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Comparison of the kinetics of chain aggregation and chain collapse in dilute polymer solutions

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The rates of chain aggregation of poly(methyl methacrylate) (PMMA) in acetonitrile (AcN) and in the mixed solvent of AcN+water (10 vol %) were determined by static light scattering and compared with the rates of chain collapse [Maki *et al.*, J. Chem. Phys. **126**, 134901 (2007)]. Dilute solutions of PMMA with the molecular weight $m_w = 6.4 \times 10^6$ and in the concentration range of $(0.8-5) \times 10^{-4}$ g/cm^3 were quenched below the cloud point, and the weight-average molecular weight M_w and z-average square radius of gyration $\langle S^2 \rangle_z$ for clusters of PMMA chains were measured as a function of the time t after the quench and the concentration c. The measurement of chain aggregation was carried out up to the cluster size of $M_w/m_w \sim 30$, which required time periods of hours to several days depending on the concentration and solvent. The chain aggregation in AcN+water occurred much faster than that in AcN. The growth of clusters in both the solvents was represented by the exponential function as $M_w \sim e^{gct}$ and $\langle S^2 \rangle_z \sim e^{hct}$, where g and h represent the intrinsic rate of chain aggregation. The ratio σ of the intrinsic rate in AcN+water to that in AcN was estimated to be 9 by taking a rough average of the ratios 9.4 obtained from g and 8.8 from h. This value is comparable to the ratio 11 of the rate of chain collapse of PMMA in AcN+water (10 vol %) to that in AcN. This close value of the ratios indicates that the nature of solvent would affect the rates of chain collapse and chain aggregation through a similar mechanism.

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I. INTRODUCTION

When a dilute polymer solution is quenched below the cloud point, chain collapse and chain aggregation occur competitively because of the same interactions between polymer segments in intra- and inter-molecules. At very low concentrations, polymer chains would collapse first and the collapsed chains would aggregate. The chain behavior below the cloud point has been studied extensively for solutions of poly(methyl methacrylate) (PMMA) in different solvents by static light scattering [1–8]. The experimental study has been carried out in the concentration range of $(0.5-6.0) \times 10^{-4}$ g/cm^3 admitting a blank time of 30 min after the quench for the thermal equilibration. The processes of chain collapse and chain aggregation for the PMMA solutions were observed for long time periods from minutes to weeks depending on the molecular weight and solvent species. For PMMA with the molecular weight $m_w = 12.2 \times 10^6$, the chain collapse finished within 90 min after the quench in pure tert-butyl alcohol (TBA) but required weeks in the mixed solvent TBA+water (2.5 vol %) [4,7]. For PMMA of $m_w = 1.57 \times 10^6$ in the mixed solvent, the chain collapse finished in the first 30 min after the quench and the chain aggregation processes were observed for long time periods [3]. The addition of water to TBA caused the slowdown of chain aggregation as well as that of chain collapse. For PMMA solutions studied with various solvents and molecular weights [1–8], the chain collapse was considered to finish before the chain aggregation became effective irrespective of the rate of chain collapse. This observation suggested that the rates of the chain collapse and chain aggregation would change in a nearly same proportion by changing the molecular weight and solvent. The present study was carried out to reveal the relation between the rates of chain collapse and chain aggregation.

Recently, we studied the relative rate of chain collapse of PMMA with $m_w = 6.4$ and 11.4×10^6 in pure acetonitrile (AcN) and in the mixed solvent AcN+water (10 vol %) by static light scattering [8,9]. The chain collapse occurred very slowly in pure AcN and was accelerated by the addition of water to AcN. The chain collapse process, which was observed at the later stage because of the thermal equilibration, was represented by the plot of the expansion factor α^2 versus $\ln t$ with t being the time after the quench. For each molecular weight, the chain collapse process in the mixed solvent was superposed on that in AcN by scaling the time as γt. The obtained value of the scale factor seemed to be independent of the molecular weight and was estimated to be $\gamma = 11$. Thus the chain collapse process in AcN+water (10 vol %) was found to occur faster by the factor $\gamma = 11$ than that in pure AcN. For the chain collapse processes observed in each solvent, the plot of α^2 versus $\ln t$ for the lower molecular weight was superposed on that for the larger molecular weight with a scale factor. The estimated scale factors suggested that the rate of chain collapse depended on the molecular weight as m_w^{-3}.

