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Slow Expansion of a Single Polymer Chain from the Knotted Globule

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ABSTRACT: Knot formation in a single polymer chain was studied by measuring chain expansion processes from a globule to a coil state. Dilute solutions of poly(methyl methacrylate) in the mixed solvent *tert*-butyl alcohol + water(2.5 vol %) were preserved in a globule state at 25.0 °C for a time period t_p and given a fast temperature jump to the θ temperature 41.5 °C to measure the chain expansion process by static light scattering. The chain expansion occurred slower with increasing t_p for the molecular weight $M_w = 1.22 \times 10^7$. For the constant time period $t_p = 7200$ min, the expansion process became slower with increasing M_w from 4×10^6 to 1.5×10^7. These observations disclose the knot formation in a single polymer chain.

Introduction

When a very dilute polymer solution is quenched into far below the θ temperature, polymer chains may collapse to compact globules of small size, while for an abrupt temperature rise from a globule state to a coil state, the polymer chains may undergo chain expansion. It has been argued that knots may be formed in a globule state and affect the chain collapse and chain expansion processes drastically.[1−3] In particular, the chain expansion process might be constrained strongly by tight knots.[3−5] However, the knot formation in a single globule has not been observed experimentally because of the chain aggregation due to phase separation. In this study, chain expansion processes from globule states were measured under various conditions, and the knot formation in the globule states was concluded from the characteristic behavior of the observed expansion processes.

The chain collapse process after an abrupt decrease of temperature has been analyzed on the basis of a phenomenological model and predicted to occur through two stages of different mechanisms.[1,2] In the first stage, the chain shrinks fast in a self-similar manner of crumpling, and in the second stage the crumpled globule contracts slowly to an equilibrium globule forming knots by means of reptation-like motion of chain.[2,3] The characteristic time of the chain collapse was predicted as $\tau_{\text{crump}} \sim \tau_0(\Delta T/\theta)N^2$ for the first stage and $\tau_{\text{rep}} \sim \tau_0(\Delta T/\theta)N^3(na^3)^2/N_e$ for the second stage, where N is the segment number per chain, N_e is the segment number in an effective entanglement length, $\Delta T = \theta - T$ is a quench depth from the θ temperature, a is the segment size, n is the globule density, and τ_0 is a microscopic time given by $\eta a^3/k\theta$.[1,2] Here, η is the viscosity coefficient of solvent and k is the Boltzmann constant.

By analogy with ropes and threads, a chain expansion process from a globule would be constrained by knots which would be formed during preservation in a globule state. For a rapid chain expansion from the globule state, loose knots may change into tight knots which are to constrain the chain expansion drastically.[4,5] Rabin et al. discussed an experimental possibility to measure metastable globules due to tight knots, which would be formed by a fast temperature jump in a time τ_{jump} ($\ll\tau_{\text{rep}}$).[3] For a slow-temperature rise in a time τ_{jump} ($>\tau_{\text{rep}}$), the chain expansion would occur as a reverse process of the chain collapse.

In previous studies, we measured chain collapse processes for poly(methyl methacrylate) (PMMA) in the single solvent isoamyl acetate and in the mixed solvent *tert*-butyl alcohol + water(2.5 vol %) by static light scattering.[6,7] The chain collapse was observed to occur for a time period from hours to weeks, depending on the solvent, molecular weight, and temperature, and in a single stage. The chain collapse process was considerably slower in the mixed solvent than in isoamyl acetate. For polystyrene of the molecular weight $M_w = 8.1 \times 10^6$ in cyclohexane, Chu et al. observed a two-stage collapse process with the characteristic times of 357 and 323 s in the first and second stages, respectively.[8] Because of the close characteristic times, this observation cannot be compared with the theoretical prediction of the two-stage collapse seriously.

It has been tried to measure a chain expansion process from globule to coil. For polystyrene in cyclohexane[9] and poly(*N*-isopropylacrylamide) in water,[10] the expansion process of the polymer chains was too fast to be followed by the experiments. For PMMA with $M_w = 1.22 \times 10^7$ in isoamyl acetate, a static light scattering measurement were carried out for a solution preserved in a globule state for a week.[6] The measurement yielded the expansion factor α^2 for the radius of gyration as 0.93 at 30 min and 0.99 at 90 min after a sudden temperature rise from the globule state to the θ-condition. This experiment suggests a possibility of observing a chain expansion process of PMMA in solutions. Thus, in this study, chain-expansion experiments were carried out for dilute solutions of PMMA in the mixed solvent *tert*-butyl alcohol + water(2.5 vol %), since the dilute solutions yield very slow phase separation and can be kept in a globule state for a long time period without chain aggregation.[7,11] Furthermore, we anticipated that the very slow chain collapse in the mixed solvent would give rise to a sufficiently slow chain expansion for our experimental observations.

