

Clustering Induced Collapse of a Polymer Brush

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Poly(ethylene oxide) (PEO) chains were grafted onto a spherical thermally sensitive poly(*N*-isopropylacrylamide) microgel with a low critical solution temperature of $\sim 32^\circ\text{C}$. The shrinking of the microgel at higher temperatures led to a dramatic decrease in its surface area, providing a convenient way to increase the grafting density of a polymer brush. As expected, we observed a repulsion-induced stretching of the PEO chains at the initial stage of the shrinking. However, as the grafting density increases, an unexpected collapse of the grafted PEO chains was observed, which can be attributed to a long predicted *n*-clustering attractive interaction among densely grafted polymer chains.

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Polymer chains can be grafted onto a surface to form a polymer brush. If the surface is planar, cylindrical, or spherical, the brush will be one, two, or three dimensional [1]. Polymer brushes are so useful that a number of theoretical models have been developed [1–6] and many experimental results have been reported [7–13]. Generally, the grafted polymer chains in a good solvent are swollen and have an extended conformation so that the brush is made of a single layer of polymer chains with an abrupt concentration drop at the outer end.

In 1993, a different scheme was also proposed for some special cases, particularly for water-soluble polymers, in which two monomers repel each other, but *n* monomers can form a certain form of “cluster” [6]. According to this scheme, there could exist two additional regimes besides the swollen state: in one regime (α), two dense phases coexist; and in another regime (β), one dense phase is in equilibrium with a dilute phase. For a given grafting density, varying temperature can, in principle, induce the transitions from the swollen state to the α regime and from the α regime to the β regime. Experimentally, the temperature range for water-soluble polymers is limited in the range $0\text{--}100^\circ\text{C}$. On the other hand, at a proper temperature, increasing the grafting density can also induce the transitions. However, it is difficult, if not impossible, to continuously vary the grafting density in practice. To our knowledge, the predicted *n*-clustering induced collapse of a polymer brush as the grafting density increases has not been observed yet.

In this study, on the basis of our previous studies of poly(*N*-isopropylacrylamide) chains (PNIPAM) [14–17], we prepared narrowly distributed spherical PNIPAM microgels grafted with linear poly(ethylene oxide) (PEO) chains. As a thermally sensitive polymer, PNIPAM is soluble only in water at lower temperatures with a lower critical solution temperature of $\sim 32^\circ\text{C}$ [18]. In the temperature range $25\text{--}35^\circ\text{C}$, the microgel can shrink ~ 3 times in its diameter; i.e., its surface area can decrease

~ 10 times, providing a convenient way to continuously increase the grafting density because the average number of the PEO chains grafted on each microgel is fixed, which is schematically shown in Fig. 1. Our previous results showed that there was no change in the spherical shape of the microgels. A control experiment, a mixture of spherical PNIPAM microgels without the grafted PEO shell and linear PEO chains free in water, reveal that there was no observable adsorption between the PEO chains and the PNIPAM microgels in both the swollen and collapsed states.

The microgels were prepared by dispersion polymerization in aqueous solution at 70°C . Into a 150 mL volume flask, a proper amount of water, 0.45 g NIPAM monomer, 0.3 g PEO macromonomer ($M_w = 5000$ g/mol), and 7 mg cross-linking agent, *N,N'*-methylene-bis(acrylamide) were added. The total volume of the reaction mixture was 50 mL. After a 30-min nitrogen purge, 0.03 g sodium persulphate aqueous solution was added to initiate the polymerization. The preparation of the PEO macromonomer can be found elsewhere [19]. The resultant microgels were successively purified by ultracentrifugation at 40°C to remove all remaining small

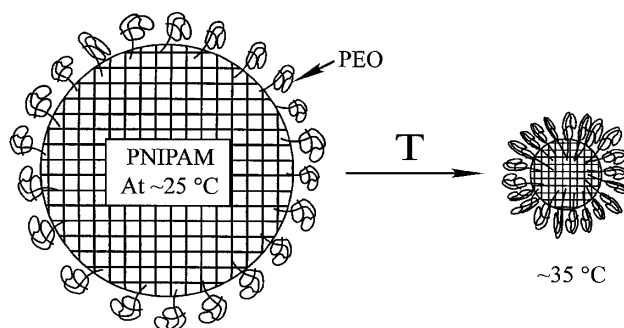


FIG. 1. Schematic of a spherical PNIPAM microgel grafted with linear PEO chains. The shrinkage of the PNIPAM microgel leads to a continuous increase of the grafting density.

molecules. The average grafting density was determined by nuclear magnet resonance (Bruker DPX300, 300 MHz spectrometer). On average, each microgel was grafted with 370 PEO chains. At 25 and 35 °C, each PEO chain occupies 320 and 48 nm², respectively. The temperature dependence of the microgels was studied by a combination of static and dynamic laser light scattering (LLS).

