

# Light-Scattering Study of Coil-to-Globule Transition of a Poly(*N*-isopropylacrylamide) Chain in Deuterated Water

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**ABSTRACT:** Using a nearly monodisperse ( $M_w/M_n < 1.1$ ) high molar mass ( $1.3 \times 10^7$  g/mol) poly(*N*-isopropylacrylamide) (PNIPAM), we studied the conformation change of individual PNIPAM chains between an extended random coil and a fully collapsed thermodynamically stable single chain globule in an extremely dilute D<sub>2</sub>O solution ( $\sim 6.3 \times 10^{-7}$  g/mL) by a combination of static and dynamic laser light scattering (LLS). In comparison with PNIPAM in H<sub>2</sub>O, the  $\Theta$ -temperature of PNIPAM in D<sub>2</sub>O is slightly higher, shifting from 30.6 to 32.1 °C. Moreover, the coil-to-globule transition in D<sub>2</sub>O showed no molten globular state, different from PNIPAM in H<sub>2</sub>O. However, the molten globular state exists in the globule-to-coil transition in D<sub>2</sub>O. The size of the PNIPAM chains near the  $\Theta$ -temperature in the globule-to-coil transition is smaller than that in the coil-to-globule transition; i.e., there exists a hysteresis, similar to PNIPAM in H<sub>2</sub>O. The hysteresis can be attributed to the intrachain interaction formed in the globular state. Our results indicate that the PNIPAM chains are stiffer in D<sub>2</sub>O than in H<sub>2</sub>O.

## Introduction

As a fundamental problem in polymer physics, the coil-to-globule transition has been extensively studied both in theories and in experiments over the past four decades.<sup>1–9</sup> Recently, using a nearly monodisperse high molar mass poly(*N*-isopropylacrylamide) (PNIPAM) sample, we successfully, for the first time, made the coil-to-globule-to-coil transition possible.<sup>9</sup> We also found that there exist two states, the crumpled coil and the molten globule, in the transition. In neutron scattering and nuclear magnetic resonance (NMR), to see how a long polymer chain can be packed into a small volume, deuterated water (D<sub>2</sub>O) has to be used to increase the contrast. Our previous study showed that deuterating a polystyrene chain could affect the chain flexibility around its  $\Theta$ -temperature.<sup>10</sup> Therefore, it is interesting to find whether the coil-to-globule-to-coil transition of PNIPAM in D<sub>2</sub>O is different from that in H<sub>2</sub>O.

## Experimental Section

**Sample Preparation.** The synthesis and fractionation of high molar mass PNIPAM samples were described before.<sup>7,9</sup> Deuterated water (D<sub>2</sub>O, 99.5% D, Aldrich) was used without further purification. We first prepared a stock solution ( $2.50 \times 10^{-5}$  g/mL). The solution was stood at room temperature for 1 week to ensure a complete dissolution. The stock solution was further diluted to a concentration in the range  $2.50 \times 10^{-5}$ – $5.07 \times 10^{-6}$  g/mL and filtered by using a 0.5  $\mu$ m Millipore Millex-LCR filter. A combination of fractionation and filtration finally led to an extremely dilute solution ( $6.3 \times 10^{-7}$  g/mL) containing narrowly distributed ( $M_w/M_n < 1.1$ , estimated from the relative line width,  $\mu_2/\Gamma^2$ , obtained in dynamic light scattering, i.e.,  $M_w/M_n \sim 1 + 4\mu_2/\Gamma^2$ ) high molar mass ( $1.3 \times 10^7$  g/mol) PNIPAM chains.

