The Coil-to-Globule-to-Brush Transition of Linear Thermally Sensitive Poly(*N*-isopropylacrylamide) Chains Grafted on a Spherical Microgel

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By using free-radical RAFT living polymerization, we successfully grafted linear poly(*N*-isopropylacrylamide) (PNIPAM) chains onto a spherical PNIPAM/HEA copolymer microgel to form a novel core−shell nanostructure. Both the tethered PNIPAM shell and the copolymer microgel core shrunk as the temperature increased, but in different temperature ranges. In the range ∼28−32 °C, the tethered PNIPAM chains underwent a coil-to-globule transition, while in the range ∼32−35 °C, the shrinking of the copolymer core induced a re-stretching of the collapsed PNIAPM chains on its surface to form a polymer brush in poor solvent. Our results showed that in the re-stretching process, the average hydrodynamic volume per tethered PNIPAM chain remained a constant, confirming a prediction made a long time ago that the collapsed chains in poor solvent were incompressible.

Introduction

The conformation of tethered polymer chains on the surface has attracted much attention in recent years due to its scientific importance[1−4] and its influence on surface properties and colloidal stability.[5,6] One could use the physisorption[3] or chemical bonding[7] to graft polymer chains onto a surface. In general, the chemical bonding has some advantages over the physisorption because such tethered polymer chains have a more explicit and stable structure.[8] The covalent binding of polymer chains to a surface can be realized by either a grafting-from or a grafting-to method. In the grafting-to approach, the chains with one functionalized end are tethered to a reactive surface. This approach is limited by the steric hindrance between grafted and adventitious chains so that the grafting efficiency of long adventitious chains is normally low. In the grafting-from approach, one could graft relatively narrowly distributed chains from a surface which was pretreated so that it could initiate anionic,[9] cationic,[10] or living free radical polymerization.[11] In spite of the fact that the grafting-from approach promises the tethered chains with a controllable and narrowly distributed chain length, the experimental success has so far been limited. This is because it is difficult to uniformly modify a surface, especially in an aqueous system, and also because the resultant grafting density was much lower than the initiator density on the surface.[10]

Recently, we tethered poly(ethylene oxide) (PEO) chains on the surface of a thermally sensitive poly(*N*-isopropylacrylamide) (PNIPAM) microgel.[12] In this way, we were able to increase the grafting density by reducing the surface area via a simple temperature variation, instead of grafting more chains on a surface. Note that PNIPAM has been studied for a long time. It has a lower critical solution temperature (LCST) of ∼32 °C.[13] The phase transitions of individual linear isolated PNIPAM chains and PNIPAM related gels have been extensively investigated in the last two decades.[14−20] There were also a few reports on the phase transition of linear PNIPAM chains constrained on the surface.[21,22] It was found that the thickness of the tethered PNIPAM layer showed a hysteresis in the heating-and-cooling cycle. Different assumptions were offered to explain the nature of such a hysteresis. One of them was the knotting of the tethered chains during the shrinking of the tethered chains. Note that the past studies used hydrophobic polystyrene latex particles as substrate, which certainly complicated the problem because it has recently been found that PNIPAM could adsorb on a hydrophobic surface at higher temperatures.[20] Such adsorption could lead to the formation of small chain loops on the surface, which was not removable when the dispersion was cooled to room temperature.[20] In our opinion, it is this adsorption that caused the hysteresis. To avoid such adsorption, we should try to graft the PNIPAM chains on a hydrophilic surface.

In the present study, our original objective was to study the conformation of the tethered PNIPAM chains on a hydrophilic surface to clarify different explanations offered to the hysteresis. We designed and prepared thermally sensitive spherical microgels by a dispersion copolymerization of *N*-isopropylacrylamide and acrylic acid 2-hydroxyethyl ester (HEA). The copolymerization of a few percent of hydrophilic HEA not only shifted its shrinking temperature from ∼32 °C to ∼35 °C, but also enabled us to modify its surface so that narrowly distributed PNIPAM chains could be grafted onto it to form a core−shell nanostructure by the reversible-addition−fragmentation−chain-transfer (RAFT) polymerization. With this core−shell nanostructure, we were able to study the coil-to-globule transition of linear PNIPAM chains tethered on a hydrophilic surface in

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the temperature range 25−32 °C. During the study, we accidentally found that the collapsed chains could re-stretch to form a polymer brush in poor solvent in the temperature range 32−35 °C when they were compressed.

