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Collapse kinetics for individual poly(*N*-isopropylmethacrylamide) chains

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ABSTRACT

The kinetics for the coil-to-globule transition of linear poly(*N*-isopropylmethacrylamide) (PiPMA) chains has been studied by use of the fluorescence and Rayleigh scattering with a fast laser pulse infrared heating. We have observed the two-stage kinetics in the collapse transition with the characteristic relaxation times, τ_{fast} and τ_{slow}, which are attributed to the nucleation and growth of pearls on the chain and the merging and coarsening of pearls to a globule, respectively. The collapse kinetics of PiPMA is similar to that of poly(*N*-isopropylacrylamide) which has one less methyl in each monomeric unit, indicating that the additional methyl groups in PiPMA chains slightly influence the kinetics. In other words, the pearls are not completely coarsened to form compact globules within τ_{slow}.

1. Introduction

The coil-to-globule transition of a flexible linear polymer chain in solution is a fundamental problem in polymer physics and of special importance for understanding the behaviors of complex biomacromolecules such as protein folding and DNA packing [1–3]. Since Stockmayer [4] predicted the collapse of a linear polymer chain from an expanded coil to a rather dense globule, the equilibrium properties of the coil-to-globule transition have been well understood both theoretically and experimentally [5–15]. However, the collapse kinetics is not so clear.

Theoretically, different models have been proposed and tested for kinetic paths of the polymer collapse transition. de Gennes [16,17] first proposed a two-stage kinetics with a rather fast crumpling of the unknotted polymer chain (crumpled globule) and a subsequent slow rearrangement of thermal blobs of the collapsed polymer chain (compact globule). Using the Gaussian self-consistent method, Kuznetsov et al. [18,19] stated that the collapse kinetics involves three stages, that is, a rapid initial spinodal process, a coarsening stage and a compaction shape optimization stage. It is believed that there exists a slow final compactification and rearrangement stage for the globule. By using the phenomenological model, Halperin and Goldbart [20] revealed a four-stage kinetics, namely, the pearling (droplets of the dense phase), bridge-stretching, the collapse of the pearl necklace, and the contact and coalescence of pearls into a single globule.

Experimentally, it is rather difficult to verify these various kinetic stages because the time for the polymer solution to reach temperature equilibrium after a temperature jump is longer than the relaxation time. Moreover, the competition between the intrachain collapse and the interchain association often spoils the experiment [21]. So far, only a few experimental methods such as laser light scattering [22–25], viscometry [26], and stopped flow [27] have been reported. The relaxation time for the collapse of a single chain predicted from theories is in the order of $10^{-3} \sim 10^{-4}$ s [16,21]. This needs not only a fast temperature jump apparatus to change the solution temperature but also detection instruments to analysis the kinetics process at least within milliseconds. The pulse laser technique is well suitable for rapidly reaction kinetics [28,29]. Recently, a combination of a ultrafast infrared heating laser pulse-induced temperature jump and the time-dependent fluorescence and Rayleigh scattering intensity measurements have been used to study the kinetics for the coil-to-globule transition of thermally sensitive linear poly(*N*-isopropylacrylamide) (PiPA) chains in dilute solutions [30]. It shows two distinct kinetic stages with two characteristic transition times ($\tau_{fast} \sim 0.1$ ms and $\tau_{slow} \sim 0.8$ ms). Note that the ultrafast infrared heating laser pulse can induce the solution temperature jumped about 8 °C within 10 ns, and the time interval between two heating laser pulses can be adjusted to 100 ms. The dead time for the change in fluorescence and Rayleigh light scattering intensity of solutions is less than ~ 20 μs. Therefore, the information about the temperature-induced the fast collapse kinetics of polymers can be obtained. Such heating induced the coil-to-globule transition in water is of particular interest due to its connection with the functionality of biological macromolecules.

