Slow knot formation by suppressed self-reptation in a collapsed polymer chain

Mitsuo Nakata, Yoshiki Nakamura, and Naoki Sasaki
Department of Polymer Science, Faculty of Science, Hokkaido University, Kita-ku, Sapporo 060-0810, Japan

Yasuyuki Maki
Department of Biological and Chemical Engineering, Faculty of Engineering, Gunma University, Kiryu 376-8515, Japan

(Received 24 April 2011; revised manuscript received 25 November 2011; published 10 February 2012)

Chain-expansion processes from knotted globules have been measured for poly(methyl methacrylate) (PMMA) in the mixed solvent tert-butyl alcohol (TBA) + water (2.5 vol %) by static light scattering. The solution was quenched from the Θ temperature of 41.5 °C to 37.0 °C, aged there for a time period t_{p}, and then returned rapidly to the Θ temperature. The chain-expansion process was determined as a time evolution of the expansion factor α^2 after the temperature increase. The measurement was carried out by changing the aging time t_{p} from 240 to 7200 min, and the molecular weight from $M_{\mathrm{w}} = 4.0 \times 10^6$ to 1.5×10^7, by taking advantage of the extremely slow chain aggregation in the solution. The chain-expansion process obtained for $M_{\mathrm{w}} = 1.22 \times 10^7$ became slow with increasing t_{p}, which revealed the knot formation in single globules. The characteristic time of the chain expansion from globules aged for $t_{\mathrm{p}} = 7200$ min was found to depend on the molecular weight as $M_{\mathrm{w}}^{2.7}$. This exponent, which is close to 3, demonstrated a disentanglement process due to self-reptation. The present data were compared with the previous data of the chain expansion from compact globules aged at 25.0 °C. The comparison made at $M_{\mathrm{w}} = 1.22 \times 10^7$ and at the same values of t_{p} revealed that the chain expansion from the globules aged at 25.0 °C was much faster than that from the globules at 37.0 °C, indicating a lower knot density in the more compact globules. It was conjectured that the knot formation due to self-reptation would be suppressed in a compact globule because an entire conformational change required by knot formation would become difficult to occur in the confined space of high segment concentration, particularly for a long polymer chain. The chain collapse of PMMA in the mixed solvent has been observed to occur extremely slowly at the later stage. This slow process was explained by the suppressed self-reptation.

DOI: 10.1103/PhysRevE.85.021802 PACS number(s): 83.80.Rs

I. INTRODUCTION

In a dilute polymer solution quenched into far below the Θ temperature, polymer chains collapse to compact globules, while on a sudden temperature rise, the globules undergo chain expansion. Since de Gennes first discussed the kinetics of chain collapse [1], many studies have been made for the chain-collapse process theoretically [2–4], experimentally [5–10], and by computer simulation [11–14]. According to the phenomenological theory [2], the chain collapse occurs at two stages: At the first stage, polymer chains collapse in a self-similar process of crumpling, and the topology of the swollen chain is reserved. At the second stage, the crumpled globules contract, forming knots by self-reptation. This contraction is realized by the penetration of the chain ends through the globules. The characteristic times at the first and second stages depend on the chain length N as N^2 and N^3, respectively. In subsequent studies [4,13], the chain collapse at the first stage was shown to proceed through multiple processes, such as formation of localized clusters along the chain, cluster growth by assimilating monomers, and coalescence into a single globule. The chain-collapse process can be determined by measuring the size of a chain as a function of the time after the quench. The knot formation in a single globule cannot be observed directly, but can be explored by measuring a chain-expansion process from the collapsed chain, because knots would act as a constraint for the chain expansion. It was argued that a rapid chain expansion would cause tight knots, by which the chain would be arrested in a metastable state of a partially collapsed conformation [15]. The structure of an arrested state and the chain expansion from a knotted globule were investigated theoretically and by using molecular dynamics simulation [16,17].

In a previous study [18], we observed the chain-expansion processes of poly(methyl methacrylate) (PMMA) in the mixed solvent tert-butyl alcohol (TBA) + water (2.5 vol %) for the molecular weight M_{w} ranging from 4×10^6 to 1.5×10^7. The dilute solution was preserved at 25.0 °C for a time period t_{p} after the quench from the Θ temperature of 41.5 °C and returned to the Θ temperature. The time period t_{p} for the aging of globules could be changed in the range of 30 to 50 000 min, taking advantage of the extremely slow phase separation in the solution. The size of the PMMA chains after the temperature rise was determined by static light scattering and expressed with the expansion factor $\alpha^2 = \langle s^2\rangle/\langle s^2\rangle_\Theta$, where $\langle s^2\rangle$ and $\langle s^2\rangle_\Theta$ are the mean-square radii of gyration at an instantaneous state and the Θ temperature, respectively. The chain expansion to $\alpha^2 = 1$ required various times up to about 500 min, depending on t_{p} and M_{w}. The initial expansion factor α_{o}^2, from which globules began to expand, changed to some extent in the experimental range of t_{p}, and was close to α_{eq}^2 of equilibrium globules at large t_{p}. The chain-expansion process was found to become slow with increasing t_{p} and M_{w}, though α_{o}^2 was insensitive to t_{p}. This chain-expansion behavior was interpreted as due to knot formation during the time period t_{p} at the globule state. Recently, the knot formation during chain-collapse processes was studied by a dynamics Monte Carlo simulation [19]. The knot formation was shown to develop more effectively with increasing chain length and with increasing quench depth. The time required for the relaxation to equilibrium knotted globules was predicted to be longer by an order of magnitude than that for the collapse to equilibrium size. Moreover, the collapse process was studied for a model polymer in which a short section of each end of the chain was kept under good-solvent conditions. The simulation with the heteropolymer chain demonstrated that the knotting was made by the tunneling of chain ends in and out of the globule, which substantiated the behavior of self-reptation [2]. These results of the simulation were compatible with the theoretical argument of the two-stage kinetics and also with our interpretation of the chain-expansion experiment in terms of knot formation. In the previous study [18], we measured an expansion process of the chain with $M_\mathrm{w} = 1.22 \times 10^7$ preserved at 20.0 °C for a time period $t_\mathrm{p} = 1.22 \times 10^5$ min (85 days) as an example of chain expansion from an aged compact globule. However, the chain expansion appeared to occur faster than that from a less compact globule aged at 25.0 °C for $t_\mathrm{p} = 7200$ min. This fast chain expansion conflicts with the Monte Carlo simulation [19], the phenomenological theory [2], and our intuitive notion on a flexible linear chain. In order to resolve this contradiction, it is necessary to compare the chain-expansion processes from globules aged at different temperatures.

In the present study, chain-expansion processes from globules aged at 37.0 °C were measured by static light scattering for the same polymer-solvent system as the previous one [18]. For PMMA of $M_\mathrm{w} = 1.22 \times 10^7$, the globules formed at 25.0 °C and 37.0 °C have different equilibrium expansion factors as $\alpha_\mathrm{eq}^2 = 0.062$ and 0.212, respectively [6]. Accordingly, the chain-expansion from the globule aged at 37.0 °C was expected to occur faster than that from the globule at 25.0 °C because of a lower degree of knotting in the less compact globule. Contrary to our expectation, however, the former chain expansion was much slower than the latter. This unexpected result required another viewpoint for knot formation in single globules. The equilibrium knot density in a globule would be determined by the size of the globule, while the kinetics of knot formation would be dominated by the mobility of the chain in the globule, as well as the size: The knot formation due to self-reptation requires an entire conformational change of the chain [2,19], and might become slow in a compact globule of high segment concentration. This consideration was compatible with the observed behavior of the chain-expansion processes and also of the chain-collapse processes [6].

II. EXPERIMENTAL AND DATA ANALYSIS

A. Light-scattering measurements

The PMMA samples used in this experiment are the same as those employed in the previous study and have the molecular weights of $M_\mathrm{w} = 0.40 \times 10^7$, 0.84×10^7, 1.22×10^7, and 1.5×10^7 [18]. The molecular weight distributions of the samples were conjectured roughly to be $M_\mathrm{w}/M_\mathrm{n} \sim 1.2$ from the characteristic ratios determined in isoamyl acetate. TBA and water were purified by standard methods to prepare the mixed solvent TBA + water (2.5 vol %) for PMMA.

The light-scattering experiment was carried out for four solutions at different concentrations less than $c = 3 \times 10^{-4}$ g/cm^3. Each solution was prepared by diluting a stock solution in an optical cell. The cell was sealed tightly with a Teflon cap and kept in a glass tube at the Θ temperature of 41.5 °C under the saturated vapor of the solvent. Impurity particles were found to sediment to the bottom in the cell in a few days, which made optical clarification effectively [6]. The optical cell was set in a thermostatted cylindrical cell filled with the solvent in the photometer, and scattered light was measured 30 min later on account of thermal equilibration. The measurement was carried out in the angular range of 30° to 135°, with the incident light at 435.8 nm of a mercury arc.

