Kinetics of chain collapse in dilute polymer solutions: Molecular weight and solvent dependences

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The molecular weight and solvent dependences of the characteristic time of chain collapse were studied for poly(methyl methacrylate) (PMMA) of the molecular weight $M_w = 6.4 \times 10^6$ and 1.14×10^7 in pure acetonitrile (AcN) and in the mixed solvent of AcN+water (10 vol %). The size of PMMA chains was measured as a function of the time after the quench by static light scattering and the chain collapse processes were expressed by the plot of the expansion factor α^2 vs ln t. The chain collapse in the mixed solvent AcN+water (10 vol %) was found to occur much faster than that in pure AcN, though the measurement of the former collapse process required several hours. In order to make a comparison between the rates of chain collapses, the fast chain collapse process was superposed on the slow one by scaling the time of the fast process as γt. The scale factor γ was determined by comparing the chain collapse processes of nearly the same equilibrium expansion factor with each other. Accordingly, the superposition of the collapse for $M_w = 6.4 \times 10^6$ on that for $M_w = 1.14 \times 10^7$ yielded $\gamma_m = 4.0 \pm 0.6$ for the process in AcN+water and 5.5 ± 0.6 in AcN. The superposition of the chain collapse process in AcN+water on that in AcN yielded $\gamma_s = 9.5 \pm 1.4$ for $M_w = 6.4 \times 10^6$ and 12.0 ± 1.8 for $M_w = 1.14 \times 10^7$. This analysis suggests that γ_m and γ_s are constant independent of each other. Thus, by assuming the molecular weight dependence of $\gamma_m \sim M^z$, the characteristic time τ_{exp} of chain collapse was conjectured as $\tau_{exp} \sim \kappa M^z$, where κ reflects the nature of solvent species. The ratio of κ for PMMA in AcN to that in AcN+water is given by γ_s. The exponent was estimated to be $z = 2.4 \pm 0.7$ for AcN+water and 3.0 ± 0.7 for AcN. These values are compatible with the theoretical prediction $z = 3$ based on a phenomenological model, though the observed characteristic times are longer by several orders of magnitude than those of the theoretical prediction. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2715596]

I. INTRODUCTION

The chain collapse has been studied by phenomenological theory,[1–4] computer simulation,[5–7] and light scattering experiment.[8–14] According to phenomenological theories,[1,2] the chain collapse occurs in two stages of different dependences on the molecular weight M. In the first stage polymer chains collapse to crumpled globules with the relaxation time $\sim M^2$, and in the second stage the crumpled globules contract slowly to compact globules with the relaxation time $\sim M^3$. The computer simulation indicates that the chain collapse occurs in two or three distinct stages and substantiates the theoretical studies. For a large molecular weight polymer, the characteristic time due to the phenomenological model is an order of millisecond at the first stage and is an order of second in the second stage. Experimental studies of the chain collapse have been carried out on solutions of polystyrene,[8] poly(N-isopropyl acrylamide),[9,10] and poly(methyl methacrylate) (PMMA).[11–14] The chain collapse in the former two solutions was too fast to be measured accurately. As for PMMA solutions, the chain collapse was observed to occur much slower than the theoretical predictions and to depend strongly on the molecular weight as well as the solvent species and the quench depth. In this study, the rate of chain collapse was estimated as a function of the molecular weight and solvent species from experimental data and compared with the theoretical predictions.

In previous studies,[11–14] we have measured chain collapse processes in the dilute solutions of PMMA in the single solvents of isoamyl acetate, tert-butyl alcohol (TBA), acetonitrile, and in the mixed solvent of TBA+water (2.5 vol %) by static light scattering. Since the solutions underwent very slow phase separation and remained transparent for long time periods from hours to weeks depending on the molecular weight, the solvent species, and the quench depth, the chain collapse process could be measured without being disturbed by the chain aggregation for the periods. The measurement, which started 30 min after the quench for thermal equilibration in the scattering cell, provided data of the chain collapse process at the later stage. The process was expressed in terms of the expansion factor $\alpha^2(t)$ as a function of the time t after the quench.

The collapse of PMMA with $M_w = 1.22 \times 10^7$ to equilibrium globules occurred very slowly in the mixed solvent TBA+water (2.5 vol %) and rapidly in pure TBA: The chain collapse in the mixed solvent required time periods from days to weeks depending on the quench depth, while the

chain collapse in pure TBA finished within 90 min after the quench. PMMA chains with $M_w = 1.57 \times 10^6$ in the mixed solvent collapsed to equilibrium globules in the first 30 min after the quench. The chain collapses of PMMA with $M_w = 1.22 \times 10^7$ in isoamyl acetate and with $M_w = 1.14 \times 10^7$ in acetonitrile were very slow and required time periods of days. The observed chain collapse processes were represented by a stretched exponential function with a small exponent.[14] The behavior due to the stretched exponential function made it difficult to estimate a rate of chain collapse properly. However, a quantitative comparison would be made between two chain collapse processes which have nearly the same values of the equilibrium expansion factor: The faster chain collapse process could be superposed on the slower one in the plot of α^2 vs $\ln t$ by scaling the time for the faster process as γt, where γ would represent the ratio of the rate of the fast collapse to the slow one. This practical method for estimating the relative rate could be used to explore the dependences of the chain collapse on the molecular weight and solvent species.

