have assumed that both the shell and the core are uniform. This assumption will not affect our discussion. Also, note that we have assumed that there is no mixing of the grafted PEO layer and the PNIPAM core. At higher temperatures, PNIPAM becomes hydrophobic so that there should be no mixing of the core and the shell. Even at lower temperatures, it would be more favorable for the PEO chains to stay on the periphery than to penetrate inside the PNIPAM gel network. Substituting eq 1 into the definition of R_g , we have

$$R_g^2 = \frac{\int_V \rho(r) r^2 dv}{\int_V \rho(r) dv} = \frac{\int_0^{R_c} 4\pi\rho_c r^4 dr + \int_{R_c}^R 4\pi\rho_s r^4 dr}{\int_0^{R_c} 4\pi\rho_c r^2 dr + \int_{R_c}^R 4\pi\rho_s r^2 dr} = \frac{3[M_c R_c^2 R^3 - (M_c + M_s) R_c^5 + M_s R^5]}{5(M_c + M_s)(R^3 - R_c^3)} \quad (2)$$

Letting the mass ratio $M_c/M_s = A$ and the radius ratio $R_c/R = x$, we can rewrite eq 2 as

$$R_g^2 = \frac{3R^2[Ax^2 - (1+A)x^5 + 1]}{5(1+A)(1-x^3)} \quad (3)$$

Replacing R with R_h , we have

$$\frac{R_g}{R_h} = \left\{ \frac{3[Ax^2 - (1+A)x^5 + 1]}{5(1+A)(1-x^3)} \right\}^{1/2} \quad (4)$$

where A is a constant for a given PNIPAM microgel grafted with a fixed number of PEO chains. From each experimental value of R_g/R_h , we can numerically find a corresponding x , and then, $\langle h \rangle_{\text{brush}}$ from $R - R_c$.

Figure 3 shows that, before the temperature reaches the lower critical solution temperature (LCST, $\sim 33^\circ\text{C}$), $\langle h \rangle_{\text{brush}}$ increases with decreasing surface area per PEO chain (s) (i.e., increasing the temperature); even $\langle h \rangle_{\text{brush}}$ obtained from two different methods do not quantitatively agree with each other due to experimental uncertainties. Such stretching of the grafted PEO chains is expected because the grafted PEO chains are forced to approach each other as s decreases. It should be stated that the shell thickness is much smaller than the average radius of the microgels (~ 100 nm) so that the grafted PEO chains can be treated as a quasi-planar brush even the microgel surface is curved. On the other hand, the PEO shell at 23°C is slightly thicker than the hydrodynamic diameter (~ 4 nm) of the PEO macromonomers in water,²³ indicating that the grafted chains are slightly elongated even at room temperature. One of possible explanations of the unexpected collapse of the PEO chains in the temperature range of $T > \sim 33^\circ\text{C}$ might be related to the formation of an equilibrium between one dilute phase and one dense phase made of collapsed chains.^{24,25}

In general, the hydration has been attributed to the dissolution of PEO in water.²⁶ It has been shown that the interchain interaction among individual PEO chains is so strong that it is rather difficult to dissolve bulk PEO into a true molecular solution in pure water.^{27,28} Nevertheless, water is peculiar due to its structured conformation and could be viewed as a polymeric solvent.²⁹ A theoretical study of PEO in aqueous solution showed that the pressure could also induced the collapse of the PEO chains.³⁰ At this moment, we still do not have a confirmed explanation of Figure 3. However, it is known that polymer chains in bulk adopt a random coil conformation. It is our opinion that as the grafting density increases, the grafted chains are pushed together, the hydration is gradually destroyed, and most of water molecules are gradually excluded. Therefore, as the grafted layer approaches the bulk state, the stretched PEO chains have to collapse at some point. It is similar to the report that, in a bad or polymeric solvent, polymer brushes would gradually collapse as more solvent molecules leave the grafted layer and the configurational entropy of solvent becomes more important.³¹

Figure 4 shows that during the stretching, i.e., before reaching $\sim 33^\circ\text{C}$, the brush height ($\langle h \rangle_{\text{brush}}$) can be scaled to the grafting density (σ) as $\langle h \rangle_{\text{brush}} \propto N\sigma^{1.0 \pm 0.2}$, where N is the degree of polymerization. The past theoretic studies and experimental results showed $\langle h \rangle_{\text{brush}} \propto N\sigma^\beta$ with $\beta = 1/3$ for polymer brush in a good solvent.^{7,12} Note that $\sigma^{-1} = s$, which is the average surface area occupied per grafted chain and $\langle h \rangle_{\text{brush}}\sigma^{-1}$ represents the average hydrodynamic volume per grafted PEO chain. Therefore, the scaling of $\langle h \rangle_{\text{brush}} \propto \sigma^{1.0 \pm 0.2}$ suggests that the average hydrodynamic volume per grafted PEO chain is close to a constant, or in other words, the average hydrodynamic volume per grafted PEO chain is incompressible during the chain stretching. Further studies of other types of grafted polymer chains are needed to differentiate whether this incompressibility is only

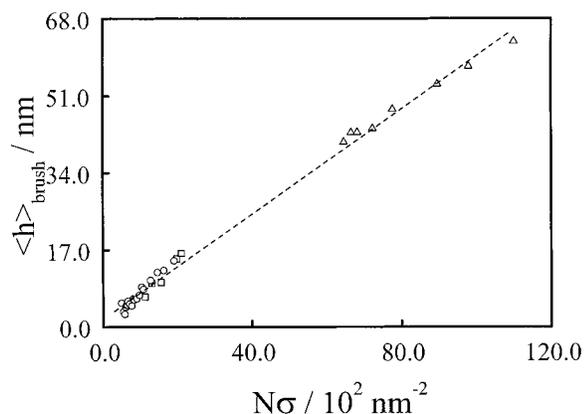


Figure 4. Grafting density (σ) dependence of average PEO brush height ($\langle h \rangle_{\text{brush}}$) during the chain stretching. The line represents a least-squares fitting of $\langle h \rangle_{\text{brush}} \propto N\sigma^{1.0 \pm 0.2}$, where N is the degree of polymerization of the grafted chain.

related to PEO or, in general, to high grafting chain density.

Conclusion

Using a newly developed novel kind of polymer brushes, i.e., grafting linear PEO chains onto a thermally sensitive poly(*N*-isopropylacrylamide) (PNIPAM) microgel, we were able to continuously change the grafting density by a simple temperature variation. Our results showed that as the grafting density increased, the steric repulsion among the grafted chains forced them to stretch. However, the average hydrodynamic volume per grafted PEO chain remained a constant, different from previously reported results. Our results also showed that a further increase of the grafting density could lead to an unexpected collapse of the grafted PEO chains. Such a collapse may be explained by a long predicted n -clustering attraction even though the exact origin of the collapse is still not clear at this moment. However, the results are inspiring. Further studies are undergoing.

Acknowledgment. The financial support of the CAS Bai Ren Project, the NNSFC projector (29974027), and the HKSAR Earmarked RGC Grants (CUHK/4266/00P, 2160135) is gratefully acknowledged.

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MA010391H