The chain aggregation process in PMMA solutions has been measured as a time evolution of the molecular weight M_w and the mean-square radius of gyration $\langle S^2 \rangle_z$ of clusters of polymer chains [2,3,5,6]. The aggregation process has been found to depend on the concentration c and time t as $M_w \sim e^{gct}$ and $\langle S^2 \rangle_z \sim e^{hct}$, where g and h represent the intrinsic rate of chain aggregation independent of the concentration, though numerically different. The exponential growth of clusters is characteristic to the reaction limited cluster aggregation (RLCA) [10]. Recently, the intrinsic rate was inferred to depend on the molecular weight as m_w^{-3} by an analysis of observed aggregation processes [11]. It should be noticed that this dependence is the same as that of the rate of chain collapse. This coincidence invokes a similarity between the chain collapse and chain aggregation suggested by Chuang *et al.* [12]. Thus it is important to make a quantitative comparison between the solvent dependences of chain collapse and chain aggregation. In this study, the intrinsic rates g and h were determined for PMMA of $m_w = 6.4 \times 10^6$ in AcN+water (10 vol %) and in AcN. The ratio of the rate in AcN+water (10 vol %) to that in AcN was estimated to be 9, which is comparable with the corresponding ratio $\gamma = 11$ for the chain collapse. The close ratio reveals an intimate correlation between the rates of chain aggregation and chain collapse. Moreover, the large values of the ratio demonstrate a strong dependence of the rates on the specific nature of solvent.

II. EXPERIMENT

The present experiment was made for the PMMA fraction which was used in the previous study on the chain collapse process in AcN and in the mixed solvent of AcN+water (10 vol %) [8,9]. The weight-average molecular weight m_w of the sample was determined as 6.4×10^6 by static light scattering, and the ratio of m_w to the number-average molecular weight m_n was determined as $m_w/m_n = 1.25$ by analytical gel permeation chromatograph (GPC). As solvents for PMMA, AcN and the mixed solvent of AcN+water (10 vol %) were used. Acetonitrile was fractionally distilled immediately before use. Water was purified by a standard method. The θ temperature has been determined to be 44.0 °C for PMMA in AcN and 50.0 °C in AcN+water (10 vol %) [8,9].

The PMMA solutions for the light scattering experiment were prepared in optical cells of 18 mm inside diameter by dilution of a stock solution to the concentrations of $c(10^{-4}\ \mathrm{g/cm^3}) = 0.86$, 1.73, 2.52, and 3.38 in AcN+water (10 vol %), and to $c(10^{-4}\ \mathrm{g/cm^3}) = 1.28$, 1.91, 2.58, 3.90, and 5.20 in AcN. Each optical cell was sealed tightly by a Teflon cap to prevent evaporation of the solvent and preserved in a glass tube partially filled with the solvent at the θ temperature. The chain aggregation experiment was performed at 32.0 °C for the solutions in AcN+water and at 15.0 °C in AcN. Each cell preserved at the θ temperature was transferred into a thermostated cylindrical cell at the center of the photometer. The intensity measurement of scattered light was started at 30 min after the setup of the cell for thermal equilibration, and was repeated at appropriate time intervals until the turbidity of the solution became perceptible to the eye. Thus the solutions were transparent and multiple scattering effect was negligibly small in the measurement. Scattered intensities were measured 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 $R_{90,vu} = 12.63 \times 10^{-6}\ \mathrm{cm^{-1}}$ at 25.0 °C [13]. The refractive index increment was estimated to be $dn/dc(\mathrm{cm^3/g}) = 0.133$ for PMMA in AcN at 15.0 °C and 0.134 in AcN+water (10 vol %) at 32.0 °C [8,9].