In this study, the solvent dependence of the chain collapse rate was investigated for PMMA in pure acetonitrile (AcN) and in the mixed solvent AcN+water (10 vol %), and the molecular weight dependence of the rate was determined for PMMA with $M_w \times 10^{-6} = 6.4$ and 11.4 in the solvents. The chain collapse processes in AcN+water (10 vol %) were determined by static light scattering, while the chain collapse processes in pure AcN have been obtained in a previous study.[13] The solvent dependence and the molecular weight dependence of the chain collapse were determined independently, and consequently, the characteristic time was conjectured as $\tau_{exp} \sim \kappa M^3$, where κ represents the nature of the solvent. The value of κ in AcN was larger by about ten times than that in AcN+water (10 vol %). The relation $\tau_{exp} \sim \kappa M^3$ was compatible with that for the second stage of the two-stage collapse,[2] though the behavior of κ was different from the theoretical predictions in a magnitude and solvent dependence.

II. EXPERIMENT

A. Samples and solution preparation

The present study was made for the PMMA fractions coded as M21A-F5 and M21-F8, which were the same fractions used in the previous study of the chain collapse process in pure AcN.[13] The weight-average molecular weights M_w of M21A-F5 and M21F8 were determined to be 6.4×10^6 and 1.14×10^7 at the θ temperature of 44.0 °C in pure AcN by static light scattering, respectively. The molecular weight distributions of M21A-F5 and M21-F8 were determined to be $M_w/M_n = 1.25$ and 1.34 by analytical gel permeation chromotography, respectively. The present experiment was carried out with the mixed solvent of AcN+water at the volume fraction $u = 0.1$ of water. Acetonitrile was fractionally distilled immediately before use. Water was purified by a standard method.

Solutions for the light scattering experiment were prepared at four polymer concentrations near $c(10^{-4} \text{ g/cm}^3) = 0.6$, 1.2, 1.8, and 2.4. Each solution was obtained by dilut-

ing a stock solution in an optical cell of 18 mm inside diameter and 1 mm in wall thickness, and the cell was sealed tightly with a Teflon cap to prevent evaporation of the solvent. Each optical cell was kept in a glass tube, which was partially filled with the solvent and immersed in a water bath thermostated at the θ temperature of 50.0 °C. In a few days impurity particles in the solution underwent sedimentation to the bottom of the cell, which made the optical purification of the solution effectively.

B. Static light scattering

The static light scattering measurements were carried out over the angular range of 30°–150° at intervals of 15° with vertically polarized incident light at 632.8 nm of a He–Ne laser. The calibration of the photometer was made with benzene taking its Rayleigh's ratio as $R_{90,vu} = 12.63 \times 10^{-6} \text{ cm}^{-1}$ at 25.0 °C.[15]

Each optical cell preserved at the θ temperature was transferred into a thermostated cylindrical cell at the center of the photometer, subjected to an intensity measurement of scattered light 30 min later on account of thermal equilibration, and back to another glass tube controlled at the experimental temperature. This measurement was carried out successively for the four solutions and repeated at appropriate time intervals until polymer chains would collapse to equilibrium sizes. At the end of the measurement, the turbidity of the solutions was not perceptible to the eye.

In order to determine the molecular weight M_w, the z-average mean-square radius of gyration $\langle s^2 \rangle_z$, and the second virial coefficient A_2, the excess Rayleigh ratio R_θ from polymer at an angle θ has been analyzed by the approximate equation[16]

$$\left(\frac{Kc}{R_\theta} \right)^{1/x} = \frac{1}{M_w^{1/x}} \left\{ 1 + \frac{1}{3x} \langle s^2 \rangle_z q^2 + \frac{2}{x} M_w A_2 c \right\}, \quad (1)$$

with $K = (4\pi^2 n^2/N_A \lambda^4)(dn/dc)^2$ and $q = (4\pi n/\lambda)\sin(\theta/2)$, where N_A is Avogadro's number, λ is the wavelength in a vacuum, and n is the refractive index of the solution. For an appropriate value of the constant x, the plot of $(Kc/R_\theta)^{1/x}$ vs $\sin^2(\theta/2)$ gives a straight line, of which the slope can be used to determine $\langle s^2 \rangle_z$. Present data were analyzed by the Zimm plot due to Eq. (1) with $x = 1.5$.

