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Solvent effect on single-chain collapse of poly(methyl methacrylate) in tert-butyl alcohol

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Kinetic and static properties of the coil-globule transition of poly(methyl methacrylate) (PMMA) in pure tert-butyl alcohol were determined by static light scattering and compared with those of PMMA in the mixed solvent tert-butyl alcohol+water(2.5 vol %) in order to examine the effect of water on the chain collapse. The measurements were carried out for the molecular weight $M \times 10^{-6} = 4.1$ and 12.2 in the concentration range of $0.6 \times 10^{-4} - 2.6 \times 10^{-4}$ g/cm³, and the mean-square radius of gyration $\langle s^2 \rangle$ was determined as a function of the time after an abrupt decrease of temperature. PMMA chains collapsed to equilibrium globules within 90 min after quenching for $M = 1.22 \times 10^7$ and within 30 min for $M = 4.1 \times 10^6$. Chain aggregation due to phase separation became noticeable after the collapse of the chain because of an increase of observed molecular weight. For PMMA in the mixed solvent tert-butyl alcohol+water(2.5 vol %), the chain collapse process has been observed for periods from hours to weeks depending on the molecular weight and temperature, and the chain aggregation was negligibly small in the chain collapse process. The expansion factor $\alpha^2 = \langle s^2 \rangle / \langle s^2 \rangle_0$ obtained for fully collapsed chains in pure tert-butyl alcohol was represented by the theoretical prediction $\alpha^3 - \alpha - C(\alpha^{-3} - 1) = B(1 - \theta/T)M^{1/2}$ with the coefficients of $B = 0.0179$ and $C = 0.054$. For PMMA in the mixed solvent, the coil-globule transition curve has been expressed by the same equation with $B = 0.0164$ and $C = 0.049$, close to the above values. The small amount of water in the mixed solvent caused a drastic slowdown in the chain-collapse rate but had little effect on the coil-globule transition curve. © 2003 American Institute of Physics.
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I. INTRODUCTION

We have recently studied the kinetic and static properties of the coil-globule transition of poly(methyl methacrylate) (PMMA) in isoamyl acetate and in the mixed solvent tert-butyl alcohol+water(2.5 vol %) by static light scattering.¹⁻⁴ Since the solutions underwent very slow phase separation, the mean square radius of gyration $\langle s^2 \rangle$ of PMMA chains was determined accurately in the temperature ranges from the θ temperature 61.0 °C to 0 °C in isoamyl acetate^{1,2} and from the θ temperature 41.5 °C to 20 °C in the mixed solvent^{3,4} by using solutions in the concentration range of $0.7 \times 10^{-4} - 5 \times 10^{-4}$ g/cm³. PMMA chains in both of the solvents collapsed completely before the onset of phase separation. The rate of chain collapse depended strongly on the molecular weight and was slower in the mixed solvent than in isoamyl acetate.^{2,4} For $M_w = 1.22 \times 10^7$, chain collapse required a period of hours to weeks depending on the solvent and quench depth. The observed chain collapse process was fitted to a stretched exponential function, with which an expansion factor for totally collapsed chains was estimated.⁴ For PMMA with $M_w = 2.84 \times 10^6$ in the mixed solvent, complete chain collapse occurred within about 60 min after a temperature decrease.

The observed expansion factor $\alpha^2 = \langle s^2 \rangle / \langle s^2 \rangle_0$ relative to $\langle s^2 \rangle_0$ at the θ temperature has been represented by^{5,6}

$$\alpha^3 - \alpha - C(\alpha^{-3} - 1) = BM^{1/2}\tau, \quad (1)$$

which was derived for a contracted chain ($\alpha < 1$), where τ is defined as $1 - \theta/T$, M is the molecular weight, and B and C are related to second and third virial coefficients among segments, respectively. These coefficients were determined to be $B = 0.0041$ and $C = 0.073$ for PMMA in isoamyl acetate^{1,2} and $B = 0.0164$ and $C = 0.049$ in the mixed solvent tert-butyl alcohol+water(2.5 vol %).^{3,4}