The refractive index increment dn/dc (cm^3/g) of PMMA in the mixed solvent has been found to depend on the temperature t (°C) as $dn/dc = 0.0994 + 3.2 \times 10^{-4} t$, which gives 0.113 at 41.5 °C and 0.111 at 37.0 °C [6].

The light-scattering data were obtained as a function of the angle θ and concentration c, and were analyzed in terms of the excess Rayleigh ratio R_θ by [20]

$$(Kc/R_\theta)^{1/x} = M_\mathrm{w}^{-1/x}\{1 + (1/3x)\langle s^2\rangle q^2 + (2/x)M_\mathrm{w} A_2 c\}, \tag{1}$$

with $K = (2\pi^2 n^2/N_\mathrm{A}\lambda^4)(dn/dc)^2$ 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 the 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 x, the plot of $(Kc/R_\theta)^{1/x}$ versus $\sin^2(\theta/2)$ at each concentration gave a straight line, which was used to estimate $\langle s^2\rangle$. In the present data analysis, we used $x = 2.0$ for $M_\mathrm{w} \times 10^{-6} = 4.0$ and $x = 1.5$ for $M_\mathrm{w} \times 10^{-6} = 8.4$, 12.2, and 15.0. The parameter x was introduced to estimate $\langle s^2\rangle$ accurately from the light-scattering data of dilute solutions of extremely large molecular weights [20]. The data analysis by Eq. (1) has been demonstrated for various solutions of large M_w.

The chain-expansion process from globules aged at 37.0 °C was determined as a time evolution of the expansion factor $\alpha^2 = \langle s^2\rangle/\langle s^2\rangle_\Theta$. After a measurement of $\langle s^2\rangle_\Theta$ at the Θ temperature, each glass tube with an optical cell inside was transferred into a water bath controlled at 37.0 °C. After a time period t_p for the aging of globules, $\langle s^2\rangle$ was determined at 37.0 °C to obtain the initial expansion factor α_o^2 at $t = 0$. Then, the temperature of the cell was raised rapidly to the Θ temperature and $\langle s^2\rangle$ was measured at a time interval of 30 min or so.

B. Analysis of single chain behavior by the Zimm plot

Figure 1 shows light-scattering data during a chain-expansion process for $M_\mathrm{w} = 1.22 \times 10^7$ by using the Zimm plot due to Eq. (1) with $x = 1.5$. The plot (a) (circles) was obtained at $t_\mathrm{p} = 7200$ min (5 days) after the quench to 37.0 °C. The plots (b) (triangles) and (c) (squares) were obtained 60 and 960 min after a temperature rise to 41.5 °C, respectively. In each Zimm plot, the plots of $(Kc/R_\theta)^{1/1.5}$ versus $\sin^2(\theta/2)$ are represented by parallel straight lines and are extrapolated to $\theta = 0$, as shown by the filled symbols, which are further extrapolated to $c = 0$ by straight lines. The intercept at $c = 0$ gives M_w, and the slope of the parallel lines and the intercept yield $\langle s^2\rangle$. The plots (a), (b), and (c) give $M_\mathrm{w} \times 10^{-7} = 1.40$, 1.37, and 1.24, respectively. The former two values are slightly larger than $M_\mathrm{w} \times 10^{-7} = 1.22$, which

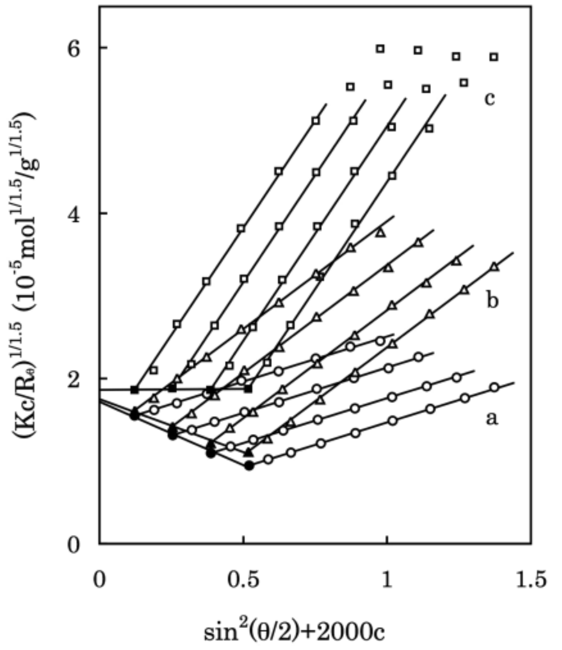

FIG. 1. Zimm plots of $(Kc/R_\theta)^{1/1.5}$ as a function of $\sin^2(\theta/2)$ and c (g/cm^3) for light-scattering data of PMMA with $M_w = 1.22 \times 10^7$ in the mixed solvent tert-butyl alcohol + water (2.5 vol %). Plot (a) (circles) was obtained 7200 min after the quench to 37.0 °C from the Θ temperature of 41.5 °C. Plots (b) (triangles) and (c) (squares) were obtained 60 and 960 min after the temperature jump to $\Theta = 41.5$ °C, respectively. The measurement was made at the concentrations $c(10^{-4}$ g/cm$^3) = 0.61$, 1.27, 1.93, and 2.58, which is far below $c^* = 0.0072$ g/cm^3 for coil overlapping.

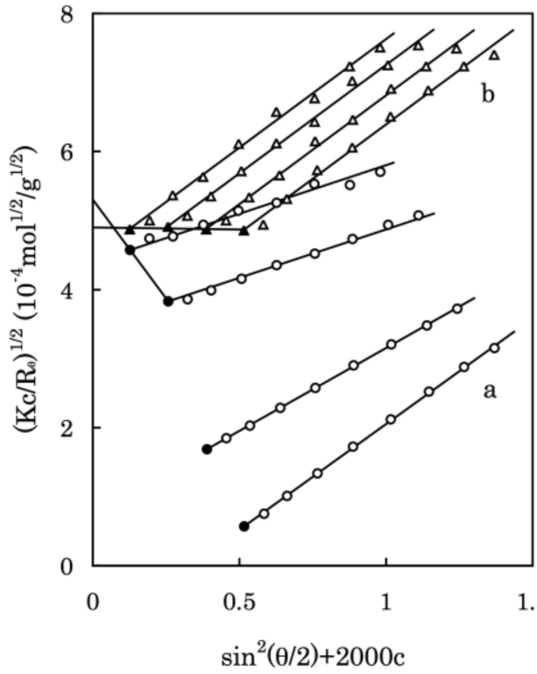

FIG. 2. Zimm plots of $(Kc/R_\theta)^{1/2}$ as a function of $\sin^2(\theta/2)$ and c (g/cm^3) for light-scattering data of PMMA with $M_w = 4.0 \times 10^6$ in the mixed solvent tert-butyl alcohol + water (2.5 vol %). Plot (a) (circle) was obtained 7200 min after the quench to 37.0 °C from the Θ temperature of 41.5 °C. Plot (b) (triangles) was obtained 60 min after the temperature jump to $\Theta = 41.5$ °C. The measurement was made at the concentrations $c(10^{-4}$ g/cm$^3) = 0.63$, 1.27, 1.93, and 2.57, which is far below $c^* = 0.0125$ g/cm^3 for coil overlapping.

would indicate an effect of chain aggregation. However, the slope of $(Kc/R_\theta)^{1/1.5}$ versus $\sin^2(\theta/2)$ in each Zimm plot is insensitive to the chain aggregation, as shown by the parallel straight lines. Thus, in order to avoid the uncertainty of the intercept at $c = 0$, we estimated the expansion factor $\alpha^2 = \langle s^2\rangle/\langle s^2\rangle_\Theta$ directly as a ratio of the slope at an instantaneous state to that at the equilibrium Θ state. Accordingly, the plots (a), (b), and (c) give $\alpha^2 = 0.208$, 0.498, and 0.988, respectively. The first value is comparable with $\alpha^2 = 0.212$ obtained as an equilibrium expansion factor [6]. The Zimm plot (c) indicates a recovery of the equilibrium Θ state.

The Zimm plot obtained for $M_w \times 10^{-7} = 0.84$ and 1.5 behaved as those in Fig. 1, and the plot of $(Kc/R_\theta)^{1/1.5}$ versus $\sin^2(\theta/2)$ yielded a slope independent of the concentration. Thus, the expansion factor was estimated from the slope as described above. For $M_w = 4.0 \times 10^6$, the measurement made 7200 min after the quench to 37.0 °C was affected by chain aggregation, as shown by the Zimm plot (a) (circles) in Fig. 2. The plots at the two higher concentrations are represented by straight lines with different slopes and are shifted below due to extra scattering from aggregates, while the straight lines for the plots at the two lower concentrations are described with the same slope, which was used to estimate α^2. The rough extrapolation to $c = 0$ with the two points gives a somewhat smaller molecular weight as $M_w = 3.6 \times 10^6$. The Zimm plot (b) (triangles) was obtained 60 min after the temperature rise to 41.5 °C. The straight lines have the same slope which yields $\alpha^2 = 0.98$. The extrapolation to $c = 0$ gives $M_w = 4.2 \times 10^6$. These values show a rapid recovery of the equilibrium Θ state.