The light-scattering data, which were obtained as a function of the scattering angle θ and the concentration c, were transformed to the excess Rayleigh ratio R_θ. For a usual dilute polymer solution, R_θ can be written as [14]

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

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 of incident light in a vacuum, and n is the refractive index of the solution. M_w, $\langle S^2\rangle_z$, and A_2 represent the weight-average molecular weight, z-average mean-square radius of gyration, and the second virial coefficient, respectively. The light-scattering data obtained in an aggregation process of polymer chains could be analyzed by Eq. (1) omitting the term due to A_2, for K remains unchanged. In this case, M_w and $\langle S^2\rangle_z$ represent the corresponding quantities for clusters of polymer chains. The plot of $(Kc/R_\theta)^{1/x}$ versus $\sin^2(\theta/2)$ for data obtained in the chain aggregation process would give a straight line for an appropriate value of the constant x, and the slope and the intercept of the plot could be used to estimate $\langle S^2\rangle_z$ and M_w. The present scattering data was analyzed by Eq. (1) with $x = 1.5$.

The refractive indices of AcN and water are close to each other and the difference between them vanishes at 49.8 °C. Accordingly, the light scattering data for PMMA in AcN +water (10 vol %) could be analyzed by Eq. (1) for single solvent [9].

The phase separation temperature of the solutions was determined by lowering the temperature by 0.5 K stepwise. At each step, an increase of forward scattered intensity caused by cluster formation was monitored for a few days or more because of the very slow phase separation. The phase separation temperature T_p was determined as the temperature at which the scattered intensity began to increase on lowering the temperature. T_p ($10^4 c\ \mathrm{g/cm^3}$) at each concentration was obtained to be 39.0 °C (0.86), 40.0 °C (1.73), 40.5 °C (2.52), and 41.5 °C (3.38) for PMMA in AcN+water, and 21.0 °C (1.28), 22.0 °C (1.91), 23.0 °C (2.58), 24.0 °C (3.90), and 25.0 °C (5.20) in AcN.

III. EXPERIMENTAL RESULTS

Figure 1 represents the time evolution of scattered light intensities from PMMA in AcN+water (10 vol %) at $c = 2.52 \times 10^{-4}\ \mathrm{g/cm^3}$ by the plot of $(Kc/R_\theta)^{1/1.5}$ versus $\sin^2(\theta/2)$. The plots from the top to the bottom were obtained at 60, 120, 180, 240, 300, and 360 min after the quench to 32.0 °C. The data points at each time are represented by a straight line, from which M_w and $\langle S^2\rangle_z$ of clusters of chains were estimated by using Eq. (1) without the term due to A_2.

Figures 2(a) and 2(b) represent the semilogarithmic plots of M_w (g/mol) and $\langle S^2\rangle_z$ (nm^2) versus time t for PMMA in AcN+water (10 vol %), respectively. The different symbols are used to distinguish the data at different concentrations as c ($10^{-4}\ \mathrm{g/cm^3}$) = 0.86 (circles), 1.73 (squares), 2.52 (tri-

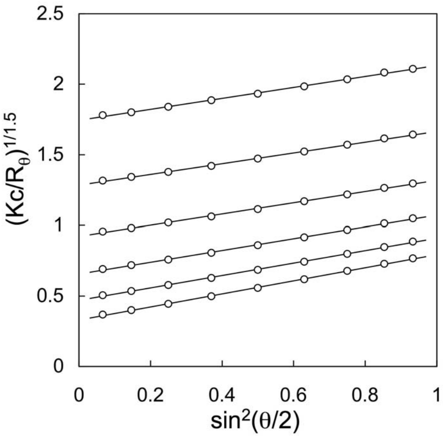

FIG. 1. Plots of $(Kc/R_\theta)^{1/1.5}$ $(10^{-5}\ \text{mol}^{1/1.5}/\text{g}^{1/1.5})$ vs $\sin^2(\theta/2)$ for scattered intensities from clusters of PMMA chains in AcN +water (10 vol %) at $c=2.52\times10^{-4}$ g/cm^3. The plots were obtained at 60, 120, 180, 240, 300, and 360 min after quench to 32.0 °C from the top to the bottom.