Experimental Section

Sample Preparation. The PMMA samples used in the present study have the molecular weight $M_w \times 10^{-6} = 4.0$, 8.4, 12.2, and 15.0 and were designated as M19-F12, M21-F6,

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M21-F9, and M23-F6, respectively. The samples M19-F12 and M21-F9 were employed in the previous study, and M21-F6 belongs to the same fraction series as M21-F9.[7] To obtain PMMA of very large molecular weight, purified monomer was polymerized in the absence of initiators and solvents in the dark at 50.0 °C for 52 h. The PMMA was fractionated into 14 fractions by the solution method in the mixture of benzene and methanol. The sample M23-F6 was the sixth fraction in the fraction series. The molecular weight distribution has been estimated to be $M_w/M_n \sim 1.20$ for M19-F12 and M21-F9 from the characteristic ratio measured with isoamyl acetate.[6] A comparable value of M_w/M_n was also suggested for M21-F6 and M23-F6 from characteristic ratios observed with the same solvent. *tert*-Butyl alcohol and water were purified by standard methods.

Light Scattering. For the light scattering experiment, a stock solution was prepared and was diluted in optical cells to obtain four solutions near the concentration c (10^{-4} g/cm^3) = 0.7, 1.4, 2.1, and 2.8. Each cell was sealed tightly with a Teflon cap and kept near the θ-temperature under the saturated vapor of the solvent for a few days to sediment impurity particles to the bottom in the cell, which made optical clarification effectively. Then, the optical cell was transferred into a cylindrical cell filled with the solvent at the center in the photometer, and the measurement of scattered light was started 30 min after the setup of the cell on account of thermal equilibration. The temperature control of the cylindrical cell was made by means of a jacket, to which thermostated water was circulated. The scattered intensity was determined in the angular range 30°−135° with the incident light at 435.8 nm as described elsewhere.[6]

The refractive index increment dn/dc (cm^3/g) as a function of temperature t (°C) has been determined as $dn/dc = 0.0994 + 3.2 \times 10^{-4}t$ in the previous study.[7]

The light-scattering data obtained as a function of the angle θ were analyzed by the equation for the excess Rayleigh ratio R_θ[12]

$$(Kc/R_\theta)^{1/a} = M_w^{-1/a}\{1 + (1/3a)\langle s^2\rangle q^2 + (2/a)M_w A_2 c\} \quad (1)$$

with $K = (2\pi^2 n^2/N_A\lambda^4)(dn/dc)^2$ and $q = (4\pi n/\lambda)\sin(\theta/2)$, where N_A is Avogadro's number, λ is the wavelength of incident light in a vacuum, and n is the refractive index of solution. M_w, $\langle s^2\rangle$, and A_2 are the weight-average molecular weight, mean-square radius of gyration, and second virial coefficient, respectively. For an appropriate value of a, the plot of $(Kc/R_\theta)^{1/a}$ vs $\sin^2(\theta/2)$ may be represented by a straight line, and $\langle s^2\rangle$ can be determined reliably from the slope of the line.[12] In the present data analysis, we used $a = 2.0$ for $M_w \times 10^{-6} = 4.0$ and $a = 1.5$ for $M_w \times 10^{-6} = 8.4$, 12.2, and 15.0.

To determine the chain-expansion process as a time evolution of the expansion factor $\alpha^2 = \langle s^2\rangle/\langle s^2\rangle_0$, we first measured $\langle s^2\rangle_0$ at the θ temperature. Then, each optical cell was sealed in a glass tube under a saturated vapor of the solvent and preserved in a water bath thermostated at 25.0 °C. After an appropriate preservation time t_p, the cell was set in the photometer controlled at 25.0 °C and $\langle s^2\rangle$ was measured to determine the initial expansion factor α_0^2 at $t = 0$. Then, the temperature of the cell was raised quickly to the θ temperature 41.5 °C, and a time evolution of $\langle s^2\rangle$ was measured at a time interval of 30 min or so.