The coil-globule transition has been studied for some other polymer solutions, for which light scattering measurements have been carried out for very large molecular weights and at extremely low concentrations in order to minimize the effect of the phase separation. Tanaka *et al.*^{7,8} obtained a coil-globule transition curve for polystyrene in cyclohexane with the molecular weight $M_w = 2.6 \times 10^7$ in the concentration range from 3×10^{-6} to 3×10^{-8} g/cm³. A recent analysis of the data has revealed that the transition curve can be represented by Eq. (1) with $B = 0.0162$ and $C = 0.026$.⁴ Chu *et al.* attempted to determine the chain collapse process for polystyrene in cyclohexane with $M_w = 8.1 \times 10^6$ at the concentration 8.7×10^{-6} g/cm³ by dynamic light scattering.⁹ Their measurements, which were carried out at a temperature of a few degrees below the phase separation temperature, suggested a two-stage collapse process with characteristic times of 357 and 323 s in the first and second stages, respectively. Wang *et al.*¹⁰ carried out static and dynamic light scattering measurements for poly(*N*-isopropylacrylamide) (PNIPAM) with $M_w = 1.3 \times 10^7$ in water at the concentration

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$6.7 \times 10^{-7} \text{ g/cm}^3$. They observed a fully collapsed chain just after attainment of temperature equilibration and detected no change in chain size for 10 h at that temperature. The coil-globule transition curve obtained experimentally for PNIPAM was compared with Eq. (1) with $B=0.0325$ and $C=0.0295$.

The results of the abovementioned experimental studies on different polymer solutions suggest that a coil-globule transition curve of polymer solutions may be expressed by Eq. (1), in which the coefficients B and C depend on the interaction between polymer and solvent. On the other hand, the time period required for chain collapse varies largely depending on the system of polymer and solvent. For the molecular weight $M \sim 10^7$, the time period required for chain collapse is roughly days for PMMA, minutes for polystyrene, and shorter than the time required for thermal equilibration in experiment for PNIPAM.

The kinetics of chain collapse has been studied on the basis of phenomenological models^{11–15} and by computer simulations.^{16–19} de Gennes first studied a mechanism of chain collapse and derived the characteristic time τ_0 as¹¹

$$\tau_0 = \eta a^3 (-\tau) N^2 / k \theta, \quad (2)$$

where η is the viscosity coefficient of the solvent, a is the segment size, N is the segment number per chain, and k is the Boltzmann constant. Grosberg *et al.* also derived a characteristic time similar to Eq. (2).¹² Since each quantity in Eq. (2) is comparable for the above polymer solutions, Eq. (2) fails to explain the large difference in the observed chain collapse duration. Moreover, the characteristic time of Eq. (2) is of an order of 10^{-1} s for the above solutions with $M \sim 10^7$ and is much smaller than the chain-collapse durations observed for PMMA and polystyrene. Theoretical analyses and computer simulations for chain collapse have been focused on the chain length dependence of the characteristic time rather than the absolute value. Equation (2) gives the characteristic time for the first stage in a two-stage collapse.^{11,12} The characteristic time in the second stage depends on N^3 and may be much longer than that in the first stage. The results of the above experiments on the chain collapse process are not compatible with the theoretical prediction of two-stage collapse.

So far, there has been little discussion on the rate of chain collapse of real polymers, because the rate of chain collapse is likely to depend on specific properties of polymer and solvent and accordingly cannot be discussed from a unified viewpoint. However, elucidation of the chain-collapse process of real polymers is important for the understanding of the fundamental behavior of linear polymer chains and conformational transitions of biopolymers. It would be interesting to examine the effect of water on the rate of chain collapse in the mixed solvent tert-butyl alcohol+water, since water is nonsolvent for PMMA but an addition of a small amount of water to tert-butyl alcohol gives rise to a strong solvent power for PMMA.

In this study, we carried out static light scattering measurements for PMMA in pure tert-butyl alcohol. The θ temperature was determined to be 66.0 °C. This high θ temperature has hampered experimental studies on the solution.

PMMA chains of $M \times 10^{-6} = 4.1$ and 12.2 collapsed to an equilibrium size within 30 and 90 min after quenching, respectively. It should be recalled that the chain collapse of PMMA with $M = 1.22 \times 10^7$ required a time period of days in the mixed solvent tert-butyl alcohol+water (2.5 vol %). The rate of chain collapse in pure tert-butyl alcohol is much faster than that in the mixed solvent. The small amount of water obviously caused the slowdown of the chain-collapse rate in the mixed solvent. The coil-globule transition curve of PMMA in pure tert-butyl alcohol was the same as that in the mixed solvent at 2.5 vol % of water. The kinetic and static properties of chain collapse were not correlated with each other.

