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

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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 ≈150 nm² 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, the alignment of diblock polymers at the interface of polymer blends or in Langmuir membranes, and photocontrolled gating. 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, cationic, or living free radical polymerization. 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. 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 distribution and the local domains. The analytical derivation, the self-consistent-field calculation, and molecular dynamic simulations have shown that the chain density profile is parabolic rather than a “steplike” one predicted earlier. Auroy and co-workers 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.

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. 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 (Mₙ = 5000, 42 000) or styrene-terminated poly(ethylene oxide) (Mₙ = 14 500) purchased from Polymer Source, Inc., were used as received. Potassium persulfate (KPS) was recrystal-

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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 were achieved by three-cycle precipitation in the reaction mixture into acetone. Further purification of the microgels 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-methylenediocrylamide (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 microgel. 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.

**Results and Discussion**

Figure 1 shows a typical change of average hydrodynamic radius (Rᵧ(Rₜ)) of PNIPAM microgels grafted with linear PEO chains. The average hydrodynamic radius (Rᵧ(Rₜ)) starts to increase when the temperature is higher than 37°C, the decrease of (Rᵧ(Rₜ)) nearly stops, but (Rᵧ(Rₜ)) still decreases. Therefore, the increase of (Rᵧ(Rₜ)) 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 2 shows a typical change of (Rᵧ(Rₜ)) 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 (hᵧbrush) 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 (Rᵧ(Rₜ)), while the stretching of the grafted PEO chains in the shell slows down the decrease of (Rᵧ(Rₜ)), according to their own definitions. This explains the decreases of (Rᵧ(Rₜ)) in the temperature range 23–33°C. To our surprise, (Rᵧ(Rₜ)) 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 > ~37°C, the decrease of (Rᵧ(Rₜ)) nearly stops, but (Rᵧ(Rₜ)) still decreases. Therefore, the increase of (Rᵧ(Rₜ)) 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 (hᵧbrush), i.e., the
average height of the grafted PEO chains, 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 \( \langle R_g \rangle / R_h \) (see text for details).

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 solvent.29 A theoretical study of PEO in aqueous solution showed that the pressure could also induce the collapse of the PEO chains.29 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 \( \sigma \) (as \( \langle h \rangle_{\text{brush}} \propto N^{0.10 \pm 0.02} \)), where \( N \) is the degree of polymerization. The past theoretical 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 \( \langle h \rangle_{\text{brush}} \propto N^{0.10 \pm 0.02} \) 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
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 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.

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