Results

Figure 1 shows light-scattering data in a chain-expansion process for $M_w = 1.22 \times 10^7$ by the Zimm plot due to eq 1 with $a = 1.5$. Plot a (○) was obtained at 25.0 °C for solutions preserved for $t_p = 49\,000$ min (34 days) at the temperature. Plots b (△) and c (□) were obtained for the solutions 30 and 330 min after an abrupt temperature rise from 25.0 to 41.5 °C. In each Zimm plot, the plots of $(Kc/R_\theta)^{1/1.5}$ vs $\sin^2(\theta/2)$ are represented by parallel straight lines and are extrapolated to $\theta = 0$ as shown by the filled symbols. The value of $\langle s^2\rangle$ was obtained from the slope of the parallel lines, and M_w was determined from the intercept at $c = 0$ of the straight line fitted to the filled symbols at $\theta = 0$. Plots a, b, and c give the molecular weight as $M_w \times 10^{-7} = 1.31$, 1.30, and 1.22, respectively. The value of $\langle s^2\rangle$ due to the plot a gives the initial expansion factor as $\alpha_0^2 = 0.064$. Plots b and c yield the expansion factor as $\alpha^2 = 0.186$ and 0.950, respectively. The Zimm plot determined at the equilibrium θ-condition overlapped plot c and was omitted. Values of $\langle s^2\rangle$ at various times after the temperature rise were determined with Zimm plots as in Figure 1 and used to describe the chain expansion process. The parallel straight lines for $\sin^2(\theta/2)$ dependence in each Zimm plot and the constant molecular weight within an experimental error demonstrate that the chain aggregation due to phase separation is negligibly small and does not affect the determination of $\langle s^2\rangle$. For the other solutions used in the present experiment, the light scattering data obtained at the time t_p after quench also yielded the correct molecular weight, and $\langle s^2\rangle$ was determined without being disturbed by an effect of chain aggregation.

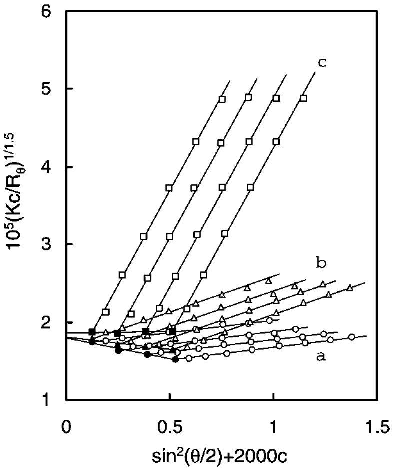

Figure 1. Zimm plots of $(Kc/R_\theta)^{1/1.5}$ as a function of $\sin^2(\theta/2)$ and c (g/cm^3) for $M_w = 1.22 \times 10^7$. Plot a (○) was obtained for solutions preserved at 25.0 °C for 49 000 min. Plots b (△)and c (□) were obtained 30 and 330 min after a temperature jump to 41.5 °C.

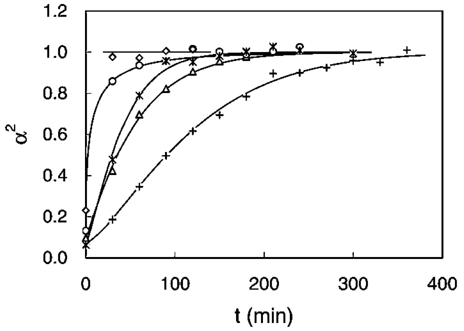

Figure 2. Chain-expansion processes for $M_w = 1.22 \times 10^7$ by the plot of α^2 (= $\langle s^2\rangle/\langle s^2\rangle_0$) vs t min after a temperature jump from 25.0 to 41.5 °C. The plots were obtained for solutions preserved for the periods t_p (min) = 30 (◇), 1440 (○), 7200 (△), and 49 000 (+). Plot (∗) was obtained for a solution preserved at 20.0 °C for t_p = 122 000 min. The curves are given by eq 2 with the values of β, τ, and α_0^2 in Table 1.