**Laser Light Scattering (LLS).** In static LLS, the angular dependence of the excess absolute time-average scattered intensity, known as the Rayleigh ratio  $R_{v}(q)$ , of a dilute

polymer solution at concentration  $C$  (g/mL) and the scattering angle  $\theta$  was measured.  $R_{v}(q)$  is related to the weight-average molar mass  $M_w$ , the root-mean-square radius of gyration ( $R_g^2$ )<sup>1/2</sup> (or written as  $\langle R_g \rangle$ ), and polymer concentration  $C$  as<sup>11</sup>

$$\frac{KC}{R_{v}(q)} \cong \frac{1}{M_w} \left( 1 + \frac{1}{3} \langle R_g^2 \rangle q^2 \right) + 2A_2 C \quad (1)$$

where  $K = 4\pi^2 n^2 (dn/dC)^2 / N_A \lambda_0^4$  and  $q = (4\pi n / \lambda_0) \sin(\theta/2)$  with  $N_A$ ,  $dn/dC$ ,  $n$ ,  $\lambda_0$ , and  $\theta$  being the Avogadro number, the specific refractive index increment, the solvent refractive index, the wavelength of light in vacuo, and the scattering angle, respectively.  $A_2$  is the second virial coefficient. For an extremely dilute solution, the angular dependence of  $R_{v}(q)$  directly leads to  $M_w$  and  $\langle R_g \rangle$ .

In dynamic LLS,<sup>12,13</sup> the cumulant analysis of the measured intensity–intensity time correlation function  $G^2(t)$  of narrowly dispersed polymer chains in a dilute solution is sufficient to determine an accurate average line width ( $\langle \Gamma \rangle$ ). For a diffusive relaxation,  $\langle \Gamma \rangle$  is related to the average translational diffusive coefficient by  $\langle D \rangle = \langle \Gamma \rangle / q^2$  and the average hydrodynamic radius by  $\langle R_h \rangle = k_B T / (6\pi\eta \langle D \rangle)$  with  $k_B$ ,  $\eta$ , and  $T$  being the Boltzmann constant, the solvent viscosity, and the absolute temperature, respectively. The Laplace inversion of  $G^2(t)$  by using the CONTIN program<sup>14</sup> leads to the hydrodynamic radius distribution  $f(R_h)$ .

The LLS instrumentation has been detailed before.<sup>7</sup> It should be noted that our LLS spectrometer has an unusual small angle range 6°–20°, very important for the study of the coil state of a long polymer chain because of the required condition of  $q \langle R_g \rangle \ll 1$ . The measured  $dn/dC$  of PNIPAM in D<sub>2</sub>O at  $T = 25$  °C and  $\lambda_0 = 532$  nm is  $0.232 \pm 0.001$  mL/g. The long-term temperature fluctuation inside the sample holder was less than  $\pm 0.02$  °C.

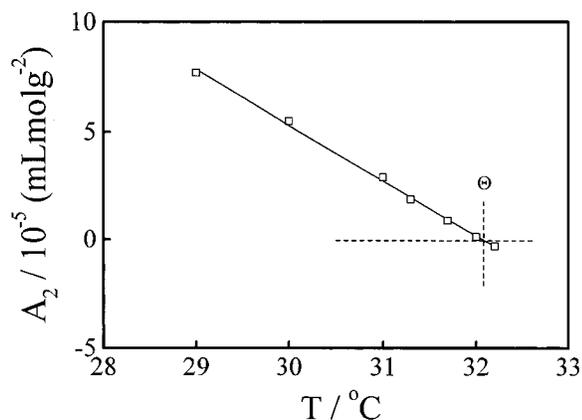
## Results and Discussion

Figure 1 shows that the second virial coefficient  $A_2$  decreases as the solution temperature increases, a characteristic of aqueous polymer solution because of the negative entropy change. The interpolation of  $A_2 \rightarrow 0$  led to the Flory  $\Theta$ -temperature (32.1 °C), which is higher than the  $\Theta$ -temperature (30.5 °C) of PNIPAM

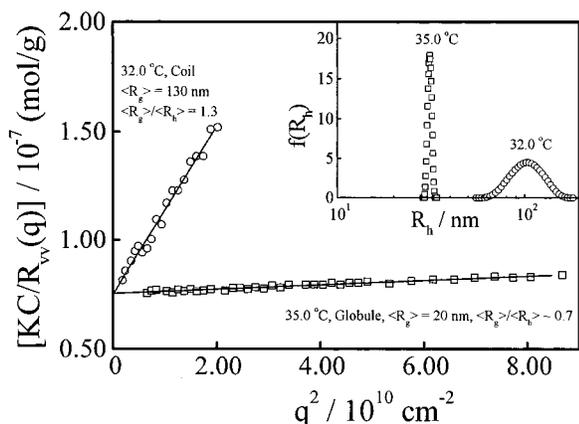
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**Figure 1.** Temperature dependence of the second virial coefficient  $A_2$  for PNIPAM in  $D_2O$ .