The refractive index increment dn/dc (cm^3/g) at a required temperature t (°C) was evaluated from the relation $(\partial n/\partial c)_u = 0.1262 + 2.5 \times 10^{-4} t$, which was determined at 632.8 nm for PMMA in the mixed solvent AcN+water at $u = 0.1$ in the range of 20 °C to 55 by using a differential refractometer of the Brice type.

Present light scattering data for PMMA in AcN+water at the volume fraction $u(=0.1)$ of water may depend on the derivative $(\partial n/\partial u)_{c=0}$ in addition to $(\partial n/\partial c)_u$ due to preferential adsorption. In the case of $(\partial n/\partial u)_{c=0}/(\partial n/\partial c)_u \ll 1$, the light scattering data can be analyzed by Eq. (1) for a single solvent. Since the refractive indices of AcN and water are close to each other, the difference between them can be measured by the differential refractometer. The difference at 632.8 nm was found to vanish at 49.8 °C, and the refractive index of the mixture has a maximum near $u = 0.5$. The de-
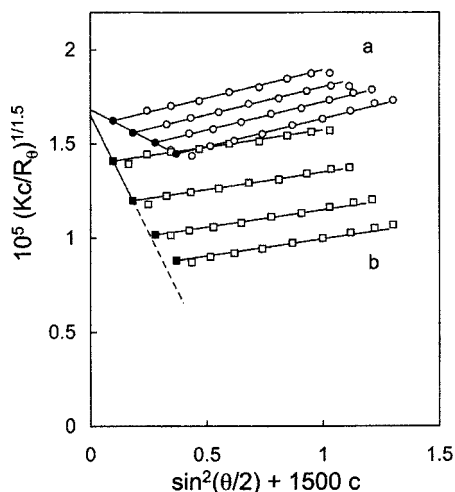
FIG. 1. Zimm plot of $(Kc/R_\theta)^{1/1.5}$ as a function of $\sin^2(\theta/2)$ and c (g/cm^3) for light scattering data of PMMA with $M_w = 1.14 \times 10^7$ in the mixed solvent of AcN+water (10 vol %). Plots a (circles) and b (squares) were obtained at 60 and 2100 min after quenching to 20.0 °C, respectively.

FIG. 2. Chain collapse processes of PMMA of $M_w = 6.4 \times 10^6$ in AcN +water (10 vol %) by the plot of $\alpha^2(t)$ vs $\ln t$ with the time t in minutes. The plots from the top to the bottom were obtained at 35.0, 30.0, 25.0, and 20.0 °C. The lines are described by Eq. (2) with appropriate values of α^2_{eq}, τ^*, and β.

rivative was obtained as $(\partial n/\partial u)_{c=0} = 0.0093 + 3.4 \times 10^{-4} t$ at $u = 0.1$ in the range of 25 °C to 50. The ratio $(\partial n/\partial u)_{c=0}/(\partial n/\partial c)_u$ was less than 0.2. Takashima et al.[17] showed that $\langle s^2 \rangle$ of polymer chain in a mixed solvent can be measured correctly by the conventional analysis with Eq. (1) under the condition of $0.8 < M^{(Y)}_{app}/M < 1.2$, where M is the true molecular weight of polymer and $M^{(Y)}_{app}$ is the apparent one which is obtained by replacing K in Eq. (1) by $K_0 = (4\pi^2 n_0^2/N_A \lambda^4)(dn/dc)_0^2$. Here, suffix 0 indicates the component of a good solvent in the mixed solvent. In the present case, K_0 was calculated from the data obtained for PMMA in pure AcN. $M^{(Y)}_{app}$ estimated at 50.0 °C for M21A-F5 and M21-F8 agreed with the respective true molecular weights determined with pure AcN within an experimental uncertainty. Thus, the conventional analysis due to Eq. (1) was found to be used to analyze the present light scattering data for a chain collapse process.

