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Can Coil-to-Globule Transition of a Single Chain Be Treated as a Phase Transition?

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The effects of the concentration (C) and heating rate on the collapse and association of poly(N -isopropylacrylamide) chains in water have been investigated by use of ultrasensitive differential scanning calorimetry. In the dilute solutions, both the phase transition temperature (T_p) and enthalpy change (ΔH) increase with the heating rate but decrease with concentration. By extrapolation to zero heating rate and zero concentration, T_p and ΔH for coil-to-globule transition of a single chain in thermodynamic equilibrium can be obtained. In semidilute solutions, both T_p and ΔH increase with the heating rate but slightly vary with the concentration. T_p and ΔH for pure interchain association in equilibrium are obtained by extrapolation to zero heating rate. Our experiments reveal that only intrachain contraction occurs when the concentration is infinitely close to zero. When the concentration is above the overlap concentration (C^*), only interchain association exists. In the range $0 < C < C^*$, both intrachain contraction and interchain association coexist.

Introduction

The conformation and phase transition of polymer chains in solution not only relate to the properties of polymer materials but have implications for protein folding,^{1,2} protein aggregation,^{3–5} and DNA packing.⁶ It has long been predicted that a flexible linear polymer chain can transit its conformation from a random coil to a collapsed globule when the solvent quality gradually changes from good to poor.⁷ Although many efforts have been made,^{8–10} it is difficult to observe the coil-to-globule transition of a single polymer chain because interchain aggregation often occurs before individual chains reach the fully collapsed globule state. In other words, the phase transition involves intrachain contraction and interchain association. So far, one of the unsolved problems in physical chemistry of polymers is how many single chain events can be treated as a phase transition.

In our previous work,^{11,12} by use of ultrasensitive microcalorimetry (ultrasensitive differential scanning calorimetry, US-DSC), we have investigated poly(N -isopropylacrylamide) (PNIPAM) chains with a lower critical solution temperature (LCST) at $\sim 32^\circ\text{C}$ in dilute and semidilute aqueous solutions. The intrachain contraction and interchain association were characterized by the energy change in the phase transition. By extrapolating the concentration (C) to zero, the enthalpy change (ΔH) for the collapse of a single chain was obtained. However, such an enthalpy change has a scanning rate dependence, and what we measured is the apparent one in nonequilibrium. In the present work, we have investigated the effects of the concentration and heating rate on the phase transition of PNIPAM. By extrapolation of both the concentration and heating rate to zero, we have obtained the enthalpy changes for intrachain contraction and interchain association in equilibrium. Accordingly, the coil-to-globule transition and phase transition can be differentiated.

Experimental Section

Sample Preparation. PNIPAM was synthesized by free radical polymerization.¹³ The resultant PNIPAM was fraction-

ated by a dissolution/precipitation process in a mixture of dry acetone and hexane at room temperature. The absolute weight-average molar mass ($M_w = 2.35 \times 10^6$ g/mol) and the z -average radius of gyration ($\langle R_g \rangle = 60$ nm) were determined by static laser light scattering. The polydispersity index (M_w/M_n) was estimated to be ~ 1.40 from the line-width distribution measured in dynamic laser light scattering.¹⁴ The overlap concentration (C^*) was estimated to be 4.3 mg/mL by $C^* = 3M/(4\pi N_A R_g^3)$, where M and R_g are the molar mass and the radius of gyration of the polymer chains and N_A is the Avogadro constant.¹⁵

US-DSC Measurements. US-DSC measurements were performed on a VP-DSC microcalorimeter from Microcal with deionized water as the reference. The PNIPAM solution and the reference were degassed at 25.0°C for 30 min and then equilibrated at 10.00°C for 120 min before heating. The PNIPAM concentration ranged from 0.25 to 20.0 mg/mL. The heating rate ranged from 0.08 to $1.00^\circ\text{C}/\text{min}$. Data analysis was done by use of Microcal software. The excess specific heat capacity is obtained by using the progress baseline as the reference. The transition temperature (T_p) was taken as that corresponding to the maximum excess specific heat capacity during the transition. The enthalpy change (ΔH) during the transition was calculated by integration of the peak area. The accuracy of the US-DSC measurements at different heating rates was determined with high-purity naphthalene as the standard. The errors for the transition temperature and enthalpy are within $\pm 0.1\%$ and $\pm 1\%$, respectively.