III. THE CHAIN-EXPANSION PROCESS AND CHARACTERISTIC TIME

Figure 3 shows chain-expansion processes from globules aged at 37.0 °C for $t_p = 7200$ min by plotting α^2 against t (min) after the temperature rise to 41.5 °C. The plot is depicted for $M_w \times 10^{-7} = 0.40$ (triangles), 0.84 (diamonds), 1.22 (circles), and 1.5 (squares), with the initial expansion factors $\alpha_o^2 = 0.43$, 0.250, 0.208, and 0.203, respectively. For $M_w = 4.0 \times 10^6$, the chain expansion appears to finish within 30 min after the temperature increase. It is clear that the chain expansion becomes slow with increasing molecular weight.

Figure 4 exhibits chain-expansion processes from globules of $M_w = 1.22 \times 10^7$ aged at 37.0 °C. The plots are obtained for different aging times as $t_p = 240$ (squares), 1440 (triangles), and 7200 min (circles), with $\alpha_o^2 = 0.391$, 0.271, and 0.208, respectively. The plot for 7200 min is the same as that in Fig. 3. The chain-expansion process requires a longer time with increasing aging time t_p.

The observed chain-expansion processes have been represented by the stretched exponential function [18]

$$\alpha^2 = 1 - \left(1 - \alpha_o^2\right) \exp[-(t/\tau)^\beta], \tag{2}$$

where β and τ are constant independent of the time t after the temperature rise. Figure 5 represents the chain-expansion

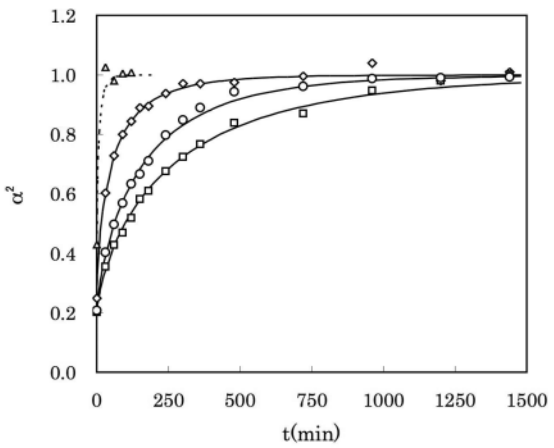

FIG. 3. Chain-expansion processes from globules aged at 37.0 °C for the time period 7200 min by the plot of the expansion factor α^2 vs the time t (min) after the temperature jump to $\Theta = 41.5\,^\circ\text{C}$. The plots were obtained for the molecular weights of $M_w \times 10^{-7} = 0.40$ (triangles), 0.84 (diamonds), 1.22 (circles), and 1.5 (squares). The solid and broken curves are described by Eq. (2).

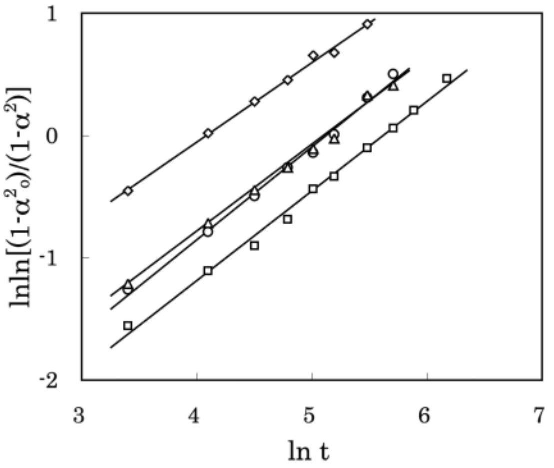

FIG. 5. Chain-expansion processes from globules aged at 37.0 °C for the time period 7200 min by the plot due to Eq. (2). The plots were obtained for $M_w \times 10^{-7} = 0.84$ (diamonds), 1.22 (circles), and 1.5 (squares) with the data in Fig. 3. The plot (triangles) was obtained by another experimental run for $M_w = 1.22 \times 10^7$.

processes given in Fig. 3 by plotting $\ln\ln[(1-\alpha_o^2)/(1-\alpha^2)]$ against lnt according to Eq. (2). The plots are for $M_w \times 10^{-7} = 0.84$ (diamonds), 1.22 (circles), and 1.5 (squares). Data in the range $\alpha^2 > 0.9$ were omitted because of a large uncertainty in $1-\alpha^2$. The plot with the triangles was obtained from another experimental run for $M_w = 1.22 \times 10^7$. The close behavior of the two plots indicates a reproducibility of the expansion process. The data in Fig. 4 were also represented by straight lines in the plot due to Eq. (2). The values of β and τ were determined from the straight lines. The plots for $t_p = 7200$ min at different M_w give $(\beta, \tau) = (0.65, 59\text{ min})$, (0.76, 168), and (0.73, 276) for $M_w \times 10^{-7} = 0.84$, 1.22, and 1.5, respectively. The plot with triangles gives $(\beta, \tau) = (0.71, 164\text{ min})$. The data for different t_p at $M_w = 1.22 \times 10^7$ in Fig. 4 yielded $(\beta, \tau) = (0.75, 30\text{ min})$ and (0.76, 85) for $t_p = 240$ and 1440 min, respectively. The solid curves in Figs. 3 and 4 are described by Eq. (2) with the above values of β and τ. Although the values of β and τ would contain experimental errors from various sources, the different experimental runs for $M_w = 1.22 \times 10^7$ and $t_p = 7200$ min yield comparable values for β and τ. Thus, the values of β and τ could be used for some numerical analysis. Since the values of β are nearly the same, the characteristic time of the chain expansion can be represented by τ, which increases with increasing t_p and M_w.

τ was assumed to depend on t_p and M_w as $\tau \sim t_p^z$ and $\tau \sim M_w^y$. Figure 6 shows the plots of $\ln\tau$ against $\ln t_p$ (triangles) and $\ln\,(M_w/20\,000)$ (circles). The straight lines are described with the slopes $z = 0.51$ and $y = 2.7$ due to a least-squares fit. The value of z would vanish in a range of large t_p because of an attainment of equilibrium knotted globules. In the plot of $\ln\tau$ versus $\ln t_p$, α_o^2 changes as 0.391, 0.271, and 0.208 for $t_p = 240$, 1440, and 7200 min, respectively, as given earlier.

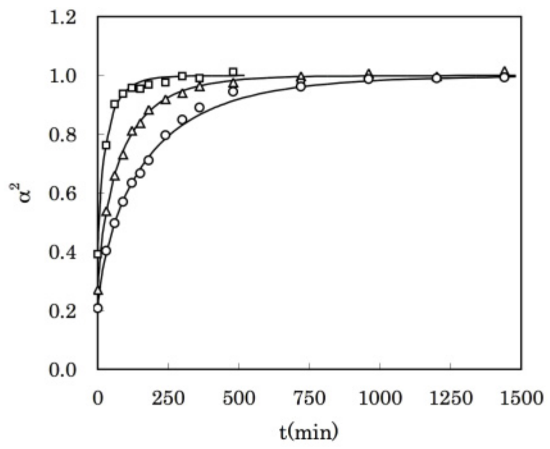

FIG. 4. Chain-expansion processes from globules aged at 37.0 °C for various time periods for $M_w = 1.22 \times 10^7$ by the plot of the expansion factor α^2 vs the time t (min) after the temperature jump to $\Theta = 41.5\,^\circ\text{C}$. The plots were obtained for the aging times of 240 (squares), 1440 (triangles), and 7200 min (circles). The solid curves are described by Eq. (2).

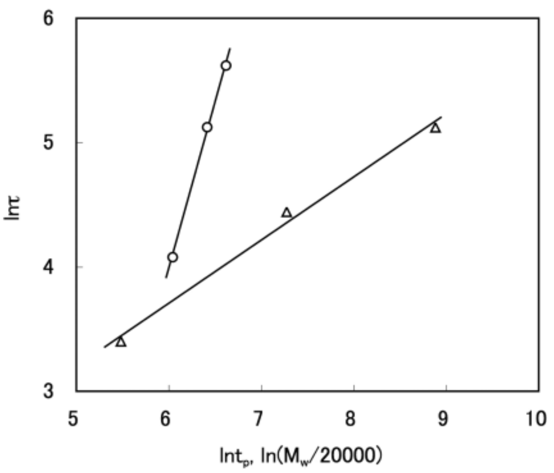

FIG. 6. Double logarithmic plots of the characteristic time τ (min) at $M_w = 1.22 \times 10^7$ as a function of the aging time t_p (min) (triangles), and τ for $t_p = 7200$ min as a function of M_w (circles).

The value of $\alpha_o^2 = 0.208$ is comparable with the equilibrium one, for which z could be estimated properly from the plot of $\ln\tau$ versus $\ln t_p$. A better estimation of z would be made by omitting the data for $t_p = 240$ min as $z \sim 0.4$. Although the relation between $\tau \sim t_p^{0.4}$ and the rate of knotting in a globule is not clear, it is suggested that the time scale to form equilibrium knotted globules is much longer than that of the chain collapse to equilibrium size, as predicted by the Monte Carlo simulation [19].