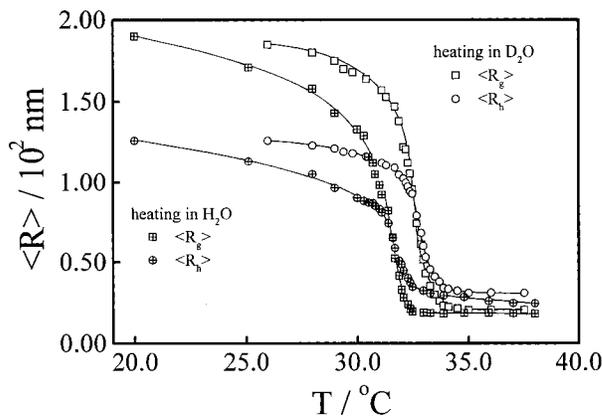


**Figure 2.** Typical angular dependence of  $KC/R_v(q)$  of the PNIPAM chains in  $D_2O$  at two different temperatures, where the polymer concentration is  $6.3 \times 10^{-7}$  g/mL. The inset shows the corresponding hydrodynamic radius distributions  $f(R_h)$  of the PNIPAM chains in the coil and the globule states.

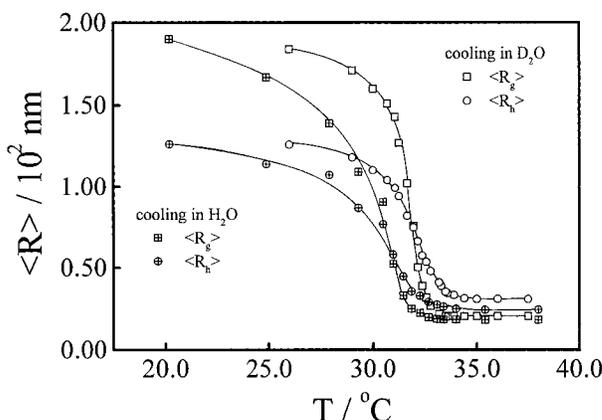
in  $H_2O$ , indicating that  $D_2O$  is a better solvent for PNIPAM than  $H_2O$ .

Figure 2 shows that after the temperature increases from 32 to 35 °C the slope of the line sharply decreases, reflecting a decrease of  $\langle R_g \rangle$  from 130 to 20 nm. It clearly indicates the collapse of the PNIPAM chains in  $D_2O$ . The chain collapse can be directly viewed from the change of hydrodynamic radius distribution  $f(R_h)$  as shown in the inset of Figure 1. The extrapolation of  $[KC/R_v(q)]_{q \rightarrow 0}$  led to the same intercept. On the basis of eq 1, this indicates no change in  $M_w$ ; i.e., the observed coil-to-globule transition was a pure intrachain process. It should be stated that the intensity of the scattered light ( $I$ ) in the globule state was independent of time, indicating that individual globules were stable because  $\langle I \rangle$  is proportional to  $M_w$  and  $M_w$  is further proportional to  $n_i M_i^2$  on the basis of eq 1, very sensitive to the interchain aggregation.

Figure 3 shows the temperature dependence of  $\langle R_g \rangle$  and  $\langle R_h \rangle$  of PNIPAM chains in the heating process, where each data point was obtained at least 2 h after the solution reached the desired temperature even though we knew that individual PNIPAM chains can reach the equilibrium state as fast as the temperature change.<sup>7</sup> Below 31.7 °C, the PNIPAM chains slightly shrinks as  $T$  increases, while in the temperature range 31.7–33.9 °C, both  $\langle R_g \rangle$  and  $\langle R_h \rangle$  dramatically decreases as  $T$  increases, indicating the coil-to-globule transition. Above 33.9 °C, both  $\langle R_g \rangle$  and  $\langle R_h \rangle$  were nearly independ-



**Figure 3.** Temperature dependence of the average radius of gyration ( $\langle R_g \rangle$ ) and hydrodynamic radius ( $\langle R_h \rangle$ ) of the PNIPAM chains in  $D_2O$  in the coil-to-globule (heating) transition. For comparison, the previous results of PNIPAM in  $H_2O$  were also plotted.