Experimental Section

Materials. *N*-Isopropylacrylamide (NIPAM, courtesy of Kohjin Co., Ltd., Japan) was purified by recrystallization in a benzene/*n*-hexane mixture. Acrylic acid 2-hydroxyethyl ester (HEA, from TCI, Japan) was distilled under reduced pressure to remove inhibitant, hydroquinone monomethyl ether. Cross-linking agent, *N*,*N*′-methylenebisacrylamide (BIS, from Aldrich, USA), was purified by recrystallization in methanol. Azobis-isobutylnitride (AIBN, from Aldrich, USA), was purified by recrystallization in ethanol. Initiator, potassium persulfate (KPS, from Aldrich, USA), was purified by recrystallization in water.

Microgel Preparation. Narrowly distributed spherical surface-modified PNIPAM/HEA microgel was prepared in water by dispersion polymerization.[17] Into a 250 mL three-neck flask equipped with a reflux condenser, a thermometer and a nitrogen-bubbling tube were added 1.92 g of NIPAM monomer, 0.076 g of HEA, 0.058 g of BIS, 0.083 g of SDS, and 93 mL of deionized water. The solution was stirred and bubbled with nitrogen for half an hour to remove oxygen before adding 0.06 g of KPS dissolved in 7 mL of deionized water to initiate the copolymerization. The reaction was conducted at 70 °C for ∼12 h. The resultant dispersion was extensively dialyzed to remove surfactant SDS and residual monomers. At 70 °C, PNIPAM became hydrophobic and collapsed so that hydrophilic HEA was presumably located on the periphery of the resultant copolymer microgels.[23] The purified dispersion was freeze-dried. Such obtained microgels are denoted as MG-core hereafter.

Grafting of Linear PNIPAM Chains. The initiator was first introduced on the surface of the MG-core. A 1.00 g sample of the MG-core and 0.50 g of α-butyl acid dithiobenzoate were dispersed in 3 mL of THF. Into this mixture was added 1 mL of dicyclohexycarbodiimide (1.00 g) THF solution to catalyze the reaction. The mixture was stirred for 24 h at room temperature and the resultant dicyclohexylurea was removed by filtration. The initiator-immobilized MG-cores were harvested by precipitation in anhydrous diethyl ether and dried at 30 °C under vacuum. The grafting polymerization was carried by RAFT polymerization.[24,25] An amount of 3 mL of THF dispersion containing 0.30 g of NIPAM, 0.50 g of the initiator-immobilized MG-cores and a tiny amount of AIBN was charged into a 5-mL reaction tube. After three cycles of freezing−thawing−evacuating, the tube was sealed under nitrogen and was incubated at 70 °C for 24 h. The resultant dispersion was poured into a large amount of diethyl ether and the precipitate was collected and dried at room temperature under vacuum. The disappearance of the characteristic peak at $\delta = 4.6$ of the initiator and the increase of the relative intensity of the peak at $\delta = 4.0$ of NIPAM in the ^{1}H NMR spectrum confirmed the grafting. The linear PNIPAM chains grafted MG-core will be denoted as PNIPAM-*g*-MG hereafter.