II. EXPERIMENT

Two fractions designated by M19-F12 and M21-F9 were used as PMMA samples in the present study. The molecular weights of M19-F12 and M21-F9 were determined to be $M_w \times 10^{-6} = 4.0$ and 12.2, respectively, in a previous study.⁴ The molecular weight distribution has been estimated from observed characteristic ratios to be $M_w/M_n \sim 1.20$. tert-butyl alcohol was fractionally distilled immediately before use.

The solution for light-scattering measurement was prepared at four concentrations near $c(10^{-4} \text{ g/cm}^3) = 0.6, 1.2, 1.8,$ and 2.4 , similar to those used in a previous study.⁴ Each solution was transferred into an optical cell of 18 mm in i.d. and 1 mm in wall thickness and sealed tightly with a Teflon cap to prevent evaporation of the solvent. The optical cells were kept under saturated vapor of tert-butyl alcohol in the dark at a temperature near 70 °C. The solutions were kept still for a few days to sediment impurity particles to the bottom of cell, which made the optical clarification of the solution effectively.

Each optical cell was immersed in a thermostated cylindrical cell at the center of a photometer. The measurements of scattered light were started 30 min after the setup of the cell to allow sufficient time for thermal equilibration and continued at time intervals of 30 min. The measurements were carried out over the angular range of 30°–135° at intervals of 15° with unpolarized incident light at 435.8 nm of a mercury arc as described elsewhere.³ The light-scattering data were obtained in the temperature ranges of 54–70 °C for M19-F12 and of 47–70 °C for M21-F9.

The refractive index increment $dn/dc(\text{cm}^3/\text{g})$ at a required temperature t (°C) for PMMA in pure tert-butyl alcohol was calculated from the relation $dn/dc = 0.0990 + 3.6 \times 10^{-4}t$, which was obtained as follows. On account of the high θ temperature for pure tert-butyl alcohol, dn/dc was determined for PMMA in the mixed solvent tert-butyl alcohol+water at the volume fraction u of water as 0.015, 0.025, and 0.05. The dependence of dn/dc on u was small in the above range of u , and dn/dc for PMMA in pure tert-butyl alcohol was determined by an extrapolation of the observed dn/dc to $u=0$ as given above. The values of dn/dc for PMMA in the mixed solvent were determined at the temperatures 30, 45, and 60 °C for $M_w = 8.8 \times 10^4$ by using a differential refractometer of the Brice-type.

In order to determine the molecular weight M_w , the mean-square radius of gyration $\langle s^2 \rangle$ and the second virial

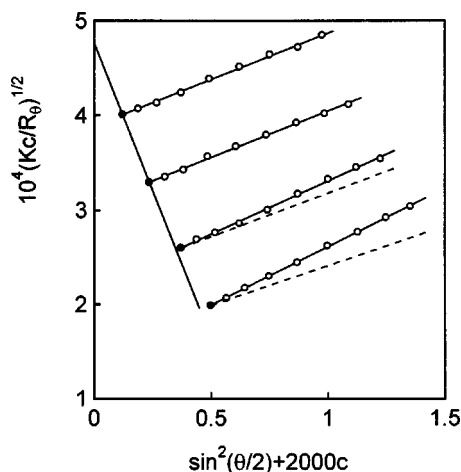


FIG. 1. Zimm plot of $(Kc/R_\theta)^{1/2}$ ($\text{mol}^{1/2}/\text{g}^{1/2}$) as a function of $\sin^2(\theta/2)$ and c (g/cm^3) for light-scattering data of PMMA with $M_w = 4.1 \times 10^6$ in tert-butyl alcohol. The data were obtained 30 min after quenching to 60.0°C . The four solid lines fitted to data points represent the dependence on $\sin^2(\theta/2)$. The solid lines at two lower concentrations are parallel to each other, and the broken lines at two higher concentrations are given parallel to these solid lines.

coefficient A_2 from the light-scattering data, the excess Rayleigh ratio R_θ at an angle θ was analyzed by the scattering equation,²⁰

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

with $K = (2\pi^2 n^2 / N_A \lambda^4) (dn/dc)^2$ and $q = (4\pi n / \lambda) \sin(\theta/2)$, where N_A is Avogadro's number, λ is the wavelength of incident light in a vacuum, and n is the refractive index of solution. The plot of $(Kc/R_\theta)^{1/a}$ vs $\sin^2(\theta/2)$ gives a straight line for an appropriate value of the constant a and $\langle s^2 \rangle$ can be obtained from the slope of the plot according to Eq. (3).^{2,20} The values of $\langle s^2 \rangle$, A_2 , and M_w were determined by using the Zimm plot with $a=2$ for the sample M19-F12 and $a=1.5$ for M21-F9.