The plot of $\ln\tau$ versus $\ln(M_w/20000)$ in Fig. 6 gives $\tau = 1.71 \times 10^{-17} \times M_w{}^{2.68}$, which predicts $\tau = 8$ min for $M_w = 4.0 \times 10^6$. The broken curve in Fig. 3 is described by Eq. (2) with $\tau = 8$ min and the assumed value $\beta = 0.73$. The agreement of the broken line with the experimental observation supports the value of $y = 2.7$. The molecular weight dependence of $\tau \sim M_w^{2.7}$ with the exponent close to 3 suggests the disentanglement process due to the self-reptation, $\tau \sim M_w^3$. In a previous study [8], we compared the chain-collapse processes obtained for different molecular weights and conjectured that the characteristic time of the process depends on the molecular weight as M_w^3. This result was compared with the self-reptation process at the second stage of the phenomenological theory [2], though the experimental time scale of chain collapse was several orders of magnitude larger than the theoretical prediction of $\tau_{\text{rep}} \sim 10^0$ sec. The process of chain expansion from aged globules was suggested to be a reverse process of a chain collapse in view of self-reptation [15].

IV. KNOT FORMATION AND SELF-REPTATION

A. Comparison of the chain-expansion processes from globules aged at 25.0 °C and 37.0 °C

The present expansion processes from globules aged at 37.0 °C were compared with those from globules aged at 25.0 °C obtained in a previous study [18]. In Figs. 7 and 8, a comparison between the data for 37.0 °C (circles) and for 25.0 °C (triangles) is made for $M_w = 1.22 \times 10^7$ at the time $t_p = 1400$ and 7200 min, respectively. The solid lines are described by Eq. (2) to make the graphical comparison clear. The values of β and τ at 25.0 °C are less reliable because of the rapid chain expansion. However, β was estimated to be around unity, except for the processes for which β was obtained nominally for lack of a data point [18]. It is noticeable that the expansion processes from globules at 37.0 °C are slower than those from globules at 25.0 °C, though the initial expansion factors at 37.0 °C are larger than those at 25.0 °C. This observation conflicts with the consideration that the knot formation would proceed effectively in compact globules [2]. The plot with squares in Fig. 8 represents the expansion process from globules aged at 20.0 °C for $t_p = 1.22 \times 10^5$ min (85 days) [18]. In spite of the very long aging time, this process is much faster than that at 37.0 °C and comparable with that at 25.0 °C. This unexpected behavior motivated the present study, as mentioned in Sec. I. In the previous study, this fast chain expansion was argued to be correlated with the very fast chain collapse observed at 20.0 °C [6], because both the chain collapse and chain expansion were considered to be associated with a same nature of the polymer-solvent system. Light-scattering behavior suggested an abrupt change of the nature of the solution at 20.0 °C, as described later. However, the slower chain expansion from globules aged at 37.0 °C than at 25.0 °C cannot be attributed to a change of the nature of the system. It is necessary to examine the expansion behavior from a different viewpoint.

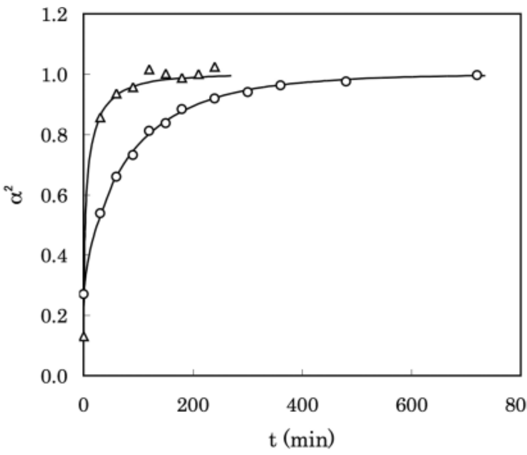

FIG. 7. Comparison of the chain-expansion processes from globules aged at 25.0 °C (triangles) and 37.0 °C (circles). Both of the processes were obtained for the aging time $t_p = 1400$ min and $M_w = 1.22 \times 10^7$. Data at 25.0 °C is from Ref. [18].

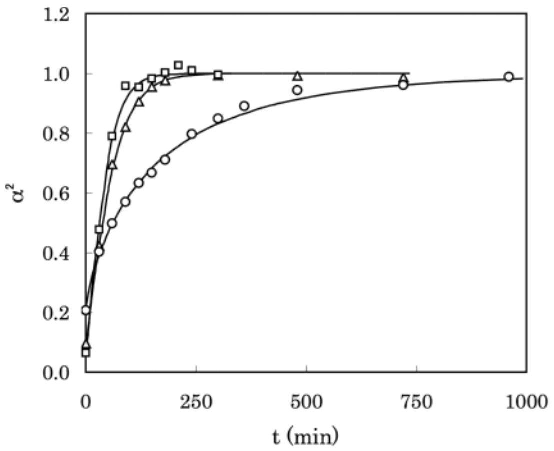

FIG. 8. Comparison of the chain-expansion processes from globules aged at 20.0 °C (squares), 25.0 °C (triangles) and 37.0 °C (circles) for $M_w = 1.22 \times 10^7$. Both of the latter two processes were obtained for the aging time $t_p = 7200$ min. The former process was obtained for $t_p = 122\,000$ min. Data at 20.0 °C and 25.0 °C are from Ref. [18].

B. Chain expansion and chain collapse by suppressed self-reptation

In the previous study [6], the chain-collapse processes for $M_w = 1.22 \times 10^7$ were measured at various quench temperatures for very long time periods of 2×10^4 to 5×10^4 min in pursuit of the equilibrium expansion factors α_{eq}^2. Figure 9 shows the early part of the collapse processes at 37.0 °C (circles), 25.0 °C (triangles), and 20.0 °C (diamonds). The horizontal short lines at the right indicate the obtained values of $\alpha_{\text{eq}}^2 = 0.212$, 0.062, and 0.053 at 37.0 °C, 25.0 °C, and 20.0 °C, respectively, and the difference $\alpha^2 - \alpha_{\text{eq}}^2$ at 1500

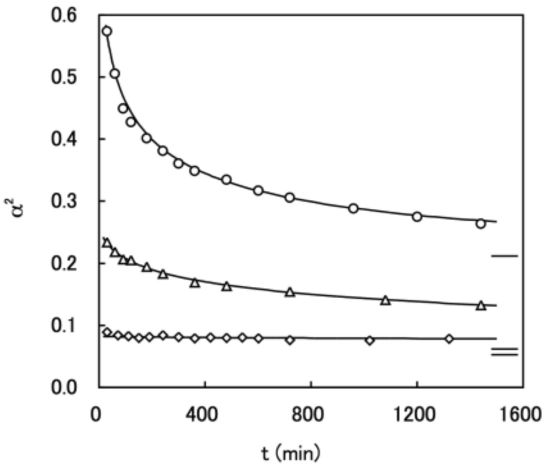

FIG. 9. Chain-collapse processes for $M_w = 1.22 \times 10^7$ by the plot of α^2 vs t (min) after the quench to 37.0 °C (circles), 25.0 °C (triangles), and 20.0 °C (diamonds) from the Θ temperature of 41.5 °C. Short lines at the right represent the equilibrium expansion factor $\alpha^2_{\text{eq}} = 0.212$, 0.062, and 0.053, at 37.0 °C, 25.0 °C, and 20.0 °C, respectively. Data are from Ref. [6].

min after the quench was estimated to be 0.055, 0.069, and 0.023, accordingly. Although the initial chain collapse at 25.0 °C appears to occur much faster than that at 37.0 °C, the difference $\alpha^2 - \alpha^2_{\text{eq}}$ at 25.0 °C is larger than that at 37.0 °C. The expansion factor at 20.0 °C decreases to $\alpha^2 \sim 0.09$ in the first 30 min after the quench and approaches $\alpha^2_{\text{eq}} = 0.053$ very slowly, indicating somewhat different behavior from that at 25.0 °C and 37.0 °C. The measurement of the chain-collapse process was carried out for a time period of 5×10^4 min at 20.0 °C and 25.0 °C, and for 2×10^4 min at 37.0 °C because of the very slow collapse at the later stage. The effect of chain aggregation on the measurement was negligibly small at 25.0 °C and was slightly observed at 37.0 °C. However, the behavior of the chain aggregation changed abruptly at 20.0 °C depending on the concentration. The solution at the highest concentration of 2.3×10^{-4} g/cm^3 yielded strong forward scattering 150 min after the quench, while the scattering from the solution at the lowest concentration of 0.6×10^{-4} g/cm^3 showed no sign of chain aggregation during the time period 5×10^4 min. Thus, expansion factors at 20.0 °C were estimated by using the slope of the plot of $(Kc/R_\theta)^{1/1.5}$ versus $\sin^2(\theta/2)$ at the lowest concentration. It has been observed for dilute solutions of PMMA in various solvents in the range $c < 5 \times 10^{-4}$ g/cm^3 that the chain aggregation becomes effective after the chain collapse finishes [9,21,22]. This observation suggests that the characteristic times of chain collapse and chain aggregation are dominated similarly by a property of the solvent. A recent experiment disclosed a relation between the characteristic times quantitatively [23]. Thus, the rapid chain collapse at 20.0 °C would be concerned with the same specific nature of the solvent that caused the fast chain aggregation, because even the segment concentration of 7.2×10^{-3} g/cm^3 in the polymer domain at the Θ temperature is much higher than the solution concentration of 2.3×10^{-4} g/cm^3 at which the rapid chain aggregation was observed.