Results and Discussion

Figure 1 shows the temperature dependence of the excess specific heat capacity (C_p) of PNIPAM aqueous solutions at different heating rates. It can be seen that T_p increases with the heating rate. This is because the chain contraction and association cannot follow the temperature change.¹¹ In other words, the phase transition occurring at a certain heating rate is not in thermodynamic equilibrium.

Figure 2 shows the temperature dependence of C_p of PNIPAM aqueous solutions at different concentrations. Generally, the phase transition shifts to lower temperature with increasing

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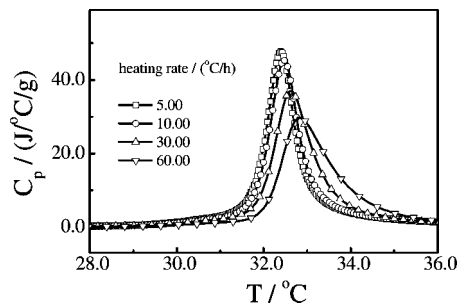


Figure 1. Temperature dependence of C_p of PNIPAM aqueous solutions at different heating rates, where the PNIPAM concentration is 0.50 mg/mL.

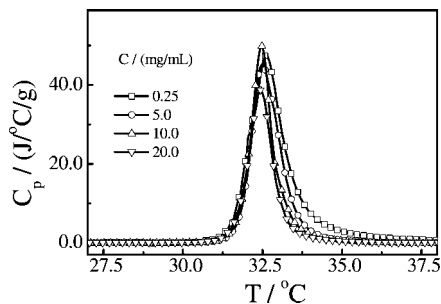


Figure 2. Temperature dependence of C_p of PNIPAM solutions at different concentrations, where the heating rate is 0.50 °C/min.

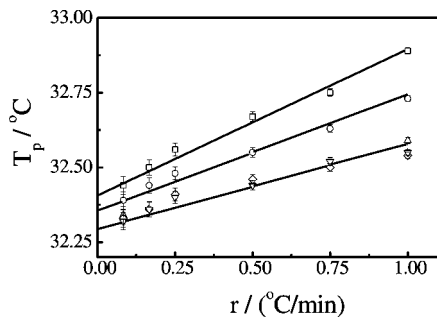


Figure 3. Heating rate (r) dependence of T_p at different concentrations, where the concentrations are 0.50 mg/mL (\square), 5.00 mg/mL (\circ), 10.00 mg/mL (Δ), 15.00 mg/mL (∇), and 20.00 mg/mL (\diamond).

concentration. Therefore, to study the phase transition, both the concentration and heating rate dependences should be taken into consideration.

Figure 3 shows the heating rate dependence of T_p . Clearly, as the heating rate increases, T_p increases, indicating that T_p is not the phase transition temperature in equilibrium. The extrapolation of T_p to zero heating rate leads to the phase transition temperature (T_e) in equilibrium at a certain concentration.

Figure 4 shows the concentration dependence of T_e , where the confidence interval is 95%. When the concentration is below C^* , T_e decreases with increasing concentration. It is known that the phase transition involves both the intrachain contraction and interchain association. It is more difficult for polymer chains to undergo intrachain contraction than interchain association because the former requires a cost of conformational entropy. At a higher concentration, the chains are closer to each other, and they have more chance to undergo interchain association upon heating, which requires lower energy. As a result, the phase transition occurs at a lower temperature. When $C > C^*$, T_e holds constant (~ 32.32 °C), indicating that the phase transition is controlled only by interchain association; that is, interchain association dominates the intrachain contraction in semidilute

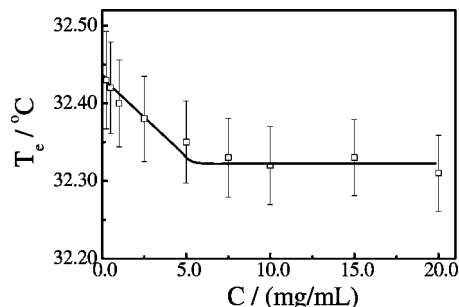


Figure 4. C dependence of T_e , where T_e is obtained by extrapolation of r to zero.