Figure 2 exhibits chain expansion processes for $M_w = 1.22 \times 10^7$ by plotting α^2 against the time t min after a temperature rise. The plots were obtained for the preservation times of t_p (min) = 30 (◇), 1440 (○), 7200 (△), and 49 000 (+). For t_p = 30 min, the PMMA chain

Table 1. Parameters of the Chain-Expansion Process in Eq 2 for PMMA of Molecular Weight M_w[a]

$M_w \times 10^{-6}$	t_p (min)	α_0^2	β	τ (min)
4.0	7200	0.103		
8.4	1600	0.126	0.61	12
	7200	0.098	1.03	46
	14400	0.086	1.22	50
12.2	30	0.234		
	1440	0.131	0.47	8
	7200	0.096	1.08	58
	7200[b]	0.093	0.97	48
	49000	0.064	1.32	132
	122000[c]	0.063	1.20	43
15.0	7200	0.112	0.81	112

[a] The process was obtained for solutions preserved at 25.0 °C for a time period t_p and given a temperature jump to 41.5 °C. [b] Obtained in a different experimental run. [c] Obtained for a solution preserved at 20.0 °C.

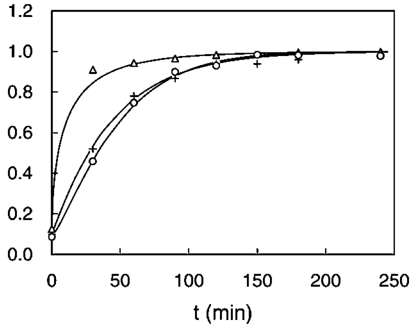

Figure 3. Chain-expansion processes after a temperature jump from 25.0 to 41.5 °C for $M_w = 8.4 \times 10^6$ as in Figure 2. The plots were obtained for solutions preserved for t_p (min) = 1600 (△), 7200 (+), and 14 400 (○). The curves are given according to eq 2.

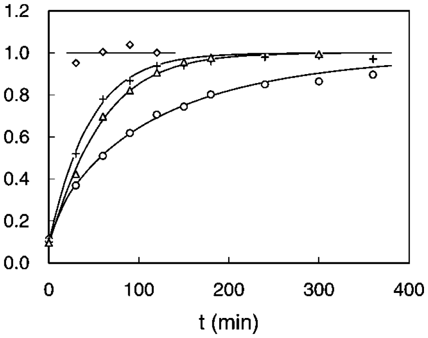

Figure 4. Chain-expansion processes after a temperature jump from 25.0 to 41.5 °C for $M_w \times 10^{-6}$ = 4.0 (◇), 8.4 (+), 12.2 (△), and 15.0 (○) for the constant period t_p = 7200 min. The curves are given according to eq 2.

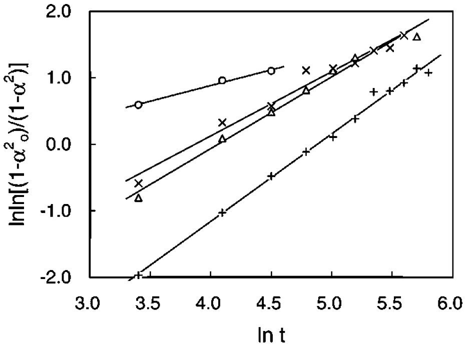

Figure 5. Chain-expansion processes for $M_w = 1.22 \times 10^7$ by the plot due to eq 2. The plots were obtained for t_p (min) = 1440 (○), 7200 (△) and 49 000 (+). Plot (×) was obtained in another experimental run for t_p = 7200 min.

expands fully to its equilibrium size within 30 min after the temperature rise. The values of α_0^2 at the initial state are given in Table 1. The dependence of α_0^2 on t_p at the constant temperature indicates a chain collapse process.

Figure 3 shows chain expansion processes for $M_w = 8.4 \times 10^6$. The plots were obtained for t_p (min) = 1600 (△), 7200 (+), and 14 400 (○). The latter two plots are close to each other.

Figure 4 shows chain expansion processes for various molecular weights for the constant time t_p = 7200 min. The plots were obtained for $M_w \times 10^{-6}$ = 4.0 (◇), 8.4 (+), 12.2 (△), and 15.0 (○). The plots for $M_w \times 10^{-6}$ = 8.4 and 12.2 are the same as those in Figures 3 and 2, respectively. For $M_w = 4.0 \times 10^6$, the PMMA chain expands fully within 30 min after the temperature rise, while for $M_w = 15.0 \times 10^6$ the chain expansion is very slow.