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Poly(*N*-isopropylmethacrylamide) (PiPMA) is a thermally sensitive polymer with an additional hydrophobic methyl group at each monomeric unit than PiPA [31]. In terms of the structure, it should have a lower critical solution temperature (LCST) lower than PiPA. In fact, its LCST (~45.0 °C) is higher than that of PiPA (~32 °C) [10–13]. Recently, we studied the phase transition behavior of PiPMA in water by use of laser light scattering and ultrasensitive differential scanning calorimetry [32]. In comparison with PiPA, the additional methyl groups in PiPMA chains restrain the intrachain collapse and interchain association, leading the phase transition to occur at a higher temperature. In the present work, we have investigated the collapse kinetics of PiPMA chains by using a home-set up fluorescence spectrometer equipped with an ultrafast pulsed infrared heating laser. Our aim is to understand the role of the methyl group in the kinetics of polymer chains.

2. Experimental section

2.1. Materials and preparation of samples

PiPMA was synthesized via radical polymerization as described in our previous papers [32]. The sample was fractionated by successive dissolution/precipitation cycles in a mixture of acetone and n-hexane at 26.0 °C. The weight-average molar mass (M_w) was measured by static light scattering (ALV/DLS/SLS-5022F spectrometer) in water at 25.0 °C. The polydispersity (M_w/M_n) was estimated from the relative line width distribution in dynamic laser light scattering. Five fraction samples with M_w 1.6 × 10^6, 1.0 × 10^6, 2.0 × 10^5, 8.2 × 10^4, and 2.6 × 10^4 g/mol were obtained; Correspondingly, M_w/M_n values were 1.3, 1.5, 1.5, 1.5, and 1.4, respectively. Each PiPMA sample was dissolved in D_2O with a concentration (C) of 1.0 mg/mL for the kinetics experiment. 8-anilinon-1-aphthalene-sulfonic acid ammonium salt (ANS) was used as a fluorescent probe with final concentration of 100 μM.

2.2. Fast infrared laser heating

The equipment and principle of the fast infrared laser heating were detailed elsewhere [30,33]. Briefly, the fast infrared heating laser pulse was generated with a Nd:YAG laser (Spectra Physics, Lab-170, 10 Hz, and pulse width = 10 ns) and two Raman cells were filled with 34 atm hydrogen. PiPMA dissolved in D_2O was placed between two quartz windows with a 200 μm spacer. The temperature of the solution was controlled by a thermostatic bath with an accuracy of ±0.1 °C. Each heating pulse (1.9 μm, ~8 mJ/pulse at 10 Hz) adsorbed by the overtone of the O-D stretching vibration in D_2O can induce about 8 °C temperature jump of solution [34,35], which is sufficient to cause the coil-to-globule transition of individual PiPMA chains.

The light source for both the fluorescence and Rayleigh scattering experiments was a 200-W high pressure mercury lamp (Shanghai Hualun Bulk Factory). The collapse kinetics was investigated by monitoring the change in fluorescence intensity or Rayleigh scattering intensity. In order to increase the signal-to-noise ratio, each data point was obtained by averaging over 512 times repeated measurements.

2.3. Fluorescence spectrometry

The fluorescence spectra were measured on an LS-55 spectrophotometer (PerkinElmer, America) with a 0.5 mm optical path length quartz cell. The sample temperature was controlled by an SDC-6 thermostatic water-circulator bath (Ningbo Tianheng Instrument Co.) with an accuracy of ±0.1 °C.

3. Results and discussion

We first examined the effect of the conformational change of PiPMA chains on the fluorescence of ANS. Fig. 1 shows the effect of temperature on the fluorescence emission spectra of ANS in D_2O solution of PiPMA. It is known that the fluorescence of ANS is weak in a polar media and strong in a nonpolar microenvironment [36,37]. When the temperature of PiPMA solution is below 46.1 °C, the fluorescence intensity (I_F) is low, indicating that ANS probe molecules locate in a polar environment. As the temperature is increased above 46.1 °C, I_F increases rapidly along with a pronounced blue shift of the maximum emission wavelength from 500 nm to 466 nm, reflecting that the microenvironment around ANS is changed from polar to nonpolar. As we know, at the temperature above the LCST, PiPMA chains collapse or aggregate to form globules. Simultaneously small amounts of ANS are trapped in its hydrophobic core, which leads to the decrease of the polarity around ANS. That is why the fluorescence intensity is enhanced along with a blue shift in the emission spectra. The temperature dependence of the fluorescence intensity at 466 nm is shown in the inset of Fig. 1. Clearly, the conformational change of PiPMA chains near 46.1 °C can markedly change the I_F of ANS.