III. EXPERIMENTAL RESULTS

A. Analyses of light scattering data

The θ temperature for PMMA in the mixed solvent AcN+water (10 vol %) was determined to be 50.0 °C from the behavior of A_2 as a function of temperature. Figure 1 gives the Zimm plots of light scattering data for PMMA of $M_w = 1.14 \times 10^7$. The plots a (circles) and b (squares) were obtained 60 and 2100 min after quenching the solution from the θ temperature to 20.0 °C, respectively. In each plot, the plots of $(Kc/R_\theta)^{1/1.5}$ vs $\sin^2(\theta/2)$ at the four concentrations are described by straight lines with the same slope and are extrapolated to $\theta = 0$, as shown by the filled symbols. The mean-square radius of gyration $\langle s^2 \rangle_z$ was estimated from the slope of the parallel straight lines. The filled points at $\theta = 0$ are extrapolated to $c = 0$ by the straight lines which have a weight on points at lower concentrations on account of an effect of the phase separation on data at higher concentrations. For example, the four filled points are used for the extrapolation in plot a, whereas the two filled points at lower
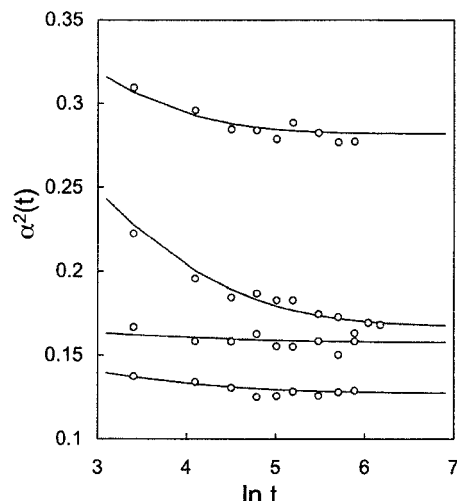
concentrations are used in plot b. The intercepts at $c = 0$ of the straight lines seem to coincide with each other within an experimental error. Thus, the parallel lines for the plot of $(Kc/R_\theta)^{1/1.5}$ vs $\sin^2(\theta/2)$ and the common intercept indicate that the determination of M_w and $\langle s^2 \rangle_z$ would be made without being affected by the phase separation. Plot b represents the data of the last measurement after the quench to 20.0 °C.

B. Chain collapse processes

Figures 2 and 3 illustrate the chain collapse processes obtained for PMMA with $M_w = 6.4 \times 10^6$ and 1.14×10^7 in AcN+water (10 vol %), respectively. The process is expressed by plotting the transient expansion factor $\alpha^2(t) = \langle s^2 \rangle(t)/\langle s^2 \rangle_0$ against $\ln t$, where $\langle s^2 \rangle_0$ is the unperturbed radius at the θ temperature and t is the time in minutes after the quench. The plots from the top to the bottom in Fig. 2 were
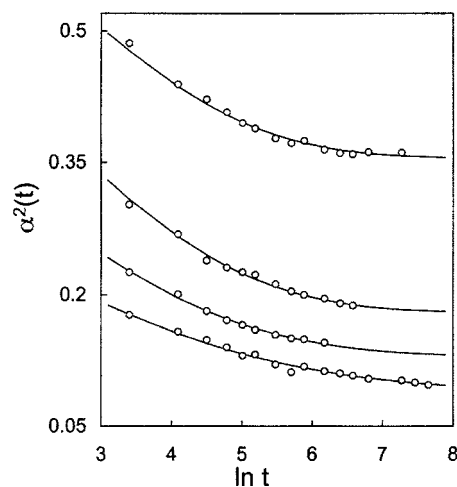

FIG. 3. Chain collapse processes of PMMA of $M_w = 1.14 \times 10^7$ in AcN +water (10 vol %) by the plot of $\alpha^2(t)$ vs $\ln t$ with the time t in minutes. The plots from the top to the bottom were obtained at 40.0, 35.0, 30.0, and 20.0 °C. The lines are described by Eq. (2) with the appropriate values of α^2_{eq}, τ^*, and β.
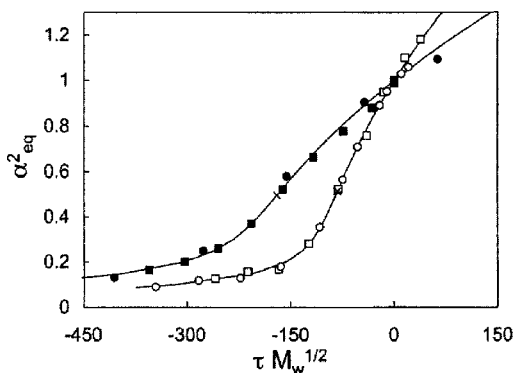
FIG. 4. Coil-globule transition curves by the plot of α_{eq}^2 vs $\tau M_w^{1/2}$ for PMMA with $M_w = 6.4 \times 10^6$ (squares) and 1.14×10^7 (circles) in pure AcN (filled symbols) and in AcN+water (10 vol %) (open symbols). The crosses represent the coil-globule crossover points calculated as an inflection point.

obtained at 35.0, 30.0, 25.0, and 20.0 °C, and those in Fig. 3 at 40.0, 35.0, 30.0, and 20.0 °C. It is obvious that the expansion factor decreases rapidly in the blank time of the first 30 min after the quench and approaches slowly an equilibrium expansion factor α_{eq}^2. At a temperature higher than those indicated above, $\alpha^2(t)$ was observed to reach α_{eq}^2 near 60 min after the quench. The chain collapse processes for $M_w = 6.4 \times 10^6$ and 1.14×10^7 require roughly 500 and 2000 min, respectively. The chain collapse for $M_w = 6.4 \times 10^6$ at the low temperatures appears almost to finish in the first 30 min.