III. EXPERIMENTAL RESULTS

Figure 1 shows light-scattering data for the sample M19-F12 obtained at 30 min after quenching to 60.0°C . The data are given in a form of the Zimm plot due to Eq. (3) with $a=2$. Each plot of $(Kc/R_\theta)^{1/2}$ vs $\sin^2(\theta/2)$ at four concentrations is described by a solid straight line, which is extrapolated to $\theta=0$ as shown by filled circle. The intercept of the solid line fitted to the two filled circles at the lower concentrations gives the molecular weight $M_w = 4.4 \times 10^6$, which is slightly larger than 4.1×10^6 obtained near the θ temperature. The second virial coefficient A_2 was not determined reliably with the slope of the solid line. The solid lines for the dependence on $\sin^2 \theta/2$ at the two lower concentrations are parallel to each other, and the broken lines at the two higher concentrations are described parallel to those lines. The solid lines fitted to data points at the higher concentrations have slopes larger than those of the broken lines indicating an effect of the chain aggregation due to phase separation. Since the effect of chain aggregation is very small at the lower concentrations as shown by the observed molecular weight,

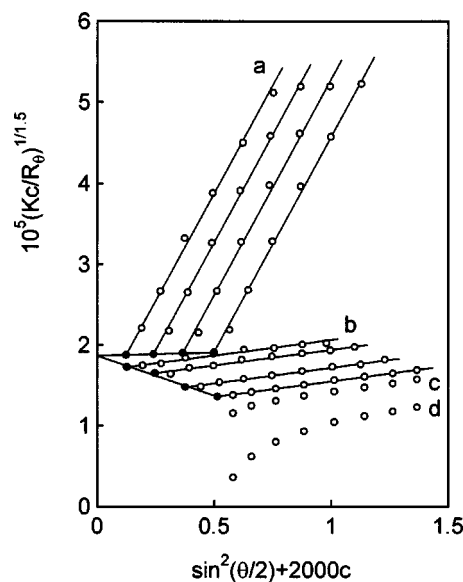


FIG. 2. Zimm plot of $(Kc/R_\theta)^{1/1.5}$ as a function of $\sin^2(\theta/2)$ and c (g/cm^3) for light-scattering data of PMMA with $M_w = 1.22 \times 10^7$ in tert-butyl alcohol. Data for plots a and b were obtained 30 min after quenching to 66.0 and 47.0°C , respectively. Plots c and d were obtained 60 min and 120 after quenching to 47.0°C for the highest concentration.

the slope of the two parallel lines at the lower concentrations was used for the determination of $\langle s^2 \rangle$. For M19-F12, Zimm plots similar to those shown in Fig. 1 were obtained at 30 min after quenching to temperatures above 54°C . Light-scattering data obtained at 60 min after quenching, however, were largely affected by the chain aggregation due to phase separation.

Figure 2 shows the Zimm plots for the sample M21-F9 according to Eq. (3) with $a=1.5$. The plots a and b were obtained 30 min after quenching to 66.0 and 47.0°C , respectively. For each of the plots, the straight lines for the $\sin^2(\theta/2)$ dependence have the same slopes and are extrapolated to $\theta=0$ as shown by filled circles. The value of $\langle s^2 \rangle$ was estimated from the slope of the parallel straight lines. M_w and A_2 were obtained from the straight line fitted to the filled circles. The fact that the lines for the $\sin^2(\theta/2)$ dependence are parallel to each other and the lines at $\theta=0$ have a common intercept indicates that chain aggregation is negligibly small at 30 min after quenching. The molecular weight was determined to be $M_w = 1.24 \times 10^7$, which agrees with that obtained in the mixed solvent tert-butyl alcohol + water (2.5 vol %). The plots c and d were obtained for the solution at the highest concentration at 60 min and 120 min after quenching to 47.0°C , respectively. The large forward scattering at 120 min is caused by an incipient phase separation. However, plots of $(Kc/R_\theta)^{1/1.5}$ vs $\sin^2(\theta/2)$ at the two lower concentrations obtained at 120 min after quenching, though not shown, were parallel to each other and yielded the correct molecular weight within an error of 5%. At temperatures above 47.0°C , the effect of phase separation on the Zimm plots was negligibly small for a time period of 180 min after quenching even at the highest concentration. The second virial coefficient A_2 , though apparent one below the phase-separation temperature, was obtained unambiguously,