The observed chain expansion processes were represented by the stretched exponential function

$$\alpha^2 = 1 - (1 - \alpha_0^2)\exp[-(t/\tau)^\beta] \qquad (2)$$

where τ and β are constant independent of the time t. Figure 5 shows the plot of ln ln[(1 − α_0^2)/(1 − α^2)] vs ln t due to eq 2 for $M_w = 1.22 \times 10^7$. The plots are obtained for t_p (min) = 1440 (○), 7200 (△), and 49 000 (+). The plot with the point (×) was obtained for another experimental run for t_p = 7200. The close behavior of the two plots for t_p = 7200 indicates a reproducibility of the data. The values of τ and β were determined from the straight lines in Figure 5. Equation 2 also can be fitted to the data for the other molecular weights. The obtained values of τ and β are listed in Table 1. The curves in Figures 2−4 are described by eq 2 with these values.

Discussion and Conclusions

In previous studies, we found that the chain collapse of PMMA with $M_w = 1.22 \times 10^7$ in isoamyl acetate[6] and in the mixed solvent *tert*-butyl alcohol + water(2.5 vol %)[7] roughly required a few days and a few weeks, respectively. On the other hand, for PMMA with $M \sim 10^7$, the theoretical prediction of the two-stage collapse mentioned in the Introduction[1,2] gives $\tau_0 \sim 10^{-11}$ s, $\tau_{\mathrm{crump}} \sim 10^{-2}$ s, and $\tau_{\mathrm{rep}} \sim 10^0$ s with $N \sim 10^5$, $N_e \sim 10^2$, $\Delta T/\theta \sim 10^{-1}$, and $\eta \sim 10^{-3}$ Pa s. Here, the globule density n in τ_{rep} may be estimated by $n = (M/m)/\kappa(4\pi/3)\langle s\rangle_0^{3/2}\alpha^3$, which reduces to $n = 7.0 \times 10^{22}/M^{1/2}\alpha^3$ with the molecular weight $m = 100$ of monomer, $\kappa = (5/3)^{3/2}$ for a sphere of uniform density, and the characteristic ratio $\langle s^2\rangle_0/M = 6.3 \times 10^{-18}$ cm^2, from which the segment size is obtained as $a = 6.1 \times 10^{-8}$ cm. It is seen that the theoretical values of τ_{crump} and τ_{rep} are several orders smaller than the observed ones. A similar discrepancy between the experimental and theoretical values of the characteristic times is also known for polystyrene in cyclohexane. It has been argued that the solvent viscosity should be replaced by an effective viscosity on account of the high segment density in a globule.[1,8] The above expression for the globule density gives the segment concentration in the globule as $c_g = 11.7/M^{1/2}\alpha^3$, which ranges from 0.07 to 0.21 g/cm^3 for the values of M_w and α_0^2 in Table 1 except for the small value $c_g \sim 0.03$ g/cm^3 for $M_w = 1.22 \times 10^7$ and t_p = 30 min. However, an actual viscosity due to the high concentration does not seem to be important.[8] The PMMA chain with $M_w = 1.22 \times 10^7$ in the single solvent *tert*-butyl alcohol collapses to small globule of $\alpha^2 \sim 0.07$ within 90 min after quench.[13] The addition of a small amount of water(2.5 vol %) to *tert*-butyl alcohol could not be considered to increase the viscosity considerably.

In previous studies for the incipient phase separation of PMMA solutions, very slow aggregation of polymer chains were observed and ascribed to the reaction limited aggregation (RLA) because of the exponential growth of chain clusters.[11,14] Correspondingly, the observed slow chain collapse would be ascribed to the RLA of segments in a single chain. Thus, the microscopic time τ_0 ($\sim \eta a^3/k\theta$) is not legitimate for the PMMA solutions, but the knot formation in a globule state, which has been argued to constrain the chain collapse and chain expansion processes strongly,[1,2,5] would occur in a single polymer chain of large molecular weight irrespective of the rate of the chain collapse because of its universal nature. The knot formation was suggested to occur in the final stage of chain collapse for $N > N_e^2$ by de Gennes[1] and for $N > N_e g$ with $g \sim 1/(na^3)^2$ by Grosberg et al.[2] According to the latter relation, the knot formation is expected to occur in densely collapsed chains as well as in chains of large molecular weight. With $N_e = 184$ for PMMA,[15] N/N_e^2 for the present molecular weights has values from 1.2 to 3.5. $N/N_e g$ ranges from 7 to 60 depending on M_w and α_0^2 except for the small value $N/N_e g \sim 1$ for the process of $M = 1.22 \times 10^7$ and $t_p = 30$ min.