The chain collapse process has been represented by the stretched exponential function[13,14]

$$\alpha^2(t) = \alpha_{eq}^2 + (1 - \alpha_{eq}^2)\exp[-(t/\tau^*)^\beta], \qquad (2)$$

where β and τ^* are constants independent of the time t. According to Eq. (2), the plot of $\ln \ln[(1 - \alpha_{eq}^2)/(\alpha^2(t) - \alpha_{eq}^2)]$ vs $\ln t$ should yield a straight line from which the values of β and τ^* could be estimated. The plot for the present data was linear for the value of α_{eq}^2, which was slightly smaller than those measured at the last stage of the chain collapse. The difference between them was no more than 5% of α_{eq}^2. The obtained value of β was found between 0.25 and 0.35, while τ^* changed with the temperature and molecular weight considerably. The solid curves in Figs. 2 and 3 were described by Eq. (2) with the estimated values of β and τ^*.

C. Equilibrium expansion factor

Figure 4 shows the coil-globule transition curves by plotting the equilibrium expansion factor α_{eq}^2 against $\tau M_w^{1/2}$, where τ is the reduced temperature defined as $\tau = 1 - \theta/T$. The open squares and open circles show the data for $M_w = 6.4 \times 10^6$ and 1.14×10^7 in AcN+water (10 vol %), respectively. The data points construct a single curve. For a comparison, the coil-globule transition curve for PMMA of $M_w = 6.4 \times 10^6$ and 1.14×10^7 in pure AcN is shown with filled squares and filled circles, respectively.[13] The coil-globule transition in the mixed solvent is much sharper than that in pure AcN.

The coil-globule transition curve has been determined for PMMA in various solvents.[11–14] It was found that the

transition curve depends markedly on the solvent species and is represented by the equation of the mean-field theory as[18,19]

$$\alpha_{eq}^3 - \alpha_{eq} - C(\alpha_{eq}^{-3} - 1) = B\tau M^{1/2}, \qquad (3)$$

where B and C stem from the second v and third virial coefficient w among polymer segments, respectively. The solvent dependence of the transition curve can be ascribed to the values of B and C. According to Eq. (3), the plot of $(\alpha_{eq}^3 - \alpha_{eq})/(1 - \alpha_{eq}^{-3})$ vs $\tau M^{1/2}/(1 - \alpha_{eq}^{-3})$ for data at various temperatures and molecular weights should yield a straight line. The plot for the present data gave a straight line, from which the values of the parameters were estimated as $B = 0.0052$ and $C = 0.045$. The transition curve of PMMA in pure AcN has been represented by Eq. (3) with $B = 0.0025$ and $C = 0.041$. The solid curves in Fig. 4 are depicted by Eq. (3) with the above values of B and C. The coil-globule crossover point was assumed to coincide with the inflection point on the curve of α_{eq}^2 vs $\tau M^{1/2}$ and was estimated as $\alpha_{eq}^2 = 0.51$ and $\tau M^{1/2} = -82.4$ for the present system by using Eq. (3). The crosses in Fig. 4 indicate the crossover point.

IV. DETERMINATION OF RELATIVE RATES OF THE CHAIN COLLAPSE

A. Molecular weight dependence of the chain collapse

A comparison between Figs. 2 and 3 indicates that the chain collapse becomes slow with increasing molecular weight. The chain collapse process for $M_w = 6.4 \times 10^6$ could be superposed on that for $M_w = 1.14 \times 10^7$ by scaling the time as $\gamma_m t$, provided that the two processes have the same value of α_{eq}^2. The factor γ_m would represent the ratio of the rate of the chain collapse for $M_w = 6.4 \times 10^6$ to that for $M_w = 1.14 \times 10^7$. The chain collapse processes for $M_w = 6.4 \times 10^6$ at 30.0 °C and for $M_w = 1.14 \times 10^7$ at 35.0 °C have nearly the same values of α_{eq}^2 as 0.17 and 0.18, respectively. In a previous study,[13] we carried out measurements on the same samples as the present ones in pure AcN and obtained the chain collapse processes shown in Figs. 2 and 3 in Ref. 13. The chain collapse processes for $M_w = 6.4 \times 10^6$ at 15.0 °C and for $M_w = 1.14 \times 10^7$ at 20.0 °C have nearly the same values of α_{eq}^2 as 0.26 and 0.25, respectively, and can be used to determine γ_m. The characteristics of the above two pairs of chain collapses are listed in Table I. In Fig. 5, $\alpha^2 - \alpha_{eq}^2$ is plotted against $\ln(\gamma_m t)$ for $M_w = 6.4 \times 10^6$ (squares) and against $\ln t$ for $M_w = 1.14 \times 10^7$ (circles). The subtraction of α_{eq}^2 from $\alpha^2(t)$ is made to correct the small difference in α_{eq}^2. Plots (a) and (b) are for AcN+water (10 vol %) and pure AcN, respectively. In order to estimate γ_m, the plots were made for various values of γ_m. By a visual observation of the plots, the superposition was found to be obtained reasonably for $\gamma_m = 4.0 \pm 0.6$ for AcN+water (10 vol %) and 5.5 ± 0.6 for AcN. The plots in Fig. 5 are given by using these values of γ_m.