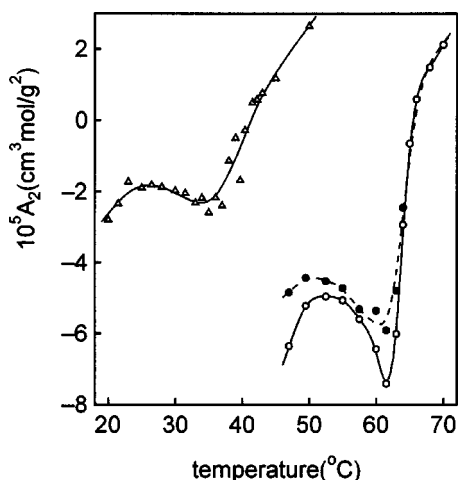


FIG. 3. Temperature dependencies of the second virial coefficient A_2 . The open circles show data obtained 30 min after quenching for PMMA with $M_w = 1.22 \times 10^7$ in pure tert-butyl alcohol, and the filled circles are data corrected for the effect of phase separation. The triangles are data for the same sample in the mixed solvent tert-butyl alcohol + water(2.5 vol %) obtained 30 min after quenching (Ref. 4).

since the points extrapolated to $\theta=0$ yielded a straight line with a well-defined slope.

In Fig. 3, the second virial coefficient A_2 , which was obtained for $M_w = 1.22 \times 10^7$ at 30 min after quenching, is plotted against temperature by open circles. To eliminate the effect due to chain aggregation, the apparent values of A_2 obtained at a time interval of 30 min were extrapolated to zero time. The extrapolated value of A_2 was taken as an equilibrium one because of the rapid collapse of the PMMA chain. The corrected values of A_2 are shown by filled circles in Fig. 3. The broken line for the corrected data and the solid line for uncorrected data show essentially the same behavior. A_2 vanishes at 66.0°C, where we obtained the characteristic ratio as $\langle s^2 \rangle / M_w \times 10^{18} = 6.1$ and 6.7 cm^2 for $M_w \times 10^{-6} = 4.1$ and 12.2 , respectively. These values agree with those obtained at the θ temperature.^{1,4} Thus, the θ temperature for PMMA in pure tert-butyl alcohol can be determined to be 66.0°C, which is 24.5°C higher than the θ temperature 41.5°C for PMMA in the mixed solvent tert-butyl alcohol + water(2.5 vol %).⁴

Figure 4 shows plots of the expansion factor α^2 vs the time (min) at various temperatures for $M_w = 1.22 \times 10^7$. The plots from the top to the bottom were obtained at 65.0, 64.0, 63.0, 61.5, 60.0, 57.5, 55.0, 52.5, 49.5, and 47.0°C, respectively. The plots at 52.5 and 49.5°C overlap each other. The plot at 47.0°C lacks data points at 150 and 180 min because of the effect of phase separation. The plot at 63.0°C exhibits a clear time dependence of α^2 . At each temperature, α^2 becomes constant at 60 min after quenching. The broken line at each temperature shows the value of the equilibrium expansion factor.