In static LLS [20], we were able to obtain both the weight-average molar mass (M_w) and the z -average root-mean-square radius of gyration ($\langle R_g^2 \rangle^{1/2}$ or written as $\langle R_g \rangle$) of the microgels in an extremely dilute dispersion ($\sim 1 \mu\text{g/mL}$) from the angular dependence of the excess absolute scattering intensity, known as Rayleigh ratio $R_{vv}(q)$, where q is the scattering vector. In dynamic LLS [21], the cumulant analysis of the measured intensity-intensity time correlation function $G^2(t)$ of nearly monodisperse microgels led to an accurate determination of the average linewidth $\langle \Gamma \rangle$. For a pure diffusive relaxation, Γ is related to the diffusion coefficient D and the hydrodynamic radius R_h by $D = (\Gamma/q^2)_{q \rightarrow 0, C \rightarrow 0}$ and $R_h = k_B T / (6\pi\eta D)$ with k_B , η , and T being the Boltzmann constant, solvent viscosity, and the absolute temperature, respectively. In LLS, we measure an average of $\sim 10^9$ microgels simultaneously so that a statistical difference from one microgel to another microgel or a statistical uneven distribution of the grafted chains should have no effect on our measured average results. The LLS instrumentation has been detailed before [14]. It should be stated that our LLS spectrometer has an exceptional small angle range down to 6°, which is vitally important for the study of large swollen microgels because a precise determination of M_w , $\langle R_g \rangle$, and $\langle R_h \rangle$ requires a condition of $q\langle R_g \rangle \ll 1$. The dispersion was so dilute that the extrapolation of $C \rightarrow 0$ was not necessary.

Figure 2 shows that the shrinking and swelling of the microgels in the heating and cooling cycle are completely reversible, where each data point was obtained long after the dispersion reached its temperature equilibrium. The inset shows that the weight average molar mass (M_w) of the microgels is independent of the temperature, indicating that there was no aggregation or degradation of the microgel in the heating and cooling cycles. Note that even in its fully collapsed state, the microgel is still much larger than the PEO chains ($\sim 3\text{--}4$ nm). Therefore, the PEO chains were grafted on a quasiplanar surface; i.e., we can consider the PEO brush to be one dimensional. Also note that due to a small difference between PEO and PNIPAM, $\langle R_g \rangle$ showed in Fig. 2 is apparent. However, the PNIPAM microgel weighs much more than the grafted PEO chains so that the error should be very small. It should be addressed that in the temperature range studied, water is a good solvent for PEO.

It is well known that the ratio $\langle R_g \rangle / \langle R_h \rangle$ reflects the conformation of a polymer chain or the density distribution of a particle. For a coiled chain in a good solvent, $\langle R_g \rangle / \langle R_h \rangle = \sim 1.5$ and for a uniform nondraining sphere,

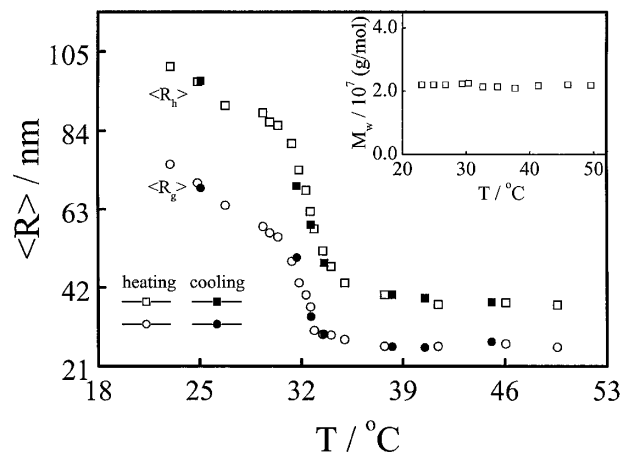


FIG. 2. Temperature dependence of average radius of gyration ($\langle R_g \rangle$) and average hydrodynamic radius ($\langle R_h \rangle$) of spherical PNIPAM microgels grafted with linear PEO chains. The inset shows a corresponding temperature dependence of the weight-average molar mass (M_w) of the PNIPAM microgels grafted with linear PEO chains.

$\langle R_g \rangle / \langle R_h \rangle = \sim 0.774$. We can view each microgel as a “core-shell” nanoparticle with a PNIPAM core and a PEO shell. In the swollen state, the core and shell have a similar chain density so that $\langle R_g \rangle / \langle R_h \rangle$ is close to ~ 0.774 (Fig. 3). As the temperature increases, the core shrinks, but not the shell. Actually, we expect the swelling of the shell as the grafting density increases because of the repulsion. Note that the core has $\sim 90\%$ mass of the microgel so that the shrinking of the core has different effects on $\langle R_g \rangle$ and $\langle R_h \rangle$; namely, $\langle R_g \rangle$ decreases faster according to their own definitions. This is why $\langle R_g \rangle / \langle R_h \rangle$ decreases in the temperature range 23–32 °C.