B. Solvent dependence of the chain collapse

The chain collapse of PMMA in the mixed solvent of AcN+water (10 vol %) occurs much faster than that in pure AcN. This is seen by comparing the plots in Figs. 2 and 3

TABLE I. Comparison between the two chain collapse processes which were superposed on each other for the estimation of γ_m and γ_s given in the last column. The θ temperature and value of B are 50.0 °C and 0.0052 for PMMA in AcN+water (10 vol %), and 44.0 °C and 0.0025 in pure AcN, respectively.

$10^{-6}M_w$	Solvent	t (°C)	α_{eq}^2	$|\tau|$	$10^4 B|\tau|$	ϕ	γ_m, γ_s
11.4	AcN+water	35.0	0.18	0.049	2.53	0.038	
6.4	AcN+water	30.0	0.17	0.066	3.43	0.058	4.0 (γ_m)
11.4	AcN	20.0	0.25	0.082	2.05	0.023	
6.4	AcN	15.0	0.26	0.101	2.52	0.030	5.5 (γ_m)
11.4	AcN	10.0	0.13	0.120	3.00	0.061	
11.4	AcN+water	30.0	0.13	0.066	3.43	0.062	12 (γ_s)
6.4	AcN	5.0	0.17	0.140	3.51	0.059	
6.4	AcN+water	30.0	0.17	0.066	3.43	0.058	9.5 (γ_s)

with those in Figs. 3 and 2 in Ref. 13, respectively. For PMMA of $M_w=1.14\times10^7$, the chain collapse in pure AcN appears to finish 10 000 min after the quench, while the chain collapse in AcN+water appears to finish 2000 min after the quench. The relative rate of the chain collapse in the mixed solvent to that in pure AcN could be estimated by the superposition of the chain collapse processes of the same values of M_w and α_{eq}^2. For PMMA of $M_w=6.4\times10^6$, both of the chain collapse processes at 5.0 °C in AcN and at 30.0 °C in AcN+water have the value of $\alpha_{eq}^2=0.17$. For PMMA of $M_w=1.14\times10^7$, both of the chain collapse processes at

10.0 °C in AcN and at 30.0 °C in AcN+water have the value of $\alpha_{eq}^2=0.13$. The characteristics of the processes are shown in Table I. In Fig. 6, $\alpha^2-\alpha_{eq}^2$ is plotted against $\ln(\gamma_s t)$ in AcN+water (squares) and against $\ln t$ in AcN (circles). The plots (a) and (b) are for $M_w=6.4\times10^6$ and $M_w=1.14\times10^7$, respectively. The plots were made for various values of γ_s and were examined visually to estimate γ_s. The superposition is obtained for $\gamma_s=9.5\pm1.4$ for $M_w=6.4\times10^6$ and 12.0 ± 1.8 for $M_w=1.14\times10^7$. The plots in Fig. 6 are described with these values of γ_s.

V. DISCUSSION AND CONCLUDING REMARKS

The chain collapse processes for the determination of γ_m and γ_s were measured just in the experimentally accessible time period. The chain collapse process was too slow for molecular weights larger than $M_w=1.14\times10^7$ in pure AcN and too fast for molecular weights smaller than $M_w=6.4\times10^6$ in AcN+water (10 vol %). For the chain collapse process of $M_w=6.4\times10^6$ at 30.0 °C in AcN+water, the range of $\alpha^2-\alpha_{eq}^2$ is narrow as <0.06 and data points scatter somewhat as seen in Fig. 2. However, this process is crucial to conclude that the rate of chain collapse is dominated independently by the molecular weight and solvent species as expressed by the product $\gamma_m\gamma_s$.

According to Eq. (2), a superposition of two chain collapse processes would be affected by the value of the exponent β. The reasonable superposition shown in Figs. 5 and 6 suggests nearly same values of β. In fact, β was estimated in the small ranges between 0.25 and 0.35 for the processes in AcN+water and between 0.25 and 0.30 in pure AcN.