Aside from this peculiar behavior at 20.0 °C, the characteristic features of the chain-collapse processes in Fig. 9 are affected by the knot formation due to self-reptation. The knot formation requires an entire change of the chain conformation [19]. It is conceivable that such a conformational change may become difficult to occur with increasing compactness of the globule. Thus, the faster chain expansion from globules at 25.0 °C than at 37.0 °C shown in Figs. 7 and 8 would be interpreted by the restricted knot formation in compact globules at 25.0 °C. Correspondingly, the very slow chain contraction after the rapid collapse at 25.0 °C may be attributed to the suppressed self-reptation in the compact globule. According to the chain-expansion behavior in Fig. 4, the collapse process at 37.0 °C in Fig. 9 accompanies topological relaxation even before 240 min, at which the expansion factor remains as large as $\alpha^2 = 0.39$. It seems that the chain of $\alpha^2 = 0.39$ would maintain high mobility and undergo topological relaxation easily. In the subsequent process up to 1440 min, the chain collapse reaches $\alpha^2 = 0.271$ relatively fast, forming a knot. In the next process up to 7200 min, the chain collapse proceeds to $\alpha^2 = 0.208$ slowly due to topological relaxation. The knotted globule at 7200 min is still far from the equilibrium one, as indicated by the plot in Fig. 6. In light of the above argument, the fast chain expansion from the globule aged at 20.0 °C for the very long time $t_p = 1.22 \times 10^5$ min may be consistent with the extremely slow chain collapse after the rapid collapse shown in Fig. 9: The knot formation cannot follow the rapid collapse at the initial stage and may become very difficult to occur in the compact globule of $\alpha^2 \sim 0.09$. Thus, the subsequent slow chain contraction observed over a time period of 5×10^4 min is likely to be ascribed to the strongly restricted self-reptation. The very compact globules may be difficult to undergo coalescence, which requires entanglement of two chains during the contact time [24,25]. As to the rapid collapse to a compact globule and fast chain expansion, the globule at 25.0 °C can be compared with that at 20.0 °C. It should be recalled that the chain aggregation was not observed at 25.0 °C during the time period of 5×10^4 min [6]. The different behavior of globules at 25.0 °C and 37.0 °C described above was assumed to explain the memory effect observed in a temperature perturbation experiment [26].

V. DISCUSSION

A. Empirical representation of chain-collapse process

In the previous study [6], the collapse process was expressed with the equation

$$\alpha^2 = \alpha^2_{\text{eq}} + \left(1 - \alpha^2_{\text{eq}}\right) \exp\left[-(t/\tau_c)^{\beta_c}\right], \tag{3}$$

where τ_c and β_c were constant independent of the time t after the quench into below the Θ temperature. The plot of $\ln\ln[(1 - \alpha^2_{\text{eq}})/(\alpha^2 - \alpha^2_{\text{eq}})]$ versus $\ln t$ yielded a straight line, from which the values of (β_c, τ_c) were determined as (0.30, 57.2 min) at 37.0 °C; (0.122, 0.57 min) at 25.0 °C; and (0.037, 5.6×10^{-13} min) at 20.0 °C. The values at 20.0 °C are nominal for lack of data at small t. Equation (3), which involves only two parameters and satisfies the initial condition of $\alpha^2 = 1$ at $t = 0$, was useful to describe the behavior of chain-collapse processes measured for long time periods. However, the unreasonably small values of τ_c and β_c show that the behavior of α^2 for a

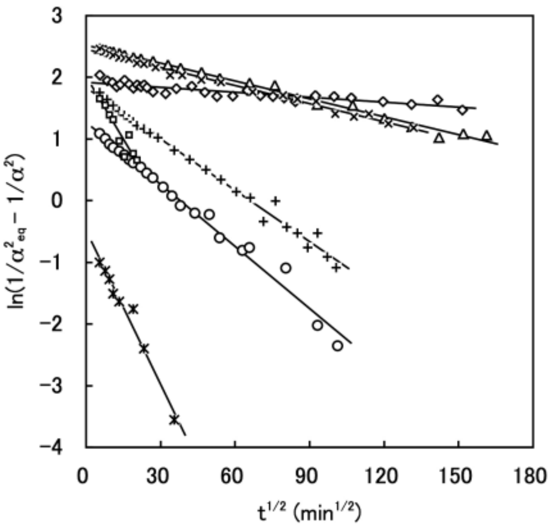

FIG. 10. Chain-collapse processes by the plot due to Eq. (5) with $\beta^* = 0.5$. The plots were obtained for $M_w = 1.22 \times 10^7$ at the quench temperatures of 20.0 °C (diamonds), 23.0 °C (x's), 25.0 °C (triangles), 35.0 °C (crosses), 37.0 °C (circles), and 39.0 °C (asterisks), and for $M_w = 4.0 \times 10^6$ at 25.0 °C (squares). Data are from Ref. [6].

long time period is not caused by a single mechanism. It is considered that the characteristic time would be determined reasonably by an equation with an effect of the suppressed self-reptation taken into account. With this anticipation, we assumed the differential expression

$$d\alpha^2/dt = -k\big(\alpha^2/\alpha_{\mathrm{eq}}^2\big)\big(\alpha^2 - \alpha_{\mathrm{eq}}^2\big)\beta^* t^{\beta^*-1}, \tag{4}$$

where k and β^* are constants and the factor $\alpha^2/\alpha_{\mathrm{eq}}^2$ is introduced to express the effect of suppressed self-reptation. Equation (4) without this factor yields Eq. (3) by using the initial condition. On the other hand, Eq. (4) gives

$$1/\alpha^2 = 1/\alpha_{\mathrm{eq}}^2 - B\exp(-kt^{\beta^*}). \tag{5}$$

As shown by a rapid initial collapse in Fig. 9, Eq. (5) cannot be expected to satisfy the initial condition of $\alpha^2 = 1$ at $t = 0$. In order to determine the three parameters B, k, and β^* in Eq. (5), $\ln(1/\alpha_{\mathrm{eq}}^2 - 1/\alpha^2)$ was plotted against t^{β^*} for the data of the collapse process by changing the value of β^*. Thus, the plot with $\beta^* = 0.5$ was found to give straight lines for the data at various temperatures [6]. Figure 10 shows the plot at 20.0 °C (diamonds), 23.0 °C (x's), 25.0 °C (triangles), 35.0 °C (crosses), 37.0 °C (circles), and 39.0 °C (asterisks). Data in the range $\alpha^2 - \alpha_{\mathrm{eq}}^2 < 0.01$ were not used on account of a large error. The different behavior of the straight line at 20.0 °C compared with the other ones reflects the peculiar collapse process mentioned earlier. The constants k and B were determined from the straight lines. Table I shows the characteristic time estimated by $\tau^* = 1/k^2$ and the expansion factor $\alpha^2(0)$ at $t = 0$ given by $1/\alpha^2(0) = 1/\alpha_{\mathrm{eq}}^2 - B$. The values of $\alpha^2(0)$ at the lower temperatures are much smaller than unity, which implies that the collapse process in the first 30 min after the quench is different from the process due to Eq. (5). τ^* becomes large with decreasing temperature and is comparable with the experimental time scale of the chain collapse. The ratio $\alpha^2(\tau^*)/\alpha_{\mathrm{eq}}^2$ was estimated roughly to be 1.4 for the processes at 23.0 °C, 25.0 °C, 35.0 °C, and 37.0 °C, and 1.15 at 20.0 °C and 39.0 °C. The latter two small values are concerned with the peculiar behavior at 20.0 °C and the large value of $\alpha_{\mathrm{eq}}^2 = 0.587$ at 39.0 °C. In light of the values of the ratio, the characteristic time τ^* is obtained with a weight on the slow process at the later stage. The lines in Fig. 9 are described by Eq. (5) with the values of τ^* and $\alpha^2(0)$ in Table I.