Laser Light Scattering. A commercial light scattering spectrometer (ALV/SP-125) equipped with an ALV-5000 multi-τ digital time correlator and a solid-state laser (Coherent, DPSS 532, output power ∼400 mw) was used. In static LLS, we were able to obtain both the weight-average molar mass (M_w) and the *z*-average radius of gyration $\langle R_g^2\rangle_z^{1/2}$ (or written as $\langle R_g\rangle$) of scattering objects in an extremely dilute solution

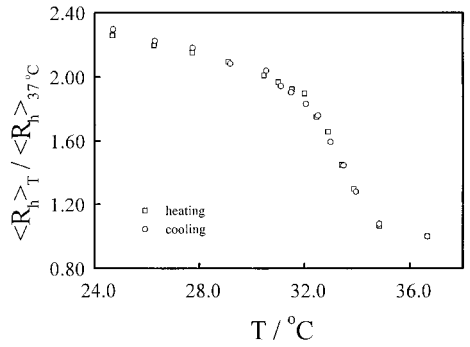

Figure 1. Temperature dependence of relative swelling ($\langle R_h\rangle_T/\langle R_h\rangle_{37°C}$) of spherical PNIPAM/HEA copolymer microgels in water before the grafting of linear PNIPAM chains on their surfaces, where $\langle R_h\rangle_{37°C} =$ 40.7 nm.

because the excess absolute scattering intensity, known as the Rayleigh ratio $R_{vv}(q)$, is dependent on the scattering vector q as

$$\frac{KC}{R_{vv}(q)} \approx \frac{1}{M_w}\left(1 + \frac{1}{3}\langle R_g\rangle^2 q^2\right) \qquad (1)$$

where $K = 4\pi n^2(dn/dC)^2/(N_A\lambda_0^4)$ and $q = (4\pi n/\lambda_0)\sin(\theta/2)$ with n, dn/dC, N_A, λ_0, and θ being the solvent refractive index, the specific refractive index increment, the Avogadro's number, the wavelength of the incident light in a vacuum, and the scattering angle, respectively. In dynamic LLS, the cumulant analysis of the measured intensity−intensity time correlation function $G^{(2)}(t)$ of narrowly dispersed 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 further related to the average translational diffusive coefficient $\langle D\rangle$ by $(\langle\Gamma\rangle/q^2)_{q\to 0,C\to 0}$ and the average hydrodynamic radius $\langle R_h\rangle$ by $k_BT/(6\pi\eta\langle D\rangle)$ with k_B, η, and T being the Boltzmann constant, the solvent viscosity, and the absolute temperature, respectively. The details of the LLS instrumentation and the theory can be found elsewhere.[26,27]

Results and Discussion

Figure 1 shows the temperature dependence of the relative swelling $\langle R_h\rangle_T/\langle R_h\rangle_{37}$ °C of the MG-cores before the grafting. As expected, the shrinking and swelling in the heating-and-cooling cycle are fully reversible without any hysteresis. It is worth noting that $\langle R_h\rangle_{37}$ °C = 40.7 nm and the relative width of the microgels was narrower than 0.05. In comparison with similar microgels made of pure PNIPAM, the volume change of these MG-cores is smoother and the temperature at which the microgels fully collapsed is shifted to ∼36 °C, higher than ∼32 °C for pure PNIPAM microgels. This is consistent with previous studies because the copolymerization of hydrophilic HEA with PNIPAM makes the microgel more hydrophilic, so that the collapsing temperature increases.[13] Note that in the range 25−32 °C, the MG-cores shrink only ∼20%.

Figure 2 shows the temperature dependence of the average hydrodynamic radius $\langle R_h\rangle$ of the PNIPAM-*g*-MG in the heating-and-cooling cycle. It is worth stating that each data point was obtained after the dispersion reached the temperature equilibrium. It has been known that both the shrinking and swelling of individual PNIPAM linear chains and spherical microgels is as fast as the temperature change.[28,29] The slight hysteresis near ∼32 °C in the cooling process was attributed to the formation of intrachain hydrogen bonding in the collapsed state.[21,30] At lower temperatures (<30 °C), water became such a good solvent that the hysteresis in $\langle R_h\rangle$ disappeared. Note that at ∼32 °C,

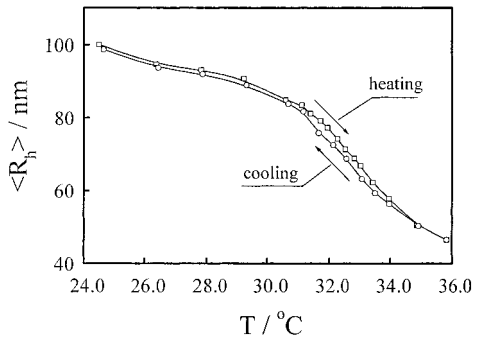

Figure 2. Temperature dependence of average hydrodynamic radius ($\langle R_h \rangle$) of spherical PNIPAM/HEA copolymer microgels in water after the grafting of a layer of linear PNIPAM chains.