The obtained factors γ_m and γ_s are interpreted as a ratio of the characteristic time of the slow chain collapse to that of the fast one. Thus, the experimental characteristic time τ_{exp} could be expressed as $\tau_{exp}\sim\gamma_s\gamma_m$. By assuming the molecular weight dependence of $\gamma_m\sim M^z$, the characteristic time would be written as $\tau_{exp}\sim\kappa M^z$, where κ represents the nature of the solvent. Although the difference between molecular weights $M_w=6.4\times10^6$ and 1.14×10^7 is not large, it is interesting to evaluate the exponent z for a comparison with the theoretical predictions.[1,2] The molecular weight was determined with an error of about $\pm5\%$, which causes an additional error of about $\pm17\%$ in the estimation of z from γ_m.
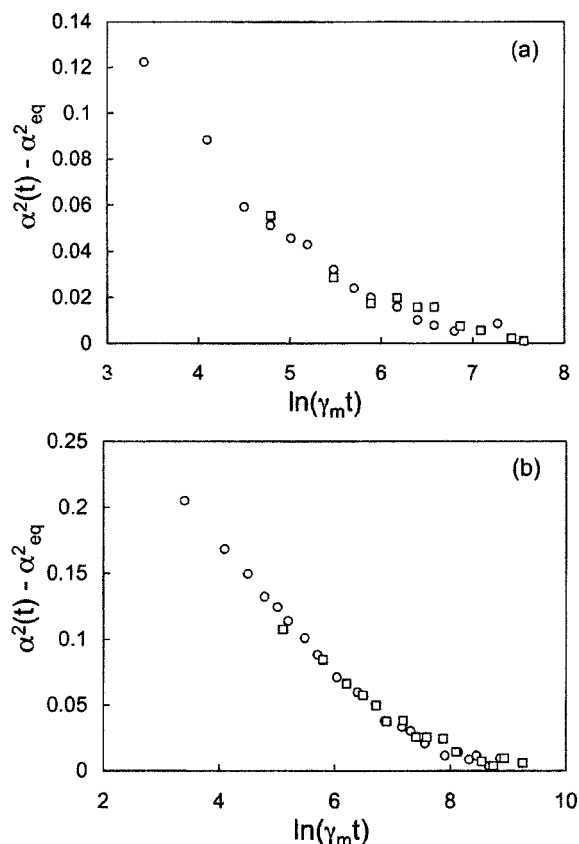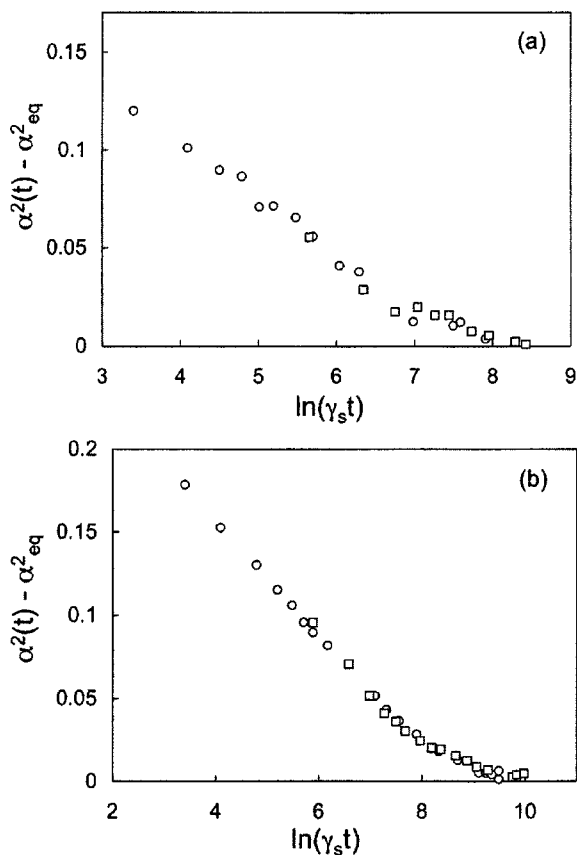

FIG. 5. Superposition of the chain collapse process for $M_w=6.4\times10^6$ (squares) on that for $M_w=1.14\times10^7$ (circles) by plotting $\alpha^2-\alpha_{eq}^2$ against $\ln(\gamma_m t)$ for $M_w=6.4\times10^6$ and against $\ln t$ for $M_w=1.14\times10^7$. Plots (a) and (b) are for AcN+water (10 vol %) and AcN, respectively. The superposition is obtained with $\gamma_m=4.0$ in AcN+water (10 vol %) and 5.5 in AcN.

FIG. 6. Superposition of the chain collapse process in AcN+water (squares) on that in AcN (circles) by plotting $\alpha^2 - \alpha^2_{eq}$ against $\ln(\gamma_s t)$ in AcN+water and against $\ln t$ in AcN. Plots (a) and (b) are $M_w = 6.4 \times 10^6$ and $M_w = 1.14 \times 10^7$, respectively. The superposition is obtained with $\gamma_s = 9.5$ for $M_w = 6.4 \times 10^6$ and 12 for $M_w = 1.14 \times 10^7$.

Thus, the exponent was estimated as $z = 2.4 \pm 0.7$ for AcN+water (10 vol %) and 3.0 ± 0.7 for AcN. An actual error of z would be smaller than those given above because the error $\pm 5\%$ of the molecular weight includes an uncertainty due to the calibration of the photometer and a partial cancellation of the errors would occur in the estimation of z from γ_m. The above values of z agree with each other within the experimental errors and suggest $z = 3$.