angles), and 3.38 (crosses). Both the plots in Figs. 2(a) and 2(b) can be represented by the straight lines except for in the region of smaller t. The deviation is noticeable at lower concentrations. Nevertheless, the main behavior of M_w and $\langle S^2\rangle_z$ can be written as

$$\ln M_w = \ln M(0) + Gt, \tag{2}$$

$$\ln \langle S^2\rangle_z = \ln S^2(0) + Ht, \tag{3}$$

where $M(0)$ and $S^2(0)$ are the values extrapolated to $t=0$, and G and H are the slopes. The rate of chain aggregation is represented by G and H, which are estimated from the straight lines as listed in Table I. The deviation from the straight line as shown in Fig. 2 has been observed for solutions of PMMA in other solvents [2,6]. The deviation did not seem to affect the slope of the straight line but caused an underestimation of the initial value.

The plots in Figs. 3(a) and 3(b) show the time evolutions of $\ln M_w$ and $\ln\langle S^2\rangle_z$ for clusters of PMMA chains in AcN at 15.0 °C, respectively. The different symbols are used for the concentrations of c $(10^{-4}\ \text{g/cm}^3)=1.28$ (circles), 1.91 (squares), 2.58 (triangles), 3.90 (diamonds), and 5.20 (crosses). The different time scales in Figs. 2 and 3 indicate that the chain aggregation for PMMA in AcN+water is faster by one order of magnitude than that in AcN. In Fig. 3, the data points at larger t are represented by the straight lines, though the data points at smaller t deviate largely from the lines especially at lower concentrations. As in the case of Fig. 2, the straight lines were used to estimate the parameters in Eqs. (2) and (3), which are listed in Table I. It should be noticed that the deviation from the straight lines occurs differently in Figs. 3(a) and 3(b). As seen clearly for the plots at the lowest concentration, the plot in Fig. 3(b) shows a minimum, which is not observed for the plot in Fig. 3(a). The initial decrease in $\langle S^2\rangle_z$ is due to the collapse of chains, and the following increase comes from the aggregation of the collapsed chains [11]. At higher concentrations the minimum is obscured by the fast chain aggregation. The chain collapse for PMMA in the mixed solvent of AcN+water occurs much faster than that in AcN and seems to finish in the first 30 min after the quench. Consequently, the minimum cannot be observed for the plots in Fig. 2(b).

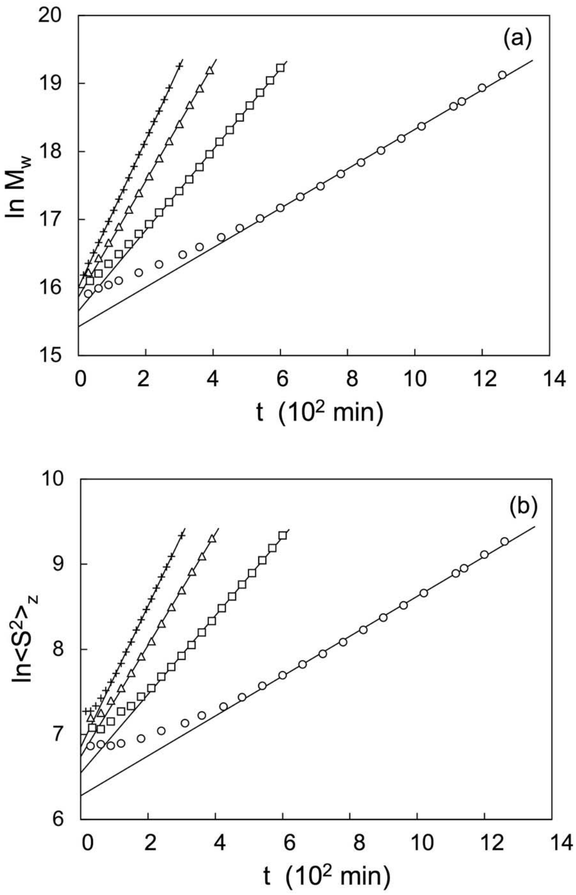

FIG. 2. Time evolution of the weight-average molecular weight M_w (g/mol) (a) and z-average square radius of gyration $\langle S^2\rangle_z$ (nm^2) (b) for clusters of PMMA chains in the mixed solvent of AcN +water (10 vol %) at 32.0 °C. Plots of $\ln M_w$ and $\ln\langle S^2\rangle_z$ vs t were obtained at the concentrations c $(10^{-4}\ \text{g/cm}^3)=0.86$ (circles), 1.73 (squares), 2.52 (triangles), and 3.38 (crosses).