Figures 2 and 3 demonstrate that the chain expansion process at the constant M_w becomes slow with increasing t_p. Figure 4 indicates that the chain expansion process becomes slow with increasing molecular weight. These characteristics of the chain expansion process would be explained reasonably by the topological constraint due to knots formed during the preservation in globule state. Figure 4 implies that the chain length plays a predominant role in knot formation. Figures 2 and 3 can be seen as a t_p dependence of knot formation because of the small change of α_0^2. In the processes for $M = 4.0 \times 10^6$ and $t_p = 7200$ min and for $M = 1.22 \times 10^7$ and $t_p = 30$ min, polymer chains expand fully at 30 min after the temperature rise indicating negligibly small knot formation. This behavior is not incompatible with the condition for knot formation mentioned above.

The chain expansion processes in Figure 2 are measured by increasing t_p by several times in successive measurements. In Figure 3 the expansion processes for $t_p = 7200$ and 14 400 min are nearly same. Though t_p is only doubled between the two measurements, the expansion processes appear to suggest asymptotic behavior started from a globule with equilibrium knot density. However, to conclude the equilibrium knot density, it is necessary to carry out an experiment for solutions preserved for a much longer time period because the knot density would increase even after the size of globule reaches a constant value. Similarly, it is not clear whether the chain expansion processes for $M = 1.22 \times 10^7$ and $t_p = 49\,000$ min is an asymptotic one or not. Nevertheless, the preservation time t_p required for the topologically equilibrium globule is suggested to increase rapidly with increasing molecular weight.

It is relevant to mention a chain-expansion experiment carried out for a solution of $M_w = 1.22 \times 10^7$ preserved at 20.0 °C for $t_p = 122\,000$ min (85 days). In this experiment, the slope of the plot of $(Kc/R_\theta)^{1/1.5}$ vs $\sin^2(\theta/2)$ was determined at the low concentration $c = 0.7 \times 10^{-4}$ g/cm^3, because chain aggregation due to phase separation affected data at higher concentrations. Thus, the expansion factor was determined as a ratio of the slope determined in the process of chain expansion to that at the equilibrium θ-condition. On account of the long time period of t_p and the small value of α_0^2, the experiment was expected to yield a very slow chain expansion process. However, the observed chain expansion was not slow as shown by the plot with the points (∗) in Figure 2. In light of a universal nature of the reptation-like motion in a chain, the relatively fast chain expansion would not necessarily mean a low degree of knot formation. It should be recalled that the chain collapse process after quench to 20.0 °C was considerably fast.[7] Thus, the relatively fast chain expansion may have a correlation with the fast chain collapse, and consequently, the topological constraint by knots is obscured. As mentioned in Introduction, we have observed a fast chain expansion for PMMA with $M_w = 1.22 \times 10^7$ in isoamyl acetate.[6] The solution was preserved at 31 K below the θ-temperature for $t_p = 7$ days. This fast chain expansion also may be correlated with its relatively fast chain collapse but would be modulated by the constraint due to knots.

Finally, it is interesting to explore tight knots formed in a process of a rapid chain expansion.[3] In the present experiment the temperature jump requires the time period of $\tau_{\text{jump}} \sim 30$ min, which is much shorter than the observed chain collapse duration τ_{col} of days or weeks.[7] For the rapid temperature rise of $\tau_{\text{jump}} \ll \tau_{\text{col}}$, some of loose knots formed in the globule state would not be adjustable to disentanglement and be converted to tight knots, which could cause very slow chain expansion in a time $\tau_{\text{ex}}(\gg\tau_{\text{col}})$. The chain expansion duration τ_{ex} of hours seen in Figures 2−4 are obviously shorter than τ_{col} of days, and consequently the formation of tight knots is not suggested.

For lack of data points near $t = 0$ min, the initial expansion processes indicated by the solid line in Figures 2−4 cannot be taken seriously. However, it should be noticed that the value of β in Table 1 increases passing through unity with increasing t_p. Equation 2 gives different characteristics for $\beta > 1$ and $\beta < 1$ because the equation with $\beta > 1$ cannot be represented by a superposition of exponential functions with various relaxation times. Equation 2 gives an infinite initial rate for $\beta < 1$ and a vanishing rate for $\beta > 1$. To disclose a new aspect of the knot formation, it is important to carry out an experiment for initial chain expansion processes.

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