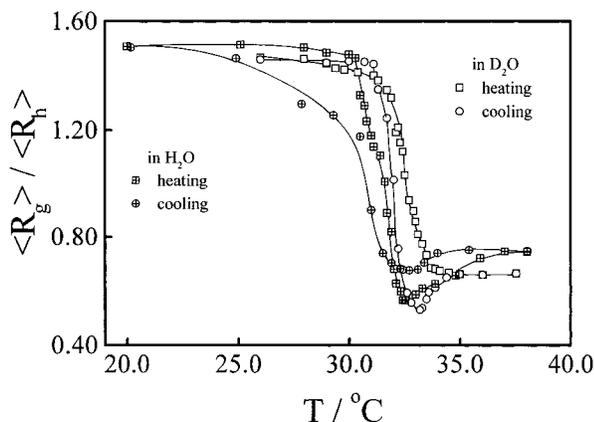


**Figure 4.** Temperature dependence of the average radius of gyration ( $\langle R_g \rangle$ ) and hydrodynamic radius ( $\langle R_h \rangle$ ) of the PNIPAM chains in  $D_2O$  in the globule-to-coil (cooling) transition. For comparison, the previous results of PNIPAM in  $H_2O$  were also plotted.

ent of the temperature, indicating that the PNIPAM chains reach the fully collapsed globular state. In comparison with our previous results of PNIPAM in  $H_2O$ , the average size of the PNIPAM chains in  $D_2O$  was larger. Therefore, the density of the globule in  $D_2O$  is slightly lower than that in  $H_2O$ .

Note that even at their respective  $\Theta$ -temperatures, the unperturbed PNIPAM chains in  $D_2O$  were more extended. It has been known that at  $\Theta$ -temperature the unperturbed chains have a size of  $\langle R \rangle = lN^{1/2}$ , where  $N$  is the number of segments per chain and  $l$  is the length of each segment. For a given PNIPAM chain, i.e., for a fixed contour length ( $lN$ ), larger  $\langle R \rangle$  means smaller  $N$  or larger  $l$ ; i.e., the chain are stiffer in  $D_2O$ . The fact that the same polymer chain under two different  $\Theta$ -temperatures has two different sizes can be attributed to different local conformations.

Figure 4 shows the temperature dependence of  $\langle R_g \rangle$  and  $\langle R_h \rangle$  of the PNIPAM chains in the cooling process. The profile is similar to that in the heating process, as shown in Figure 3. However, some points should be noted. (1)  $\langle R_g \rangle$  did not increase until  $T$  was cooled to 33.3 °C, while  $\langle R_h \rangle$  started to increase at 33.9 °C; (2) in the transition range 31.0–33.9 °C, the PNIPAM chains in the cooling process had a smaller size, revealing a hysteresis similar to the case of PNIPAM in  $H_2O$ , which



**Figure 5.** Temperature dependence of the ratio of the radius of gyration to the hydrodynamic radius ( $\langle R_g \rangle / \langle R_h \rangle$ ) of the PNIPAM chains in  $D_2O$  in the coil-to-globule (heating) and the globule-to-coil (cooling) transitions. For comparison, the previous results of PNIPAM in  $H_2O$  were also plotted.