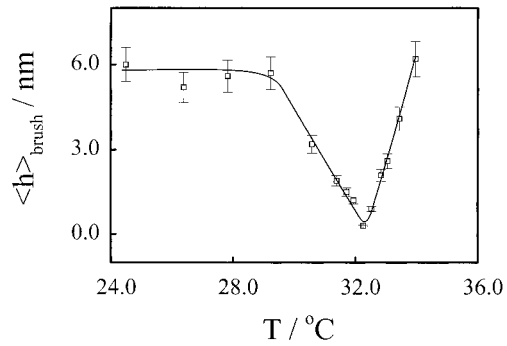

Figure 3. Temperature dependence of average layer thickness (i.e., the brush height, $\langle h \rangle_{brush}$) of grafted linear PNIPAM chains in water, where $\langle h \rangle_{brush}$ was calculated from the difference between the average hydrodynamic radii of the microgels after and before the grafting of linear PNIPAM chains.

the MG-core used was still hydrophilic, which makes this study different from previous ones.[22]

After being grafted with linear PNIPAM chains, the microgel has an even smoother temperature dependence of $\langle R_h \rangle$ than the MG-core. This is because when the temperature increases, there exists two processes, which affect $\langle R_h \rangle$ differently; namely, the shrinking of the MG-core reduces $\langle R_h \rangle$, but it increases the grafting chain density because the surface area decreases. The increase of the grafting density forces the tethered PNIPAM chains to stretch so that $\langle R_h \rangle$ increases. The compensation of these two opposite effects on $\langle R_h \rangle$ smoothes the change of $\langle R_h \rangle$. This can be better viewed in terms of the thickness change of the tethered PNIPAM layer, as shown in Figure 3, where $\langle h \rangle_{brush}$ was calculated from the size difference between the PNIPAM-*g*-MG and the MG-core.

Previously, we obtained the scaling law between M_w and R_h for PNIPAM in solution.[31] The molar mass of the tethered PNIPAM chains in water at 25 °C, estimated from $\langle h \rangle_{brush}$, was $\sim 1 \times 10^4$ g/mol. On the basis of eq 1, the increase of the scattering-intensity after the grafting led to the average mass of PNIPAM grafted on the MG-core. It was deduced that there were c.a. 6800 PNIPAM chains per MG-core if we assume that each immobilized initiator could lead to one grafted chain. This is certainly over-estimated. Considering the average mass of PNIPAM grafted on each core and the molar mass of individual chains, we estimated that on average, there were ~700 chains grafted on each core and that the average distance between two tethered PNIPAM chains on the surface was ~12 nm. It is helpful to note that for the tethered linear PNIPAM chains, there existed two opposite effects as the temperature increases. The tethered chains shrunk with increasing temperature, but at the same time, the shrinking of the MG-core increased the grafting density and forced the tethered PNIPAM chains to stretch to reduce the chain overlapping. These two opposite effects in the range 25−29 °C compensated with each other so that $\langle h \rangle_{brush}$ nearly remains a constant. Further increase of the temperature in the range 29−32 °C led to a sharp decrease of $\langle h \rangle_{brush}$, indicating that the collapse of the tethered chains becomes dominant because water is a poor solvent when the temperature is higher than ~30.6 °C.

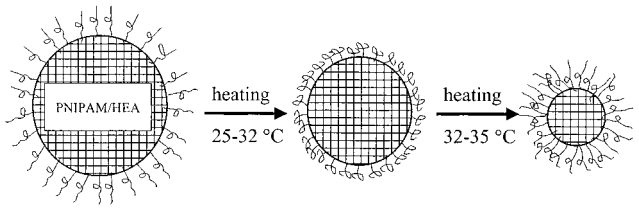

Figure 4. Schematic of the coil-to-globule-to-brush transition of linear PNIPAM chains grafted on a thermally sensitive microgel.