B. Comparison with two-stage kinetics

The phenomenological theory of the two-stage process of crumpling and a reptationlike mechanism is based on the globular state at which the segment density in a globule becomes independent of the molecular weight [2]. The two-stage collapse was conjectured from the argument that the knot formation may occur only in a compact globule [27]. Grosberg *et al.* derived the relaxation times of the first and second processes, respectively, as [2]

$$\tau_{\mathrm{crum}} = \tau_0 N^2/[1 + \mathrm{const}(\mathrm{a}^6/CN_{\mathrm{e}})], \tag{6}$$

$$\tau_{\mathrm{rep}} = \tau_0 N^3/N_{\mathrm{e}} g, \tag{7}$$

with

$$\tau_0 = \eta_{\mathrm{s}} \mathrm{a}^6 |B|/k_{\mathrm{B}}\Theta C. \tag{8}$$

Here, N is the number of chain segments, k_{B} is the Boltzmann constant, Θ is the Θ temperature, a is the segment size, η_{s} is the solvent viscosity, N_{e} is the entanglement length, and B and C are the two- and three-body interaction constants, respectively. g is the number of segments in a blob given by $1/(n_{\mathrm{eq}}a^3)^2$, where n_{eq} is the density of the equilibrium globule and is represented by $|B|/C$. For $N < gN_{\mathrm{e}}$, the chain collapse occurs in a single step of crumpling, while for $N > gN_{\mathrm{e}}$, the chain collapse occurs in two steps of crumpling and self-reptation.

In order to examine the globular state, the segment concentration $c_{\mathrm{eq}} = M_{\mathrm{w}}/\{N_{\mathrm{A}}(4\pi/3)[(5/3)\langle s^2\rangle]^{3/2}\}$ in the equilibrium globule was estimated by assuming the characteristic ratio $\langle s^2\rangle_\Theta/M_{\mathrm{w}} = 6.3 \times 10^{-18}$ cm^{2}mol/g, and using the equilibrium expansion factor α_{eq}^2 due to the theoretical equation in which the parameters for segment interactions have been determined with experimental data [6]. Accordingly, the concentration c_{eq} was calculated to be 0.19, 0.20, 0.20, and 0.21 g/cm^3 at 25.0 °C, and 0.019, 0.030, 0.035, and 0.038 at 37.0 °C for $M_{\mathrm{w}} \times 10^{-7} = 0.40$, 0.84, 1.22, and 1.5, respectively. c_{eq} at 20.0 °C was obtained as 0.28 g/cm^3 for $M_{\mathrm{w}} = 1.22 \times 10^7$. On the other hand, c_{eq} at the globular state was estimated to be 0.29, 0.22, and 0.057 g/cm^3 at 20.0 °C, 25.0 °C, and 37.0 °C, respectively. The globules at 20.0 °C and 25.0 °C are close to those at the globular state, while the globular state at 37.0 °C would be attained at much larger M_{w}, because c_{eq} remains to be 0.051 even at $M_{\mathrm{w}} = 8 \times 10^7$. Thus, the chain-collapse processes at 37.0 °C and 39.0 °C also should be compared with the theoretical prediction with some reservation.

The estimation of τ_0, τ_{crum}, and τ_{rep} was made by using the relation $|B|/C = c_{\mathrm{eq}}/(m/N_{\mathrm{A}})$ with $m = 100$ being the molecular weight of segment and the segment size $a = 6.1 \times 10^{-8}$ cm due to $\langle s^2\rangle_\Theta/M_{\mathrm{w}} = 6.3 \times 10^{-18}$ cm^2. τ_{crum} was obtained by neglecting the term of a^6/CN_{e} in the bracket. The solvent viscosity at each temperature was calculated from

TABLE I. Analyses of chain-collapse processes of PMMA of $M_w = 1.22 \times 10^7$ after quench into the indicated temperatures. α_{eq}^2 and c_{eq} are the expansion factor and segment concentration of an equilibrium globule, respectively. $\tau^* = 1/k^2$ and $\alpha^2(0) = 1/(1/\alpha_{eq}^2 - B)$ is due to (5). τ_{crum}, τ_{rep}, and τ_d in the ratios are given by Eqs. (6), (7), and (10), respectively. N/gN_e is a measure of the transition from the crumpling process of τ_{crum} to the self-reptation process of τ_{rep}. Data are from Ref. [6].

Temp. (°C)	α_{eq}^2	c_{eq}(g/cm^3)	$\alpha^2(0)$	τ^*(10^3 min)	N/gN_e	$10^{-5}\tau^*/\tau_{crum}$	$10^{-4}\tau^*/\tau_{rep}$	τ^*/τ_d
20.0	0.053	0.274	0.083	137	171	52	3.0	4.7
23.0	0.055	0.259	0.153	10.4	153	4.9	0.32	0.42
25.0	0.062	0.216	0.273	10.6	107	6.6	0.62	0.74
35.0	0.119	0.081	0.462	1.30	15.1	3.5	2.3	1.71
37.0	0.212	0.0342	0.860	0.89	2.7	6.1	23	15.7
39.0	0.587	0.0074	0.918	0.145	0.13	5.0	395	249
25.0[a]	0.081	0.253	0.205	0.221	48	1.1	0.23	0.83

[a] Obtained for $M_w = 4.0 \times 10^6$.

an empirical relation between η_s and the temperature, and N_e was assumed to be 100 [28]. The value of N/gN_e is given in Table I. On account of the small value of $N/gN_e = 0.13$, the chain collapse would occur in a single step of crumpling at 39.0 °C, which appears to be compatible with the value of $\alpha^2(0)$ close to unity. On the other hand, the value of N/gN_e suggests the collapse process of the two steps of crumpling and self-reptation at the lower temperatures. A transition from the single-step process to the two-step process is suggested to occur near 37.0 °C from $N/gN_e \sim 2.7$. Table I gives the ratios of τ^*/τ_{crum} and τ^*/τ_{rep} for a comparison of τ^* with the theoretical prediction. Except at 20.0 °C, τ^*/τ_{crum} seems to be constant, while τ^*/τ_{rep} decreases with decreasing temperature because of the factor N/gN_e. τ^* is several orders of magnitude longer than τ_{crum} and τ_{rep}.

In the previous study [6], the chain-collapse process was measured at 25.0 °C and 35.0 °C for $M_w = 4.0 \times 10^6$. The data were analyzed by Eq. (5) and the plot at 25.0 °C is shown with squares in Fig. 10. This plot yields $\alpha^2(0) = 0.205$ and $\tau^*{}_{40} = 221$ min, as shown in Table I. The data at 35.0 °C were not accurate enough for this analysis because of the rapid chain collapse. A comparison of τ_{40}^* with $\tau_{122}^* = 1.06 \times 10^4$ min for $M_w = 1.22 \times 10^7$ was made with the ratio $\tau_{122}^*/\tau^*{}_{40} = 48$, which is close to $(122/40)^{3.5} = 50$. This comparison supports the molecular weight dependence of M^3, which has been obtained experimentally in a previous study [8]. Thus, τ^* obtained at 25.0 °C is compatible with the large N/gN_e and should be compared with τ_{rep}. The large values of τ^*/τ_{rep} at 37.0 °C and 39.0 °C is attributed to the small value of N/gN_e, which indicates a transition from the self-reptation process to the crumpling process. On the other hand, the collapse process at 37.0 °C has been explained as a knot formation process on account of the expansion processes in Fig. 4. The chain-collapse behavior in the transition region cannot be predicted properly by the theory of the two-stage kinetics, and N/gN_e is a rough measure for a self-entanglement. An upper bound for the characteristic time of the self-reptation process would be given by $\tau_{rep,u} = \tau_0 N^3/N_e$ [15]. A close correlation between $\tau_{rep,u}$ and τ^* is recognized because of $\tau_{rep,u} = 1.22 \times 10^3 \tau_{crum}$, though τ^* is much longer than $\tau_{rep,u}$. The large numerical discrepancy between τ^* and τ_{rep} would stem from the use of the solvent viscosity η_s in τ_0. The viscosity η_s in dense globules has been argued to be replaced with a redefined viscosity or effective viscosity [1,5]. Nevertheless, the dependence of τ^* on the quench depth seems to be represented by τ_0 through $n_{eq} = |B|/C$.

The chain-collapse processes at 20.0 °C and 25.0 °C in Fig. 9 may be compared with the scenario of the theoretical prediction of two-stage kinetics. The compact globules observed 30 min after the quenches to 25.0 °C and 20.0 °C appear to be crumpled globules which maintain the topology at the swollen chain. In fact, the chain expansion from globules aged at 25.0 °C for 30 min finished within 30 min after the temperature rise to 41.5 °C [18]. The collapse process at 37.0 °C accompanies marked topological relaxation even in the range of large α^2, as shown in Fig. 4: In the collapse process at 37.0 °C, crumpling and self-reptation appear to occur at a comparable rate, while at 20.0 °C and 25.0 °C, crumpling causes rapid chain collapse to compact globules in which self-reptation occurs very slowly. Thus, the observed behavior of chain collapse is characterized by the competition between the rates of crumpling and self-reptation. In Fig. 9, the initial decrease of α^2 in the first 30 min after the quench is larger than the decrease during the subsequent process to an equilibrium globule. The initial chain collapse appears to become fast with decreasing temperature, contrary to the theoretical prediction of τ_{crum}. An experiment in the first 30 min after the quench is expected to disclose a new aspect of the chain collapse.