Fig. 2 shows that, when the fast infrared heating laser pulse induces the temperature of PiPMA solution jump, the fluorescence intensity of ANS increases abruptly within a few milliseconds. This is very important since the measured kinetic data are extracted from this initial stage. After ~80 ms, I_F relaxes back to its original level, implying the heat dissipation and the globules of PiPMA unfold back into individual chains. Accordingly, to ensure no residual heating effect before the next heating laser pulse, the time interval between two heating laser pulses should be not less than 80 ms. Here, we set it 100 ms.

Fig. 3 shows a magnification of the initial time dependence of normalized fluorescence intensities of ANS in D_2O solutions after a fast infrared heating laser pulse with and without PiPMA, respectively. For the solution without PiPMA, I_F remains constant, implying that the polarity around ANS does not change. With PiPMA, I_F increases rapidly in the first 0.4 ms, followed by a much slower and gradual increase and then levels off after ~3 ms, reflecting that the binding site of ANS is rapidly altered from polar to nonpolar. This change suggests that PiPMA chains transform from an extended coil to a globule state. In order to confirm that the polymer chains collapse into single chain globules without

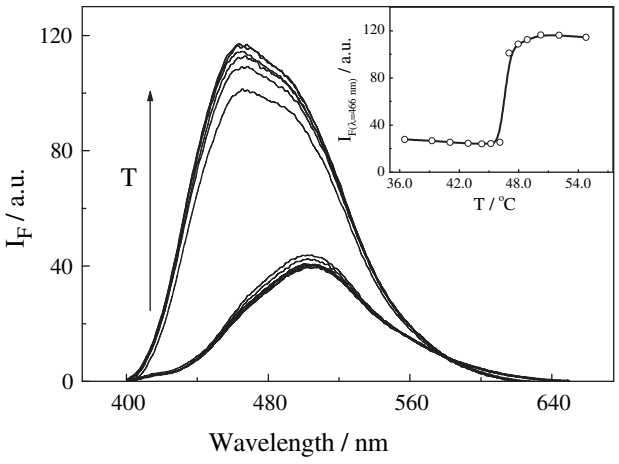

Fig. 1. Effect of temperature on the fluorescence emission spectra of ANS in D_2O solution of PiPMA. The inset shows the temperature dependence of the fluorescence intensity ($\lambda_{emission}$ = 466 nm), where M_w = 1.6 × 10^6 g/mol, C = 5 × 10^{-4} g/mL.

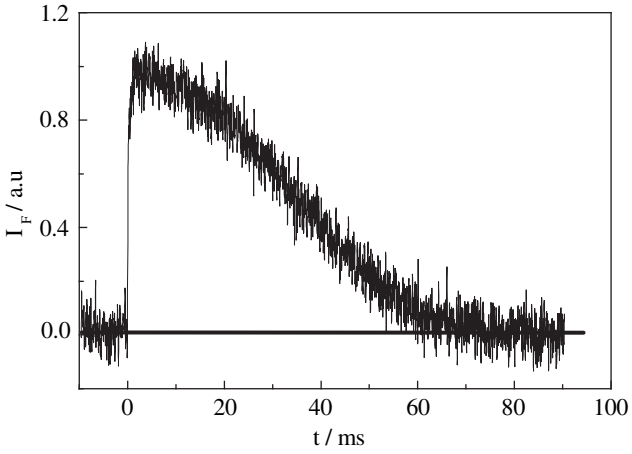

Fig. 2. Temperature jump-induced change in the normalized fluorescence intensity ($\lambda_{emission}$ = 466 nm) of ANS in D_2O solution of PiPMA, where $M_w = 1.6 \times 10^6$ g/mol, $C = 1 \times 10^{-3}$ g/mL.