Originally, we expected that as the temperature increases, $\langle R_g \rangle / \langle R_h \rangle$ would continuously decrease until the core is fully collapsed. However, in Fig. 3 we observed

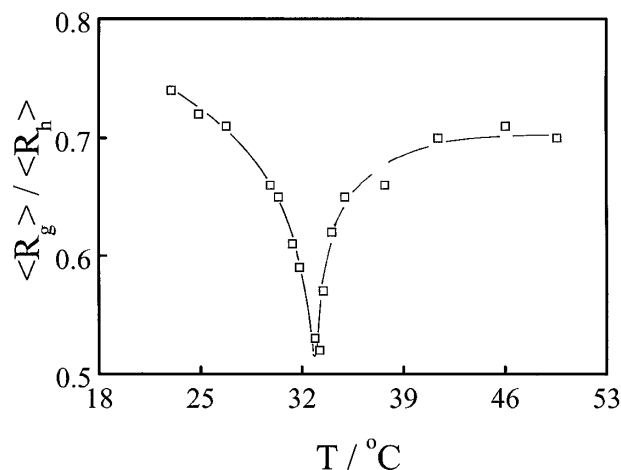


FIG. 3. Temperature dependence of the ratio of average radius of gyration to average hydrodynamic radius ($\langle R_g \rangle / \langle R_h \rangle$) of spherical PNIPAM microgels grafted with linear PEO chains.

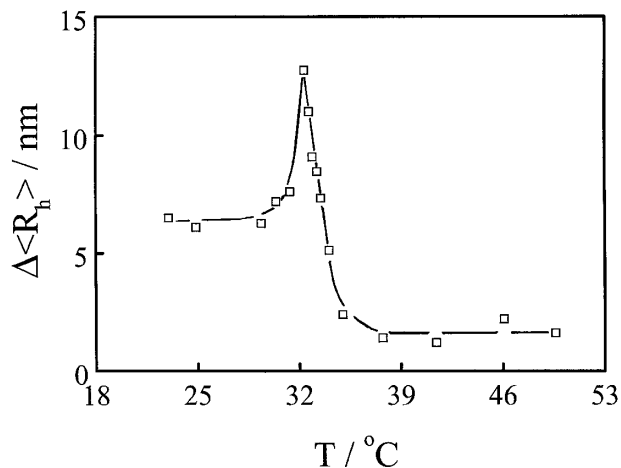


FIG. 4. Temperature dependence of hydrodynamic thickness ($\Delta\langle R_h \rangle$) of the PEO brush grafted onto spherical PNIPAM microgels, where $\Delta\langle R_h \rangle = \langle R_h \rangle - \langle R_h \rangle_0$ with $\langle R_h \rangle$ and $\langle R_h \rangle_0$ being the hydrodynamic radii of the microgel with and without the grafted PEO chains.

an unexpected increase of $\langle R_g \rangle / \langle R_h \rangle$ at $T > \sim 33^\circ\text{C}$. A careful check of Fig. 2 reveals that the increase of $\langle R_g \rangle / \langle R_h \rangle$ is attributed to the fact that at $\sim 33^\circ\text{C}$, $\langle R_g \rangle$ approaches a constant, but $\langle R_h \rangle$ continues to decrease. A near constant $\langle R_g \rangle$ indicates that the shrinking of the PNIPAM core essentially stops at $T \sim 33^\circ\text{C}$, consistent with our previous results [14–17]. The decrease of $\langle R_h \rangle$ actually reflects the collapse of the PEO chains, which can be attributed to the n -clustering attractive interaction at higher grafting densities [6]. Figure 4 shows a better and direct view of the stretching of the PEO chains as the temperature approaches $\sim 33^\circ\text{C}$ and the shrinking of the PEO chains at higher temperatures in terms of the temperature dependence of the hydrodynamic thickness ($\Delta\langle R_h \rangle$) of the PEO brush.

In summary, a novel way of grafting linear PEO chains onto a thermally sensitive PNIPAM microgel enables us to continuously increase the grafting density because the shrinking of the PNIPAM microgel as the temperature increases dramatically reduces its surface area. As the grafting density increases, we observed the stretching of the PEO chains when the temperature is lower than $\sim 33^\circ\text{C}$. However, at temperatures higher than $\sim 33^\circ\text{C}$, we found an unexpected shrinking of the grafted PEO layer, which can be attributed to a long prediction; namely, as the grafting density increases, the n -clustering attractive interaction can induce the collapse of a polymer brush.

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