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Notes

Single-Chain Expansion from the Collapsed Globule of Polystyrene in Cyclohexane to the Θ Coil

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Introduction

The two-stage kinetics of single-chain collapse, as first predicted by de Gennes[1] and Grosberg, et al.,[2] has been observed experimentally by quenching a dilute solution of polystyrene in cyclohexane from the Θ temperature to just below its phase separation temperature in the metastable two-phase region.[3,4] It was noted that the characteristic times for the contraction process were several orders of magnitude slower when compared with the theoretical estimate based on the de Gennes model, provided that our experimental observations could include the initial contraction process as described by de Gennes. This huge discrepancy led us to speculate on other physical mechanisms which could slow down the contraction process: the topological constraints, entanglements and knotting in the collapsed but not fully relaxed chain and the effective viscosity, η_{eff}, which is much higher than the pure solvent viscosity, as experienced by a collapsing globule.[4] In order to test whether knotting could play an important role, we now report our experimental findings on the single-chain expansion from the freshly collapsed globule to the Θ coil.

Experimental Section

The polystyrene (PS) [$M_w = 8.12 \times 10^6$ and $M_w/M_n = 1.08$] sample, the concentration ($C = 8.7 \times 10^{-6}$ g/mL), and the method of solution preparation were the same as those in ref 4. The dynamic light scattering (DLS) experiments, including the thin-walled cylindrical cell (0.3 mm wall thickness and 10 mm diameter) and the method of data analysis, were also as in ref 4. By taking advantage of our knowledge on the dual effects between the coil-to-globule transition and phase separation, experiments were performed by first quenching the polymer solution from the Θ temperature (35 °C) to just below the phase separation temperature (e.g., 28 °C) for a fixed time period ($t \sim 600-900$ s) such that most of the polymer coils in the Θ state ($R_h = 62.7$ nm) had time to become collapsed globules ($R_h \simeq 21$ nm) with the presence of only a small amount of phase-separated large aggregates before the sample temperature was jumped back to 35 °C. Three sets of experiments were performed, as shown schematically in Figure 1. Sequence A represents DLS measurements performed soon (about 800−900 s) after a temperature jump from 35 to 28 °C. After the initial temperature jump (from 35 to 28 °C; $t = 0$) and the appropriate waiting period, the sample temperature was returned to 35 °C. Sequence B represents quenching the sample temperature from 35 °C to liquid nitrogen temperature (−120 °C). After a 40 s equilibration time at −120 °C, the sample temperature was jumped back to 35 °C ($t = 0$). Sequence C denotes the temperature jumps as follows: 35 to −120 °C; 40 s at −120 °C; −120 °C to the melting point of cyclohexane (~6 °C); 917 s at ~6 °C; ~6 to 35 °C ($t = 0$).

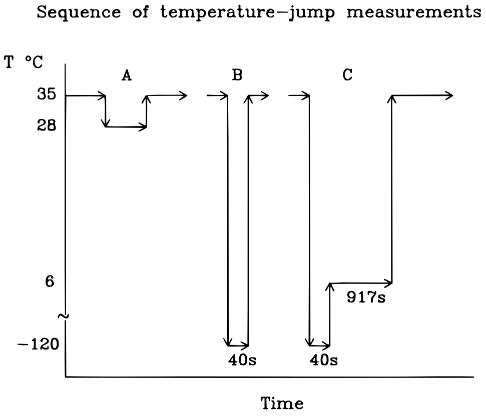

Figure 1. Schematic representation of three temperature-jump experiments. Time axis not to scale.

Results and Discussion

Sequence A. Figure 2a shows plots of average hydrodynamic radius R_h and variance ($\mu_2/\bar{\Gamma}^2$, which is a measure of polydispersity) as a function of time after an abrupt temperature change. It is noted that the coil collapse kinetics agrees with that of ref 4. No attempts have been made to separate the two modes, representing translational motions of single coils (fast mode) and of the aggregates (slow mode). Thus, the average hydrodynamic radius, which exhibited a two-stage kinetics, showed an apparent increase in R_h due to the presence of a small amount of aggregates and a corresponding increase in variance ($\mu_2/\bar{\Gamma}^2$) at about 600 s after the initial jump. After the second jump (from 28 to 35 °C), the initial recovery time to the Θ-coil size appeared to be very fast. In a couple of hundreds of seconds, R_h appeared to have reached close to about 90% of its Θ-state value, as shown in Figure 2b. The Θ-state value was recovered in about a few thousand seconds, as demonstrated by three separate runs (plus signs, hollow triangles, and hollow circles in Figure 2a). Thus, the chain-knotting process probably plays a minor role in the coil−globule transition process for a polystyrene globule which has been quenched to a hydrodynamic radius of ~20 nm. More precisely, if the chain-knotting process is present, the knotting and deknotting times for the particular class of knots which can be observed within our experimental time range are comparable. It is noted that we have not excluded all classes of knots as a mechanism for the coil-to-globule transition.