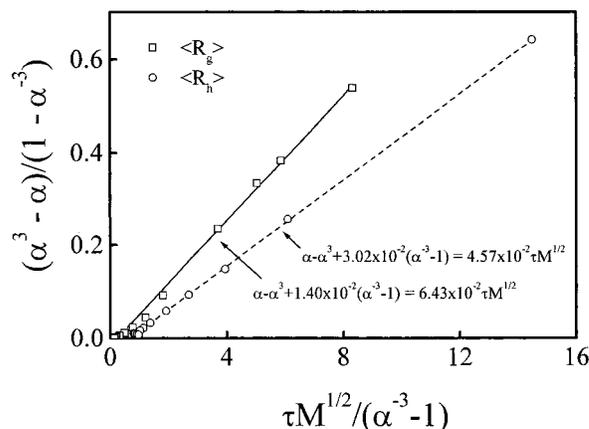
was attributed to the formation of some intrachain structures, presumably the intrachain hydrogen bonding, in the globular state.

Figure 5 shows that in both the heating and cooling processes  $\langle R_g \rangle / \langle R_h \rangle$  is nearly a constant ( $\sim 1.4$ ) when  $T$  is lower than the  $\Theta$ -temperature. In the transition range of the heating process,  $\langle R_g \rangle / \langle R_h \rangle$  decreases sharply from 1.4 to 0.7 and remains  $\sim 0.7$  when  $T > 33.7$  °C. In comparison with PNIPAM in  $H_2O$ ,  $\langle R_g \rangle / \langle R_h \rangle$  for PNIPAM in  $D_2O$  shows no dip, but in the cooling process,  $\langle R_g \rangle / \langle R_h \rangle$  has a dip around 33.1 °C, similar to the case of PNIPAM in  $H_2O$ . At the dip,  $\langle R_g \rangle / \langle R_h \rangle$  is only 0.54, corresponding to the molten globule state; i.e., the surface of the globule has a lower density than the center. A combination of Figures 4 and 5 shows that the dip of  $\langle R_g \rangle / \langle R_h \rangle$  is attributed to the increase of  $\langle R_h \rangle$  as the temperature decreases because  $\langle R_g \rangle$  is nearly a constant in the same temperature range. The missing of the dip in the heating process implies that the collapse of the PNIPAM chain in  $D_2O$  is more uniform from center to surface, which is different from that in  $H_2O$ .

Birshtein and Pryamitsyn suggested that the contraction factor  $\alpha$ , defined as  $\langle R \rangle_T / \langle R \rangle_\Theta$ , is related to the reduced temperature ( $\tau = (T - \Theta) / \Theta$ ) and the molar mass of a polymer chain ( $M$ ) by<sup>11</sup>

$$\alpha - \alpha^3 + C(\alpha^{-3} - 1) = B\tau M^{1/2} \quad (2)$$

where  $B$  and  $C$  are two constants, independent of  $M$  and  $T$  for a given polymer/solvent system. On the basis of eq 2, the plot of  $(\alpha^3 - \alpha) / (1 - \alpha^{-3})$  vs  $\tau M^{1/2} / (\alpha^{-3} - 1)$  is a straight line and give out the  $B$  and  $C$  as shown in Figure 6. The balance between the deformation of a Gaussian chain and the ternary-segment intrachain interaction, i.e.,  $\alpha - \alpha^3 = C(\alpha^{-3} - 1)$ , is defined as the crossover point from the coil region to the globule region. Our results show that the crossover points are far away



**Figure 6.** Plot of  $(\alpha^3 - \alpha) / (1 - \alpha^{-3})$  vs  $\tau M^{1/2} / (\alpha^{-3} - 1)$ , where  $\alpha = \langle R_g \rangle_T / \langle R_g \rangle_\Theta$  or  $\langle R_h \rangle_T / \langle R_h \rangle_\Theta$ . The solid and dashed lines respectively represent the best fitting of  $\alpha - \alpha^3 + C(\alpha^{-3} - 1) = B\tau M^{1/2}$ .

from the  $\Theta$ -temperature but close to the temperature at which  $\langle R_g \rangle$  and  $\langle R_h \rangle$  approach their respective constants. In comparison with PNIPAM in  $H_2O$ ,<sup>9</sup>  $C$  is nearly the same, which is expected because the ternary-segment intrachain interaction is independent of solvent, but  $B$  is larger, indicating a larger binary-segment interaction.

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