In Fig. 5, the equilibrium expansion factor is plotted against $\tau M^{1/2}$. The open circles show the data for $M_w = 1.22 \times 10^7$, and the triangles show the data for $M_w = 4.1 \times 10^6$ obtained at 30 min after quenching. The agreement between the data for the two molecular weights indicates that

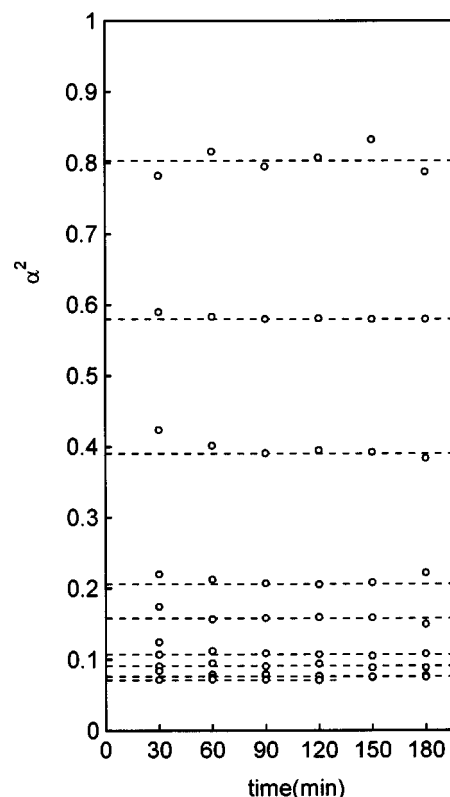


FIG. 4. Time dependencies of the expansion factor α^2 for PMMA with $M_w = 1.22 \times 10^7$ in tert-butyl alcohol. Plots from the top to the bottom were obtained at 65.0, 64.0, 63.0, 61.5, 60.0, 57.5, 55.0, 52.5, 49.5, and 47.0°C. The data at 52.5°C and 49.5°C cannot be distinguished because of overlapping. Dotted lines indicate the equilibrium expansion factors at each temperature.

the expansion factor for $M_w = 4.1 \times 10^6$ is also an equilibrium one.

According to Eq. (1), the plot of $(\alpha^3 - \alpha)/(1 - \alpha^{-3})$ vs $\tau M^{1/2}/(1 - \alpha^{-3})$ for $\alpha < 1$ should give a straight line, whose slope and intercept may be used to estimate B and C , respectively. Figure 6 shows the plot with the same symbols as

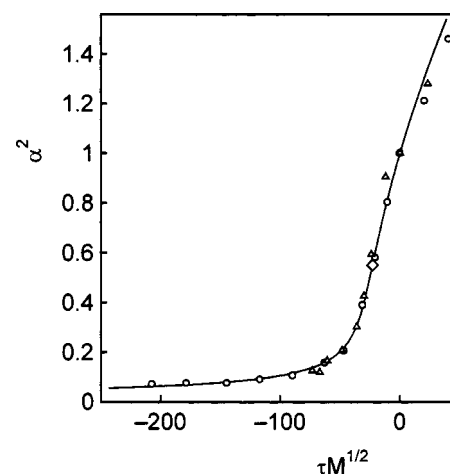


FIG. 5. Plot of the equilibrium expansion factor α^2 vs $\tau M^{1/2}$ for PMMA in tert-butyl alcohol. The open circles and triangles are data for $M_w \times 10^{-6} = 12.2$ and 4.1 , respectively. The solid line is described by Eq. (1) with $B = 0.0179$ and $C = 0.054$. The open square represents the crossover point between coil and globule regions.

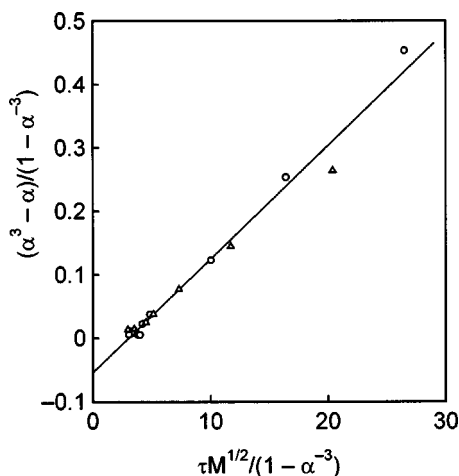


FIG. 6. Plot according to Eq. (1) for PMMA in tert-butyl alcohol. The open circles and triangles are for $M_w \times 10^{-6} = 12.2$ and 4.1 , respectively. The slope and intercept of the straight line give the coefficients in Eq. (1) as $B = 0.0179$ and $C = 0.054$, respectively.

those used in Fig. 5. Data points near the θ temperature are omitted because of a large scattering. From the straight line for the data points, we obtained $B = 0.0179$ and $C = 0.054$. In Fig. 5, the solid line is described by Eq. (1) with these values of B and C . The crossover point between coil and globule states was assumed to be located at the inflection point on the curve of α^2 vs $\tau M^{1/2}$ and was calculated with Eq. (1) to be $\alpha^2 = 0.55$ and $\tau M^{1/2} = -23.0$. The open square on the solid line shows the crossover point.