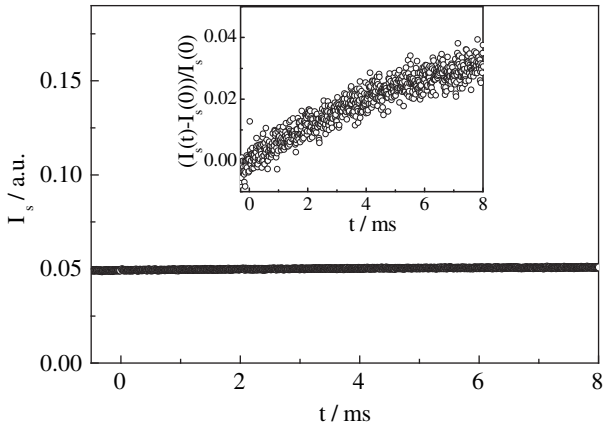

Fig. 4. Time dependence of the scattering light intensity of PiPMA in D_2O solution. The inset shows the ratio of the change of the scattering light intensity $[I_s(t)-I_s(0)]$ to $I_s(0)$, where $M_w = 1.6 \times 10^6$ g/mol, $C = 1 \times 10^{-3}$ g/mL.

interchain aggregation, Rayleigh scattering intensity (I_S) from PiPMA solution was measured by blocking the fluorescence light with a filter. The result is shown in Fig. 4. I_S is barely changed within the first 8 ms, indicating that no interchain association occurs. It is well known that I_S is proportional to the square of the mass of a scattering object. Small amounts of interchain association can cause a significant increase of I_S. By meticulously analyzing the scattering intensity change, we discover that I_S increases about 3% (the inset). In the collapse process of PiPMA chains, some ANS molecules are entrapped inside globules. In addition, the dehydration of PiPMA chains after the temperature increment might cause a slight increase of the refractive index increment (dn/dC) [30]. Both of them would slight increase I_S. We noticed that the change of I_S for PiPA is only 0.3%. The difference between PiPMA and PiPA samples may be due to that our temperature jump is 8 °C (2 °C for PiPA samples), which leads to a more increase in dn/dc. Moreover, the significant collapse of PiPMA chains caused by the higher temperature jump and the higher concentration of PiPMA (2×10^{-4} g/mL for PiPA samples) result in a big change of Rayleigh scattering intensity because it was measured at 90°. Thus, we are sure what we observed in Fig. 3 is the coil-to-globule transition of a single PiPMA chain. In our previous paper, the association

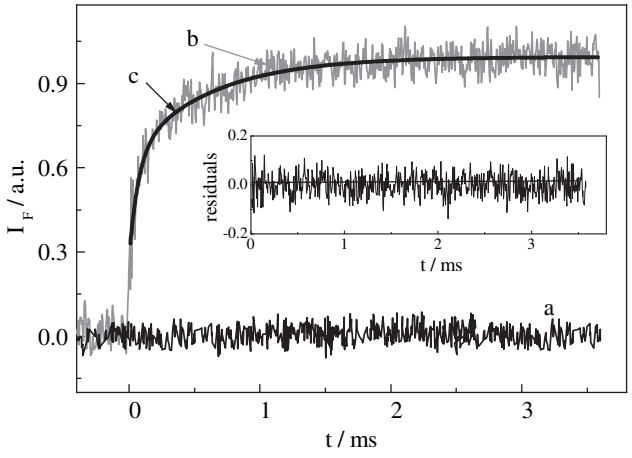

Fig. 3. Time dependence of temperature jump-induced the normalized fluorescence intensity of ANS in D_2O solution (a), PiPMA solution (b), and the double exponential fitting curve (C), where $M_w = 1.6 \times 10^6$ g/mol, $C = 1 \times 10^{-3}$ g/mL. The inset is plots of the fitting residual.

behavior of PiPMA chains in water has been investigated by laser light scattering with the concentration fixed at 2.0×10^{-5} g/mL [32]. In the present work, no interchain association observed is because that the fast laser pulse infrared heating induces the temperature jump within 10 ns and the measurement was finished within 100 ms. In addition, each data point was normally averaged over measurements repeated 512 times. If there was any aggregation, it would take more time to dissociate the aggregates [32,38], which would result in gradual increase of I_S with the measurement times rather than remaining consistent for every time.