Sequence B. Figure 3 shows plots of R_h and $\mu_2/\bar{\Gamma}^2$ as a function of elapsed time after a temperature jump from −120 to 35 °C. There was no assurance for the polystyrene in cyclohexane to have reached the collapsed globular state. Over the short time period for the polymer coils to contract, the solvent cyclohexane would be frozen, preventing the coil from reaching the collapsed globular state. Upon heating at 35 °C, the polymer coil recovered to its Θ state in less than a thousand seconds, as shown by the sequence of size

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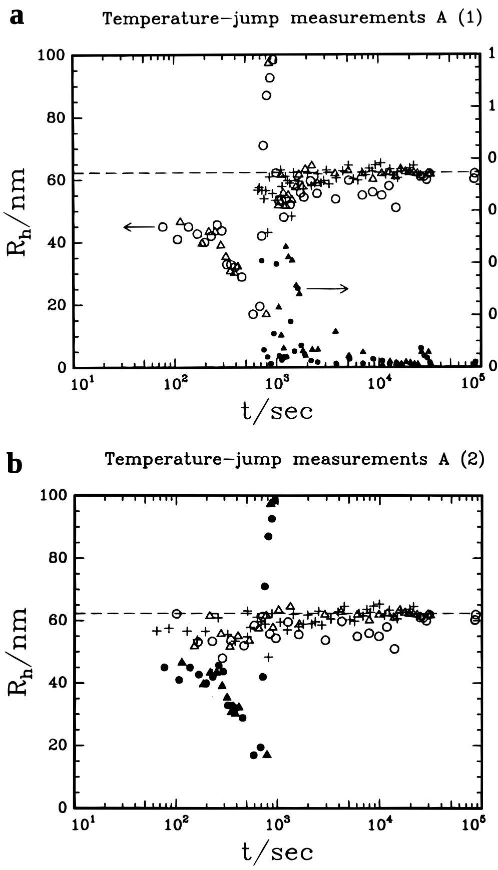

Figure 2. Temperature-jump experiment based on sequence A of Figure 1. (a) Hydrodynamic radius (hollow symbols) and μ_2/Γ^2 (filled symbols) of PS in cyclohexane in the coil-to-globule and globule-to-coil transitions. The starting time (t = 0) corresponds to the time of the first jump from 35 to 28 °C. The time axis is expressed in logarithm of time in order to ascertain the equilibrium hydrodynamic radius of the Θ coil. (b) The same hydrodynamic radius is plotted with two separate starting times. For the coil-to-globule transition (filled symbols) the starting time (t = 0) corresponds to the time of the first jump from 35 to 28 °C, as shown in (a). Then, after 800–900 s at 28 °C, the sample temperature was jumped from 28 to 35 °C (new t = 0) for the globule-to-coil transition (open symbols). The various symbols denote independent separate runs. In the coil-to-globule transition, an increase in the average hydrodynamic radius R_h denotes an increase in the amount of aggregate. See ref 4 for definition of R_h and μ_2/Γ^2.

distribution plots from CONTIN (see ref 4). It is noted that at $t \approx 500$ s, $\langle R_h \rangle_{ave}$ ($\equiv R_h$) = 36 nm, as shown in Figure 3a, indicating that quick quenching has contracted the polymer coil with no proof of achieving the collapsed globular state.

Sequence C. In order to ensure sufficient time for the polymer coil to reach the collapsed state, sequence C of Figure 1 first followed the initial two steps of sequence B, i.e., by quenching the polymer solution to −120 °C and equilibrating at −120 °C for 40 s. Then, the frozen solution was quickly heated to near the melting point of cyclohexane (~6 °C) in order for the partially collapsed polystyrene coil to have an opportunity to contract further. A time period of 917 s was based on the results of sequence A (Figure 2), which showed that about 900 s was available for chain contraction from 35 to 28 °C. The solvent viscosity should be higher near its melting point, and consequently, the slower aggregation process and lower temperature should permit this experimental procedure to produce a *smaller* collapsed globule at ~6 °C without appreciable aggregation. The fluctuations of the results, as shown in Figure 4, prevented us from making a definitive quantitative statement. Nevertheless, it appears to show that, in the presence of a small amount of aggregates which could slow down the apparent recovery process, the collapsed globule prepared by sequence C took a slightly longer time to reach the equilibrium Θ-coil value.