In Fig. 7, α^{-3} is plotted against $\tau M^{1/2}$ in order to inspect the behavior in the globule region.¹ The symbols are the same as those used in Fig. 5. The solid line is described by Eq. (1) with the above values of B and C . The open square indicates the crossover point between the coil and globule regions. Taking into account the uncertainty due to small values of α^2 in the globule region, the data points fit the solid line reasonably.

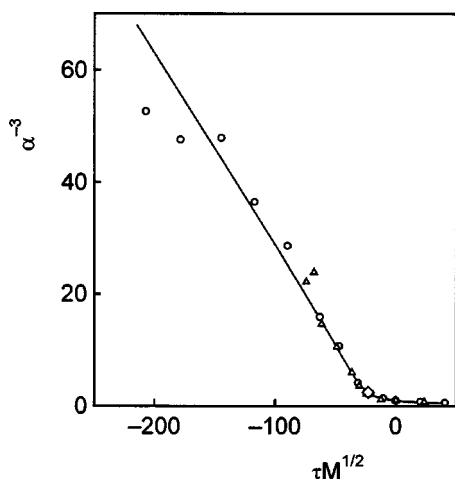


FIG. 7. Plot of α^{-3} vs $\tau M^{1/2}$ for behavior in the globule region. The symbols and line are the same as those in Fig. 5.

IV. DISCUSSION AND CONCLUSION

The behavior of A_2 given by open circles in Fig. 3 has a minimum near 61.5°C , which is somewhat below the coil–globule crossover temperature 63.8°C . The minimum near the crossover point has been predicted by a theoretical calculation based on a mean-field model with chain collapse taken into account.²¹ The correction for chain aggregation is large near the minimum and near 47.0°C . The large correction reflects a fast phase separation. In our previous study, we measured A_2 for PMMA with $M = 1.22 \times 10^7$ in the mixed solvent tert-butyl alcohol+water(2.5 vol %) at 30 min after quenching. The triangles in Fig. 3 show the data for the mixed solvent. Since the solution of the mixed solvent underwent very slow phase separation, the value of A_2 is not affected by chain aggregation. However, the value may be a transient one because of the slow chain collapse. Analysis of the light-scattering data obtained for a long period showed that A_2 decreased slowly with contraction of the polymer chain. The Zimm plots in Fig. 2 in Ref. 4 gave $A_2 = -2.5 \times 10^{-5} \text{ cm}^3 \text{ mol/g}^2$ at 30 min and -5.2×10^{-5} at 178 560 min after quenching to 23.0°C . The high values of A_2 in the mixed solvent compared with the present ones are attributed mainly to the slow chain collapse. Thus, the values of A_2 in the single solvent and in the mixed solvent may be comparable. Correspondingly, B and C in Eq. (1) are also comparable in these two solvents as seen later. For the solution of the mixed solvent, the phase separation became fast at temperatures below 20.0°C , while for the present solution, the phase separation became faster at temperatures below 47.0°C . It would be interesting to compare these threshold temperatures with the spinodal temperature between the metastable and unstable regions. Angular dependencies of scattered light may be different above and below the threshold temperatures.

In previous studies, we obtained $B = 0.0164$ and $C = 0.049$ for PMMA in the mixed solvent tert-butyl alcohol+water(2.5 vol %).^{3,4} These values of B and C are close to the values obtained in this study. In Figs. 5 and 7, the coil–globule transition curves for PMMA in pure tert-butyl alcohol and in the mixed solvent cannot be distinguished. The small amount of water does not affect the shape of the coil–globule transition curve but shifts the θ temperature from 66.0°C to 41.5°C . The large drop in the θ temperature is known to be a phenomenon of cosolvency. Cowie *et al.* suggested a mechanism of the cosolvency of alcohol+water for PMMA.²² The cosolvency of tert-butyl alcohol+water for PMMA may not be caused by a preferential sorption of the solvent, because the characteristic ratio $\langle s^2 \rangle_0 / M$ obtained in the mixed solvent agrees with those obtained in pure tert-butyl alcohol and in isoamyl acetate.^{1,4} The correct characteristic ratio could not be obtained at the θ temperature defined by $A_2 = 0$ in the presence of a preferential sorption.²³