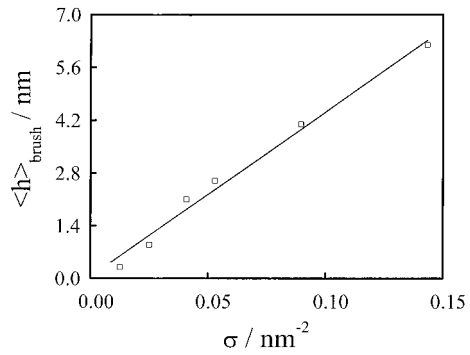

Figure 5. Grafting density (σ) dependence of average brush height ($\langle h \rangle_{brush}$) when water became a poor solvent for linear PNIPAM chains in the temperature range 32−36 °C, where the line represents a least-squares fitting of $\langle h \rangle_{brush} \approx 45\sigma$.

It is known that linear PNIPAM homopolymer chains already collapse at $T > 32$ °C. To our surprise, $\langle h \rangle_{brush}$ increased with the temperature in the range 32−36 °C. Figure 1 shows that in the range 32−36 °C, $\langle R_h \rangle$ decreased two times with increasing the temperature, i.e., the surface area reduced four times or the grafting chain density increased four times. Therefore, the increase of $\langle h \rangle_{brush}$ could be attributed to a strong steric repulsion among the chains grafted on the shrunken MG-core, which forced the tethered PNIPAM chains to stretch into a brush-like conformation on the surface. Note that in this temperature range, water is a very poor solvent for linear PNIPAM chains. To our knowledge, this is the first observation of a polymer brush formed in poor solvent because we have not been able to make such a dense polymer brush before. Figure 4 is a schematic of the coil-to-globule-to-brush transition of linear PNIPAM chains grafted on the surface of a thermally sensitive microgel.

Figure 5 indicates that the average height of such a formed polymer brush in poor solvent is proportional to the grafting density (σ). This is consistent with an existing predication of polymer brushes in poor solvent.[10] It is helpful to note that $1/\sigma$ is the average surface area occupied per grafted PNIPAM chain. Therefore, the ratio $\langle h \rangle_{brush}/\sigma$ represents the average hydrodynamic volume per grafted chain on the surface. The scaling of $\langle h \rangle_{brush} \propto \sigma$ in Figure 5 reveals that the average hydrodynamic volume per grafted PNIPAM chain remained a constant (~45 nm^3) during the chain stretching. This means that the grafted linear chains in poor solvent are incompressible. Otherwise, we would see the bending of the plot of $\langle h \rangle_{brush}$ versus σ as the

grafting density increases. The increase of the grafting density on the surface squeezed and elongated the collapsed chain into a brush-like structure.

Conclusion

Narrowly distributed linear poly(*N*-isopropylacrylamide) (PNIPAM) chains can be effectively grafted on spherical PNIPAM/HEA copolymer microgels via free-radical RAFT living polymerization, resulting in a novel core−shell nanostructure. Our results showed that such a structure had two different kinds of temperature-induced transitions in terms of the thickness of the grafted PNIPAM layer. In the low temperature range 25−32 °C, the layer thickness decreased, which was related to the coil-to-globule transition of linear grafted PNIPAM chains. While in the high temperature 32−35 °C, the layer thickness increases linearly with the grafting density due to the repulsion among the grafted chains on the surface, which was related to the globule-to-brush transition of the collapsed PNIPAM chains on the PNIPAM/HEA microgel. Using such a novel core−shell nanostructure, we were able to study, for the first time, the behavior of the grafted polymer chains in poor solvent. Our results revealed that the hydrodynamic volume per grafted chain remained a constant during the second transition in the high temperature range, i.e., the tethered chains were incompressible in poor solvent.

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