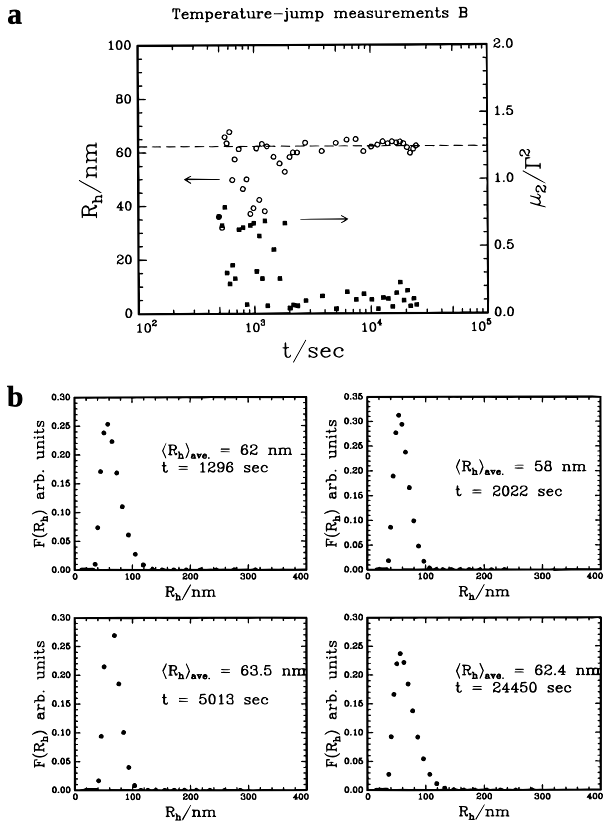

Figure 3. Temperature-jump experiment based on sequence B of Figure 1. (a) Hydrodynamic radius (R_h, hollow circles) and variance (μ_2/Γ^2, filled squares) as a function of elapsed time (t = 0 when the sample temperature jumped from −120 to +35 °C). (b) Selected average hydrodynamic radius $\langle R_h \rangle_{ave}$ and size distribution $F(R_h)$ fron CONTIN (see ref 4) as a function of elapsed time, in order to show that the contracted coils could be recovered to the Θ state within a comparable time period of 10^3 s.

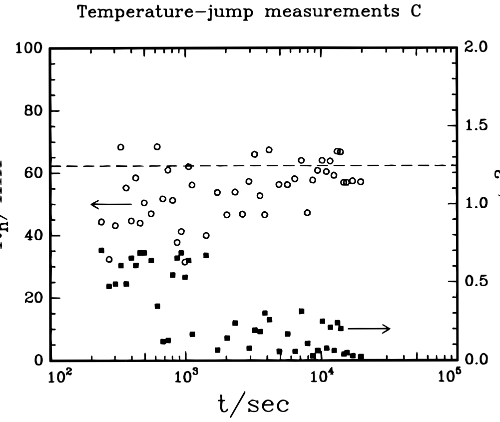

Figure 4. Temperature-jump experiment based on sequence C of Figure 1. Plots of R_h (hollow circles) and μ_2/Γ^2 (filled squares) as a function of elapsed time, with the starting time corresponding to the last temperature jump from ~6 to 35 °C. The recovery time appeared to be slower, although the presence of aggregates (as indicated by the higher values of μ_2/Γ^2 during 10^3–10^4 s) could not be ignored.

In conclusion, when compared with the coil-to-globule transition time of 10^2 s, the recovery time from the collapsed globule ($R_h \sim 20$ nm) to the Θ coil ($R_h \sim 63$ nm) appeared to be comparable even though it appeared to take a somewhat longer time ($\sim 10^3$ s) to reach the final 10% of the Θ-coil value. However, if the collapsed coil could be made more compact, as shown in sequence C, the final recovery time seemed to increase, although the higher variance suggested the presence of aggregates which also took a longer time to dissolve. Thus, chain knotting, at least the type with knotting times much faster than deknotting times, does not appear to play a dominating role in the (slow) coil–globule transition process, in contrast with the de Gennes type theory,[1] which predicted a much faster process.

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References and Notes

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