The relaxation curve in Fig. 3 is fit by a single and double exponential function, respectively. Such a curve could be well fit by the later, i.e., $I_F = A_1\exp(-t/\tau_{fast}) + A_2\exp(-t/\tau_{slow})$, where τ_{fast} and τ_{slow} are the characteristic relaxation times of the initial and later stages, respectively. The double exponential fitting curve and the fitting residual are also shown in Fig. 3. For PiPMA ($M_w = 1.6 \times 10^6$ g/mol), τ_{fast} and τ_{slow} are 0.07 ms and 0.62 ms, respectively, which are similar to those of PiPA with $M_w = 1.2 \times 10^6$ g/mol (τ_{fast} = 0.11 ms and τ_{slow} = 0.60 ms) [30]. Kikuchi et al. [21] predicted that the total average collapse time (τ) for a polymer with polymerization degree $N \sim 10^4$ is 10^{-4} s; the characteristic time of the initial pearl formation would be only a few percent of τ and the collapse kinetics is dominated by the packing and merging of the pearls. Therefore, our observed τ_{fast} and τ_{slow} are in a reasonable to agree with the theoretical values.

Fig. 5 shows the effect of PiPMA chain length on the two characteristic times. Note that the LCST of PiPMA shifts to higher temperature as M_w decreases [32], so we correspondingly set the initial solution temperature at 43.0 °C for the samples with $M_w \geq 2.0 \times 10^5$ g/mol, while it was increased to 45.0 °C for PiPMA with $M_w = 8.2 \times 10^4$ and 2.6×10^4 g/mol to ensure the same temperature difference for each sample. τ_{fast} is nearly independent of the chain length, especially at $M_w > 2.0 \times 10^5$ g/mol. A similar phenomenon has been observed for PiPA [30]. Kuznetsov et al. [18,19] showed that the earliest kinetic stage is characterized by the rapid formation of numerous small collapsed globules, whose duration is quite independent of the degree of polymerization. Halperin and Goldbart [20] also reported that the characteristic times for the pearls formation and growth are $\tau \sim N^0$ and $\tau \sim N^{1/5}$, respectively. Therefore, our experiments confirm that this fast process is related to the initial pearl formation and growth. On the other hand, when $M_w > 2.0 \times 10^5$ g/mol, the chain length does not influence the τ_{slow}. This is similar to the collapse of PiPA, where τ_{slow} remains constant as M_w increases from 1.2×10^6 to 7.7×10^6 g/mol [30]. However, in the collapse of the pearl necklace stage [19], the

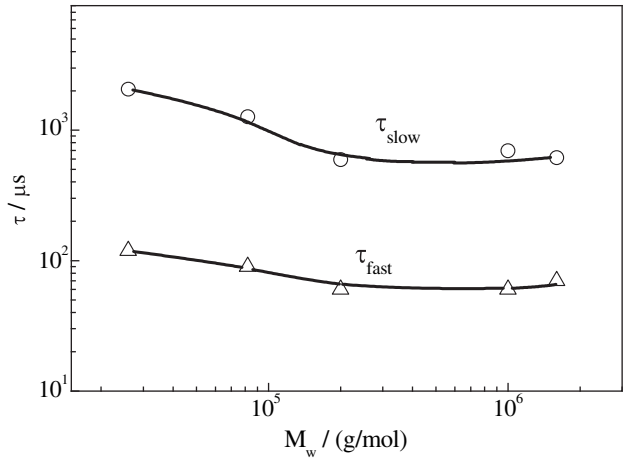

Fig. 5. Effects of PiPMA chain length on the characteristic times (τ_{fast} and τ_{slow}) of fast and slow processes during the coil-to-globule transition.