C. Other experimental studies on chain-collapse process

In order to observe the chain-collapse process, Chu *et al.* carried out a dynamic light-scattering experiment on polystyrene of $M_w = 8.0 \times 10^6$ in cyclohexane at $c = 8.7 \times 10^{-6}$ g/cm^3 [5]. The hydrodynamic radius after the quench from $\Theta = 35.0$ °C to 28.5 °C decreased to an equilibrium size of $R_h = 19.5$ nm in the two steps, with the characteristic time 357 s for the first step and 323 s for the second step. The chain collapse finished 10 min after the quench and, thereafter, an effect of the chain aggregation became perceptible. The observed characteristic times were much longer than the theoretical prediction of Eqs. (6) and (7). This discrepancy, which might be compared with the large ratios of τ^*/τ_{crum} and τ^*/τ_{rep} obtained for the present solution, remains unsolved.

Wu *et al.* made a fluorescence intensity measurement for pyrene-labeled poly(N-isopropylacrylamide) (PNIPAM) with $M_w = 3.64 \times 10^5$ [10]. A solution of PNIPAM-Py copolymer in pure methanol was mixed with an equal volume of water in a stopped-flow device. The ratio of excimer to monomer emission intensities was determined in the range $c < 2 \times 10^{-6}$ g/cm^3 for 5 s after the mixing, and was expressed by a double exponential function with the characteristic times of $\tau_{\rm fast} = 11.6$ ms and $\tau_{\rm slow} = 257$ ms. The former time was compared with that of the crumpling process of the two-stage model. However, the latter time was not explained reasonably because the self-reptational process was not conceivable for chains of the low molecular weight as $M_{\rm w} = 3.64 \times 10^5$. Wu *et al.* also carried out a fluorescence measurement on very dilute solutions of PNIPAM containing a fluorescence probe in the range of $M_{\rm w}$ from 1.2×10^6 to 2.3×10^7 [29]. The time dependence of fluorescence intensity obtained after the quench indicated the two characteristic times of $\tau_{\rm fast} \sim 0.1$ ms and $\tau_{\rm slow} \sim 0.8$ ms. These times were explained to be associated with conformational changes of chain before chain collapse. A Rayleigh intensity measurement was made to support this explanation.

The chain collapse and chain aggregation in polystyrene and PNIPAM solutions occur much faster than those in PMMA solutions and are difficult to observe accurately. The kinetics of chain collapse should be studied systematically by changing the molecular weight, temperature, and solvent species. PMMA solutions are suitable for this study because of the slow chain aggregation.

D. Chain-expansion processes

The chain expansion from a globule occurs depending on the globular size and degree of knotting at the initial state. The degree of knotting increases with increasing aging time. Rabin *et al.* argued that the chain expansion from heavily knotted globules is associated with the two characteristic times of the cooperative diffusion time $\tau_{\rm coop} = R_{\rm G}{}^2/D_{\rm coop}$ and the stress relaxation time $\tau_{\rm stress}$, where $R_{\rm G}$ is the size of the globule and $D_{\rm coop}$ is the cooperative diffusion coefficient [15]. In the absence of tight knots, $\tau_{\rm stress}$ was considered to be of the same order as $\tau_{\rm rep}$ for chain collapse. Since the relation $\tau_{\rm rep} \gg \tau_{\rm coop}$ holds in the typical case of $R_{\rm G} \sim 10^{-6}$ cm and $D_{\rm coop} \sim 10^{-6}$ cm^2/s, the chain expansion would be dominated by $\tau_{\rm rep}$ due to self-reptation. For a fast temperature jump to good solvent conditions as $\tau_{\rm jump} \ll \tau_{\rm rep}$, the resulting large concentration difference between the globule and an expanded coil would cause a strong swelling force, which may produce tight knots. The presence of tight knots would affect the chain-expansion process by stabilizing a partially swollen globule. In the present study, the thermal equilibration in the cell required $\tau_{\rm jump} \sim 30$ min, which is much shorter than the experimental time scales of chain collapse and chain expansion. However, the plots in Figs. 3 and 4 are described by smooth lines due to Eq. (2) and do not indicate an effect by partially swollen globules.

Lee *et al.* studied the chain-expansion process with an attention to the initial state of the globule [17]. The chain expansion from globules with concentrations such as those of the present globules was considered to occur in two steps. First, the globule swells with preserved topology and reaches an arrested state with a characteristic time proportional to $N^{2/3}$. In the second step, the topological constraints for the arrested globule relax by a threading mechanism in a time proportional to N^2. This expansion process of the two steps can be compared with the one suggested by Rabin *et al.*, though the second step is due to a different mechanism from self-reptation and the tight knot is not considered. The first step with preserved topology would be very fast as predicted by $\tau_{\rm coop}$ and finish in a small increase of α^2. Consequently, the chain expansion would appear to occur in a single step, as shown in Figs. 3 and 4, and be dominated by self-reptation directly. On the other hand, the chain-collapse processes in Fig. 9 are associated with crumpling, self-reptation, and suppressed self-reptation in a different way depending on the temperature. In the present study, the obtained characteristic time τ^* for chain collapse is much longer than the observed τ for chain expansion. τ depends on the knot density in a globule at the initial state, which is determined by the aging time and temperature. The chain expansion from globules of $M_{\rm w} = 1.22 \times 10^7$ aged at 37.0 °C has been described with $\tau = 30$, 80, and 168 min for $t_{\rm p} = 240$, 1440, and 7200 min, respectively. These characteristic times are much longer than $\tau_{\rm rep} = 3.9 \times 10^{-3}$ min at 37.0 °C by Eq. (7).

The stretched exponential form has been used to represent the relaxation function of glass-forming materials and explained in terms of the cooperative nature of relaxing elements in the dense systems [30,31]. The stretched exponential form $\sim \exp[-(t/\tau_{\rm K})^{\beta_{\rm K}}]$ was expressed by a superposition of exponentials and the average relaxation time $\langle \tau_{\rm K} \rangle$ was derived as

$$\langle \tau_{\rm K} \rangle = (\tau_{\rm K}/\beta_{\rm K})\Gamma(1/\beta_{\rm K}), \tag{9}$$

where $\Gamma(x)$ is the gamma function [32]. In connection with the present experiment, the ratio $\langle \tau_{\rm K} \rangle/\tau_{\rm K}$ is estimated to be 1.22 for $\beta = 0.73$, and 2 for $\beta = 0.5$. These differences between $\langle \tau_{\rm K} \rangle$ and $\tau_{\rm K}$ are of minor importance in the present study. The fractional exponent β in Eq. (2) may be attributed to a property of each globule or to an average property of globules with different characteristic times. In the latter case, the distribution of characteristic times may be associated with the distribution of initial knot densities in globules, which may become wide with the aging time $t_{\rm p}$. Thus, the distribution of characteristic times would become broad with $t_{\rm p}$, and β would decrease with $t_{\rm p}$. However, this is not the case of the present study, in which β was estimated as 0.75, 0.76, and 0.76 for $t_{\rm p} = 240$, 1400, and 7200 min, respectively. Consequently, the fractional exponent β may be attributed to a property of an individual globule, though the mechanism of the cooperative nature is not clear in a single globule. The exponent β^* for the chain-collapse process would be also associated with a property of a single globule.

E. Comparison with viscoelastic property

The characteristic time of chain collapse may have a correlation with viscoelastic properties of the concentrated solution in the terminal flow zone. Viscoelastic measurements in the range of concentration comparable with those of the equilibrium globules in the present study are very few. Masuda *et al.* carried out viscoelastic measurements on PMMA of different molecular weights less than $M_{\rm w} = 3 \times 10^5$ at 220 °C [33], and on concentrated PMMA solutions with $M_{\rm w} = 1.19 \times 10^5$ and 2.29×10^5 in diethyl phthalate

(DEP) [34]. The zero shear viscosity η_0 was estimated from the master curve of the loss modulus in the terminal flow zone and was found to depend on M_w as $\eta_0 \sim {M_w}^4$. The concentration dependence of η_0 was represented as $\eta_0 \sim w^4$ in the range of $w = 0.2$ to 1.0 at the iso-free-volume state of $f = 0.062$, resulting in the relation $\eta_0 \sim (wM_w)^4$, where w is the weight fraction of PMMA. Thus, the dependence of η_0 P on M_w and w could be written as $\eta_0 = 8.0 \times 10^{-15}\ (wM_w)^4$, where the numerical factor was determined with $\eta_0 = 1.06 \times 10^7$ P for PMMA of $M_w = 1.19 \times 10^5$ at 220 °C. It is interesting to compare the characteristic time τ^* of the chain collapse with the maximum relaxation time τ_d, which is estimated from η_0 as [35]

$$\eta_0 = (\pi^2/12)(cRT/M_e)\tau_d, \tag{10}$$

where c is the concentration. Although the density of DEP and PMMA at the room temperature is 1.12 g/cm^3 and 1.17, respectively, the weight fraction w could be replaced by the concentration c for the present purpose. The solution of PMMA in DEP around $c \sim 0.2$ g/cm^3 is at the iso-free-volume state of $f = 0.062$ near 20 °C. Thus, we estimated η_0 at c and M_w of the equilibrium globule with $\eta_0 = 8.0 \times 10^{-15}\ (cM_w)^4$ and calculated τ_d by Eq. (10). The value of the ratio τ^*/τ_d is given in Table I. The ratio becomes very large at 37.0 °C and 39.0 °C. This is attributed to the relation of $\eta_0 \sim (cM_w)^4$, which cannot be used at the low concentrations such as 0.03 g/cm^3 far below $c \sim 0.2$ g/cm^3. Except for at 20.0 °C, 37.0 °C, and 39.0 °C, the variation of τ^*/τ_d with the temperature and M_w is very small compared with that of τ^*, which indicates a correlation between the characteristic time of chain collapse and the maximum relaxation time. The comparable values of τ^* and τ_d cannot be taken seriously because these two experiments are made with different solvents and at different conditions. A quantitative comparison between τ^* and τ_d requires viscoelastic measurements on PMMA in the mixed solvent below the Θ temperature. This experiment is important to explore the mechanism of chain collapse and the origin of the very slow chain collapse in the system.