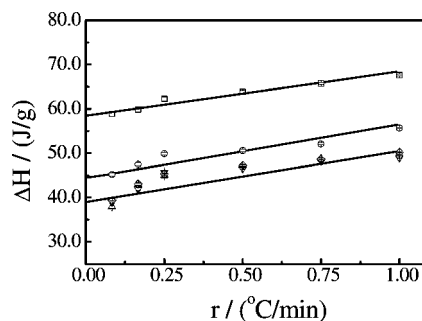


Figure 5. r dependence of ΔH at different concentrations, where the concentrations are 0.50 mg/mL (\square), 5.00 mg/mL (\circ), 10.00 mg/mL (Δ), 15.00 mg/mL (∇), and 20.00 mg/mL (\diamond).

solutions. Thus, T_e can be taken as the temperature (T_a) for the occurrence of only interchain association.

It is known that PNIPAM chains are expected to undergo only intrachain contraction or coil-to-globule transition in an extremely dilute solution.⁹ In the present study, due to the limited accuracy of US-DSC measurement, the data at a concentration below 0.1 mg/mL cannot be obtained. Certainly, a more sensitive technique is desirable in the future. However, since the phase transition only involves intrachain collapse and interchain aggregation, and the enthalpy change has a linear dependence on the concentration in the range we investigated, the extrapolation of T_e to zero concentration can lead to the temperature ($T_s \approx 32.44$ °C) for the coil-to-globule transition of a single chain. The difference between T_a and T_s clearly indicates that the coil-to-globule transition cannot be simply treated as a phase transition.

Figure 5 clearly shows that ΔH during the phase transition of PNIPAM increases with the heating rate; that is, ΔH is the enthalpy change in nonequilibrium. The extrapolation of ΔH to zero heating rate yields the enthalpy change (ΔH_e) in equilibrium at a certain concentration.

Figure 6 shows the concentration dependence of ΔH_e , where the confidence interval is 95%. It is known that the enthalpy change relates to both the intrachain contraction and interchain association of PNIPAM chains. A fast heating leads to more intrachain contraction and less interchain association, so that the enthalpy change increases with heating rate.¹¹ When $C < C^*$, ΔH_e increases with decreasing concentration. The extrapolation of ΔH_e to zero concentration leads to the enthalpy change ($\Delta H_s \approx 61.0$ J/g) for the coil-to-globule transition of a single PNIPAM chain. When $C > C^*$, ΔH_e holds constant ($\Delta H_a \approx 38.8$ J/g). This is because interchain association dominates the intrachain contraction when the chains overlap each other. It is known that the enthalpy change relates to the dehydration of the chains. In the case of intrachain contraction, water molecules are trapped between the segments of the folded chain, which

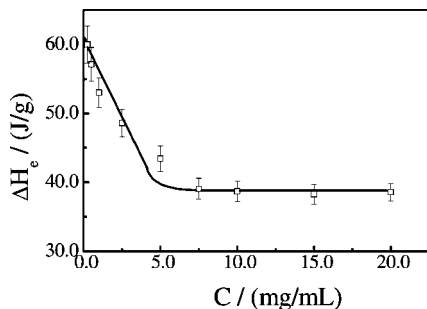


Figure 6. C dependence of ΔH_e , where ΔH_e is obtained by extrapolation of r to zero.

makes the dehydration more difficult than that in interchain association. Thus, it is not surprising that $\Delta H_s > \Delta H_a$. In the range $0 < C < C^*$, ΔH increases with decreasing concentration in that the intrachain contraction increases. Obviously, the phase transition involves only intrachain contraction when C is infinitely close to zero and only interchain association at $C > C^*$. In the range $0 < C < C^*$, both intrachain contraction and interchain association would occur. The difference between ΔH_s and ΔH_a further clearly indicates that a coil-to-globule transition is different from a phase transition.

Conclusion

We have investigated the phase transition of PNIPAM chains in water by use of ultrasensitive differential scanning calorimetry. Both C and the heating rate have effects on T_p and ΔH . By extrapolation to zero heating rate and zero concentration, T_p and ΔH for coil-to-globule transition of a single chain in thermodynamic equilibrium can be obtained. T_p and ΔH for pure interchain association in equilibrium are obtained by extrapola-

tion to zero heating rate because they do not have a concentration dependence when the concentration is above C^* . The present study indicates that the phase transition involves only intrachain contraction when C is close to zero and only interchain association at $C > C^*$. In the range $0 < C < C^*$, it involves both intrachain contraction and interchain association. The coil-to-globule transition of a single chain cannot be simply treated as a phase transition.

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