In the present experiment, the PMMA chain in pure tert-butyl alcohol was found to collapse completely within 90 min after quenching for $M = 1.22 \times 10^7$ and within 30 min for $M = 4.1 \times 10^6$. For PMMA in the mixed solvent tert-butyl alcohol+water(2.5 vol %), the chain collapse process was observed over periods of hours to weeks depending on the temperature and the molecular weight.⁴ It is clear that the

presence of the small amount of water caused a drastic slow-down of the chain collapse process contrary to the unchanged behavior of the coil-globule transition curve. The fast chain collapse in pure tert-butyl alcohol is in accord with the fast phase separation. The chain aggregation due to phase separation causes an apparent molecular weight which can be used as a measure for the rate of phase separation. For PMMA in pure tert-butyl alcohol, the apparent molecular weight was obtained as 7×10^6 for $M_w = 4.1 \times 10^6$ at 60 min after quenching to 60.0 °C and 1.7×10^7 for $M_w = 1.22 \times 10^7$ at 24 h after quenching to 55.0 °C. The effect of chain aggregation indicated by these large apparent molecular weights made the determination of $\langle s^2 \rangle$ unreliable, though the solutions were transparent by the eye. On the other hand, for PMMA in the mixed solvent tert-butyl alcohol + water (2.5 vol %), the increase in observed molecular weight due to chain aggregation was negligibly small for a day after quenching for $M_w = 4.0 \times 10^6$ and at least for a week after quenching for $M_w = 1.22 \times 10^7$. Thus, it is obvious that the phase separation occurs much faster in pure tert-butyl alcohol than in the mixed solvent.

According to theories based on phenomenological models,^{11,12} the rate of chain collapse may be related to the nature of the polymer and solvent by Eq. (2). With the use of the relations $\langle s^2 \rangle_0 = a^2 N/6$ and $m = M/N$ for the molecular weight m per segment, the segment size for the monomer unit $m = 100$ is estimated to be $a^2 = 0.366 \text{ nm}^2$ from $\langle s^2 \rangle_0/M = 6.1 \times 10^{-4} \text{ nm}^2$. Then, for $M = 1.22 \times 10^7$ we obtain $\tau_0 = 0.5 \text{ s}$ for tert-butyl alcohol at 50 °C with $\eta = 1.40 \times 10^{-3} \text{ Pa s}$ and $\tau_0 = 0.4 \text{ s}$ for the mixed solvent tert-butyl alcohol + water (2.5 vol %) at 35 °C with $\eta = 2.6 \times 10^{-3} \text{ Pa s}$. On the other hand, the observed duration of chain collapse is roughly one hour in pure tert-butyl alcohol and several days in the mixed solvent as mentioned above. Thus, the theoretically predicted and experimentally observed durations of the chain collapse are very different in a time scale and in a dependence on the solvent nature. It is clear that the chain-collapse rate of PMMA in the two solvents is governed by a different mechanism from that in the theories of de Gennes¹¹ and Grosberg *et al.*¹²

The results of the present experiment together with the results of previous experiments suggest that the rate of chain collapse increases with increase of the rate of chain aggregation.^{24–26} The chain aggregation process observed for PMMA in the mixed solvent and in isoamyl acetate was represented by an exponential function. It is known that the exponential growth of clusters is not caused by diffusion-limited cluster aggregation (DLCA) but by reaction-limited cluster aggregation (RLCA).²⁷ An elementary reaction between polymer chains stems from a reaction between polymer segments, which are identical irrespective of whether the segments belong to the same chain or to different chains.

Thus, the rates of chain collapse and chain aggregation are closely correlated with each other through the reaction between polymer segments. The role of water in the rates of chain collapse and chain aggregation in the mixed solvent may be revealed by an experiment which is carried out by changing the water content. When the temperature was lowered, the rate of chain aggregation of PMMA suddenly increased near 20.0 °C in the mixed solvent and near 47.0 °C in pure tert-butyl alcohol. A comparison of scattering functions above and below the threshold temperature would give information on the mechanism of the chain collapse and chain aggregation from a different point of view.

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