The theoretical study on the chain collapse has been made on the basis of a phenomenological model.[1,2] For the two-stage chain collapse, the relaxation times τ_{crum} and τ_{eq} for the first and second stages are written, respectively, as[2]

$$\tau_{crum} \sim \frac{\eta v |\tau|}{k\theta} \left(\frac{a^6}{w}\right) \left(1 + \frac{a^6}{wN_e}\right)^{-1} N^2, \qquad (4)$$

$$\tau_{eq} \sim \frac{\eta v |\tau|}{k\theta} \left(\frac{a^6}{w}\right) \left(\frac{N^3}{gN_e}\right), \qquad (5)$$

where η is the viscosity of the solvent, a and N are the segment size and number, respectively, N_e is the number of segments between two neighboring entanglements, v and w are the second and third virial coefficients, respectively. g is the number of segments of a blob and is expressed as $g \sim \phi^{-2}$, with ϕ being the segment volume fraction of the equilibrium globule. The experimental characteristic time $\tau_{exp} \sim \kappa M^3$ can be compared with Eq. (5) for the second

stage of the two-stage process. It should be noticed that the knot formation in compact globules, which characterizes the second stage of the two-stage chain collapse, is indicated by chain expansion experiments.[20,21]

It is possible to examine the temperature and solvent dependences of Eqs. (4) and (5). The segment volume fraction ϕ may be estimated by $\phi = (M/\rho N_A)/(\sigma\langle s^2\rangle_0^{3/2} \alpha^3_{eq})$, with $\sigma = (4\pi/3)(5/3)^{3/2}$ and ρ being the density of PMMA. The values of N_e and ρ are given as $N_e = 184$ and $\rho = 1.2$ g/cm^3.[22] The factor $k\theta$ and the solvent viscosity η are nearly the same for the solutions in pure AcN and in AcN+water (10 vol %). The virial coefficients v and w can be related to the coefficients B and C in Eq. (3) by $B = 1.09v(N/M)^{1/2}/a^3$ and $C = 3.55w/a^6$, respectively.[13] Since the coefficient C was estimated to be 0.045 and 0.041 for PMMA in AcN+water and in pure AcN, respectively, the values of w for the solutions are nearly the same. The quench depth $|\tau|$ appears in Eqs. (4) and (5) as the product $v|\tau|$ of which the behavior can be seen by $B|\tau|$. Table I lists the values of the relevant quantities. According to Eqs. (4) and (5), it is seen that the characteristic time does not seem to be affected largely by the quench depth and solvent.

For PMMA of $M_w = 1.14 \times 10^7$, Eq. (5) gives $\tau_{eq} = 300$ ms at 10.0 °C in AcN and 260 ms at 30.0 °C in AcN+water (10 vol %). Here, we used $\eta = 0.392$ cP for AcN at 10.0 °C and 0.329 cP for the mixed solvent of AcN+water (10 vol %) at 30.0 °C. The segment size a was estimated from the characteristic ratio $\langle s^2\rangle_0/M = 5.4 \times 10^{-18}$ cm^2 with the relation $\langle s^2\rangle_0 = Na^2/6$. It is obvious that the calculated values of τ_{eq} are far from the experimental observations in a magnitude and in a dependence on the solvent species. The chain collapses of PMMA in isoamyl acetate, TBA, and TBA+water (2.5 vol %) were also very slow and observed for long time periods of hours to weeks. Moreover, the characteristic time of the chain collapse of polystyrene in cyclohexane was observed to be ~ 300 s,[8] which is still much longer than those due to Eqs. (4) and (5). The characteristic times for PMMA and polystyrene are not largely different when compared with those by Eqs. (4) and (5), which suggests a common mechanism for the chain collapse of polymers.

It has been argued that the solvent viscosity in Eqs. (4) and (5) should be redefined as an effective viscosity for the reptationlike motion of chain in compact globules.[1,8] In order to explain the observed slow chain collapses, the effective viscosity should change in the range of several orders of magnitude depending on the system of polymer and solvent. The effective viscosity would be induced by an interaction between polymer chain and solvent. In the mixed solvent, the preferential adsorption would be associated with the interaction. The present light scattering data were analyzed by Eq. (1) as in the case of a single solvent because of the small refractive index difference between AcN and water. However, this does not mean that the preferential adsorption is negligibly small.

The behavior of PMMA chains in the mixed solvent AcN+water is markedly different from that in the mixed solvent of TBA+water.[14] The coil-globule transition curve changes by an addition of water to AcN, as shown in Fig. 4,

while the transition curve in pure TBA and in TBA+water (2.5 vol %) seem to agree with each other.[12] The chain collapse in pure AcN is extremely slow and accelerated by an addition of water, while the chain collapse in pure TBA is very fast and decelerated by an addition of water. A comparative study on the systems of PMMA in AcN+water and in TBA+water would provide a hint on the dynamics of chain collapse.

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