characteristic time is estimated to be $\tau \sim N^{6/5}$. The difference between the experimental and theoretical values is probably because the chain length is not high enough in our experiments. When $M_w < 2.0 \times 10^5$ g/mol, τ_{slow} decreases with M_w, which cannot be interpreted with previous theories. PiPMA with an isobutyronitrile end group was prepared via radical polymerization using 2,2′-azobis(isobutyronitrile) as an initiator, Xia et al. [39,40] have reported that the end group effect of polymer is most pronounced for low M_W polymers but diminishes rapidly when M_W is above 1.0×10^4 g/mol. Therefore, we think that the end group effect is negligible for PiPMA with $M_w = 2.6 \times 10^4$ g/mol. In the previous reports, it has been confirmed that the coil-to-globule transition time is inversely related to the quenching depth (ΔT) of the process [18,24,30]. For PiPMA with $M_w = 8.2 \times 10^4$ and 2.6×10^4 g/mol, the phase transition temperature are in the range 45.7 ~ 51.1 °C and 47.0 ~ 57.0 °C, respectively [32]. It is known that short chains often exhibit a broader transition than longer chains. The broad transition here implies that only part of the chains collapse after the same temperature jump. That is why τ_{slow} decreases with M_w.

Fig. 6 illustrates the coil-to-globule transition of PiPMA chains. The collapse kinetics for individual PiPMA homopolymer chains in dilute D_2O solutions has two distinct kinetic stages. The fast stage can be related to the formation and initial growth of some pearls on the chain by adsorption of the monomer chains joining them, while the slower process is corresponded to the pearls merging and coarsening of the crumpled chain to the globule. Clearly, PiPMA has the kinetics stages similar to that of PiPA. Thus, the steric hindrance of methyl groups does not influence the kinetics. As we know that temperature has an effect on the collapse kinetics of polymer chains, especially for the collapse time. However, PiPMA and PiAM have similar structure except that PiPMA has an additional methyl group in each monomeric unit, thus both have two-stage collapsing kinetics. It should be noted there are some differences in the experiment conditions, so it is not easy to directly compare their relaxation times. In the fast stage, the dimension and conformation of the chain as a whole are only slightly altered. The formed pearls

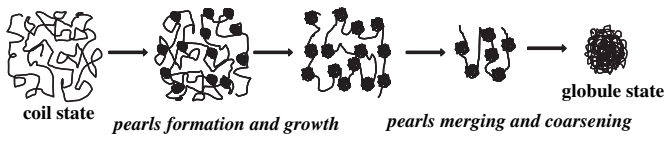

Fig. 6. Schematic of the two kinetics stages for individual PiPMA chains in D_2O solution.

are quite mobile and permit shape fluctuations that allow the merging of comparatively close pearls [20]. In the slow stage, the merging and coarsening of the pearls lead to the overall shrinking of the chain to a collapsed state. In such a short time ($\tau_{slow} = 0.62$ ms), the pearls may not completely collapse to form compacted globules. Byrne et al. [41,42] demonstrated that the final compactification of the globule is a slow equilibration process competing with the interchain association. In the present case, only a molten globule is probably formed. Namely, each chain already collapses into a globule with a rough surface made of many small chain loops [10,11]. A fair degree of mobility of the methyl groups persists even inside the collapsed globules. So, the additional methyl groups in PiPMA chains restraining the chain conformational change do not occur within τ_{slow}.

4. Conclusion

The present studies lead to the following conclusions. The coil-to-globule transition of individual linear PiPMA chains is a two-stage process with two distinct characteristic relaxation times, namely, the fast nucleation and growth of pearls along a random coil and the slow merging and coarsening of the crumpled chain to the globule. The collapse kinetics of PiPMA is similar to that of PiPA, where the globules formed are uncompacted.

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