VI. SUMMARY AND CONCLUSIONS

The chain-expansion process from globules aged for the time period t_p at 37.0 °C was measured by static light scattering for the dilute solution of PMMA in the mixed solvent TBA + water (2.5 vol %) and was discussed in terms of the expansion factor α^2. The chain expansion developed more slowly with an increase of the molecular weight M_w and the aging time t_p, which indicated a knot formation due to self-reptation in a single chain. The characteristic time of chain expansion showed the molecular weight dependence of $\sim {M_w}^3$. The chain expansion from compact globules aged at 25.0 °C occurred faster than that from less compact globules aged at 37.0 °C. It was considered that the self-reptation would be suppressed in compact globules of high segment concentration.

The chain-collapse process has been measured for PMMA in the mixed solvent at various quench depths for long time periods [6]. The very slow chain collapse at the later stage was explained to be caused by the suppressed self-reptation. The characteristic time τ^* of chain collapse was estimated with an equation which was derived with the suppressed self-reptation taken into account. The chain-collapse processes observed for $M_w \times 10^6 = 4.0$ and 12.2 at 25.0 °C were analyzed with the equation and suggested the molecular weight dependence of $\tau^* \sim {M_w}^3$ [8]. The characteristic times τ^* observed at various quench depths were compared with the theoretical prediction of the two-stage kinetics [2], though τ^* was several orders of magnitude longer than the theoretical ones.

The above experimental observations on PMMA in the mixed solvent were obtained by taking advantage of the very slow phase separation. In the concentration range of $c < 5 \times 10^{-4}$ g/cm^3, the chain collapse finished before an effect of chain aggregation became noticeable [6,9,36]. The chain-collapse process for $M_w = 1.22 \times 10^7$ was measured for a time period of 5×10^4 min at 25.0 °C, and 2×10^4 min at 37.0 °C. An effect of chain aggregation was not observed during the measurement at 25.0 °C and slightly observed at 37.0 °C. The aggregation of chains has been argued to be caused by chain entanglement during the contact time [24,25]. Accordingly, the aggregation of compact globules at 25.0 °C would be more difficult than that of less compact globules at 37.0 °C because of the suppressed self-reptation. The slower chain aggregation at a deeper quench has been also observed for PMMA of $M_w = 1.57 \times 10^6$ in the mixed solvent [36]. The characteristic time of chain aggregation has been found to depend on the molecular weight as $\sim {M_w}^3$, suggesting a chain entanglement due to reptation-type motion in the contact time [9,23].

The kinetics of single chain behavior discussed in the present study would reflect the fundamental behavior of homopolymer chains far below the Θ temperature because of the universal nature of the reptation-type motion. However, the rates of chain collapse and chain aggregation in PMMA solutions have been found to depend strongly on the solvent species [21–23]. The chain collapse of PMMA with $M_w = 1.22 \times 10^7$ in pure TBA was observed to finish within 60 min after the quench [22]. The chain aggregation became perceptible just after the chain collapse. The mechanism of this solvent dependence is interesting, but remains unclear. The solution of PMMA in the mixed solvent TBA + water is a suitable system for a study of this problem because the kinetics of chain collapse and chain aggregation has been found to change dramatically depending on the temperature and water content [6,22]. A viscoelastic measurement on the concentrated solution of PMMA below the Θ temperature is intriguing in connection with the slow chain collapse.

ACKNOWLEDGMENTS

This work was partly supported by KAKENHI (Grant-in-Aid for Scientific Research) on Priority Area “Soft Matter Physics” from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

---

[1] P. G. de Gennes, J. Phys. Lett. **46**, L639 (1985).
[2] A. Yu. Grosberg, S. K. Nechaev, and E. I. Shakhnovich, J. Phys. Fr. **49**, 2095 (1988).
[3] L. I. Klushin, J. Chem. Phys. **108**, 7917 (1998).
[4] A. Halperin and P. M. Goldbart, Phys. Rev. E **61**, 565 (2000).

[5] B. Chu, Q. Ying, and A. Yu. Grosberg, Macromolecules **28**, 180 (1995).

[6] Y. Nakamura, N. Sasaki, and M. Nakata, Macromolecules **34**, 5992 (2001).

[7] M. Nakata and T. Nakagawa, J. Chem. Phys. **110**, 2703 (1999).

[8] Y. Maki, T. Dobashi, and M. Nakata, J. Chem. Phys. **126**, 134901 (2007).

[9] M. Nakata, Y. Nakamura, N. Sasaki, and Y. Maki, Phys. Rev. E **76**, 041805 (2007).

[10] J. Xu, Z. Zhu, S. Luo, C. Wu, and S. Liu, Phys. Rev. Lett. **96**, 027802 (2006).

[11] A. Byrne, P. Kiernan, D. Green, and K. A. Dawson, J. Chem. Phys. **102**, 573 (1995).

[12] Yu. A. Kuznetsov, E. G. Timoshenko, and K. A. Dawson, J. Chem. Phys. **103**, 4807 (1995).

[13] Yu. A. Kuznetsov, E. G. Timoshenko, and K. A. Dawson, J. Chem. Phys. **104**, 3338 (1996).

[14] G. Tanaka and W. L. Mattice, Macromolecules **28**, 1049 (1995).

[15] Y. Rabin, A. Yu. Grosberg, and T. Tanaka, Europhys. Lett. **32**, 505 (1995).

[16] N.-K. Lee, C. F. Abrams, A. Johner, and S. Obukhov, Phys. Rev. Lett. **90**, 225504 (2003).

[17] N.-K. Lee, C. F. Abrams, A. Johner, and S. Obukhov, Macromolecules **37**, 651 (2004).

[18] M. Nakata, Y. Nakamura, Y. Maki, and N. Sasaki, Macromolecules **37**, 4917 (2004).

[19] M. L. Mansfield, J. Chem. Phys. **127**, 244902 (2007).

[20] M. Nakata, Polymer **38**, 9 (1997).

[21] T. Nakagawa, Y. Nakamura, N. Sasaki, and M. Nakata, Phys. Rev. E **63**, 031803 (2001).

[22] Y. Nakamura, N. Sasaki, and M. Nakata, J. Chem. Phys. **118**, 3861 (2003).

[23] Y. Maki, T. Dobashi, and M. Nakata, Phys. Rev. E **78**, 041802 (2008).

[24] J. Chuang, A. Yu. Grosberg, and T. Tanaka, J. Chem. Phys. **112**, 6434 (2000).

[25] H. Tanaka, Macromolecules **25**, 6377 (1992).

[26] Y. Maki, N. Sasaki, and M. Nakata, J. Chem. Phys. **121**, 12690 (2004).

[27] A. Yu. Grosberg and D. V. Kuznetsov, Macromolecules **26**, 4249 (1993).

[28] T. Masuda, K. Kitagawa, and S. Onogi, Polymer J. **1**, 418 (1970).

[29] X. Ye, Y. Lu, L. Shen, Y. Ding, S. Liu, G. Zhang, and C. Wu, Macromolecules **40**, 4750 (2007).

[30] K. L. Ngai, C. H. Wang, G. Fytas, D. L. Plazek, and D. J. Plazek, J. Chem. Phys. **86**, 4768 (1987).

[31] D. Boese and F. Kremer, Macromolecules **23**, 829 (1990).

[32] C. P. Lindsey and G. D. Patterson, J. Chem. Phys. **73**, 3348 (1980).

[33] S. Onogi, T. Masuda, and T. Ibaragi, Kolloid Z. Z. Polym. **222**, 110 (1968).

[34] T. Masuda, N. Toda, Y. Aoto, and S. Onogi, Polymer J. **3**, 315 (1972).

[35] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, Oxford, 1986).

[36] Y. Nakamura, T. Nakagawa, N. Sasaki, A. Yamagishi, and M. Nakata, Macromolecules **34**, 5984 (2001).