In Fig. 4, the values of G and H given in Table I are plotted against c. The closed and open symbols represent the data for PMMA in AcN+water and in pure AcN, respectively. The circle and square represent G and H, respectively. The data points of G and H for both the systems fit to the straight lines given by $G=gc$ and $H=hc$, where g and h represent the intrinsic rates independent of the concentration. The values of g and h (cm^3 min^{-1} g^{-1}) were estimated as 32.0 and 21.8 for PMMA in AcN+water (10 vol %), and 3.40 and 2.48 for PMMA in pure AcN, respectively.

Figures 5(a) and 5(b) show the double-logarithmic plots of $\langle S^2\rangle_z^{1/2}$ (nm) vs M_w (g/mol) for PMMA in AcN+water and in AcN, with the same symbols as those in Figs. 2 and 3, respectively. In each plot, data points except for at smaller t construct a single straight line irrespective of the concentration. Data points deviating from the straight line in Fig. 5(b) are attributed to the chain collapse because of a decrease of $\langle S^2\rangle_z$ with increasing M_w. The slight deviation observed in

Fig. 5(a) would be also caused by the effect of chain collapse, which is not clear in Fig. 2. The relation between M_w and $\langle S^2\rangle_z$ in the process of the chain aggregation can be expressed by the power law as

$$\langle S^2\rangle_z^{1/2} = AM_w^{1/D}. \tag{4}$$

A least-squares fit of data points free from the effect of chain collapse gives $D=2.59$ and $A=7.49\times10^{-2}$ for PMMA in AcN+water, and $D=2.59$ and $A=6.33\times10^{-2}$ in AcN. The same value of D suggests that the size distribution and structure of clusters of chains behave similarly in AcN+water and in AcN, though the rates of chain aggregation in these solvents are very different.

IV. DISCUSSION AND CONCLUSION

The chain aggregation process depends on the quench depth, polymer concentration, molecular weight, and polymer-solvent system. The quench depth could be measured by the product $v\tau$, where v is the second virial coefficient of segment interaction and τ is the reduced temperature defined by $\tau=1-\theta/T$. The value of v has been estimated from observed coil-globule transition curves as $0.87\times10^{-23}\text{cm}^3$ for PMMA in AcN+water and $0.42\times10^{-23}\ \text{cm}^3$ in AcN [8,9]. The quench depth in the present experiment is estimated as $v\tau=-5.1\times10^{-25}\ \text{cm}^3$ in AcN+water at 32.0 °C and $-4.2\times10^{-25}\ \text{cm}^3$ in AcN at 15.0 °C, which are comparable with each other. The very different rates of chain collapse in these solvents could be attributed to a specific nature of solvent. A quantitative comparison between the two rates could be made by taking the ratio σ of the intrinsic rate in AcN+water to that in AcN. The value of σ was obtained as 9.4 from g and 8.4 from h. Since the intrinsic rates g and h are related by $g/h=D/2$ due to Eq. (4), the values of σ from g and from h should agree with each other for the same value of $D=2.59$ in AcN+water and in AcN. The different values of σ may be attributed to an experimental uncertainty. Thus we employ the rough average $\sigma=9\pm1$ of the two above values as a ratio of the aggregation rate in AcN+water to that in AcN. The difference of the two values was taken as a measure of error.

TABLE I. Values of the parameters G and H in Eqs. (2) and (3) for PMMA in the mixed solvent of AcN+water (10 vol %) (a) and in AcN (b).

c (10^{-4} g/cm^3)	G (10^{-4} min^{-1})	H (10^{-4} min^{-1})
	(a) PMMA in AcN+water (10 vol %)	
0.86	29.0	23.4
1.73	59.3	46.2
2.52	85.3	65.5
3.38	108	83.0
	(b) PMMA in AcN	
1.28	3.31	2.62
1.91	5.56	4.28
2.58	7.66	5.86
3.90	12.2	9.05
5.20	16.6	12.4

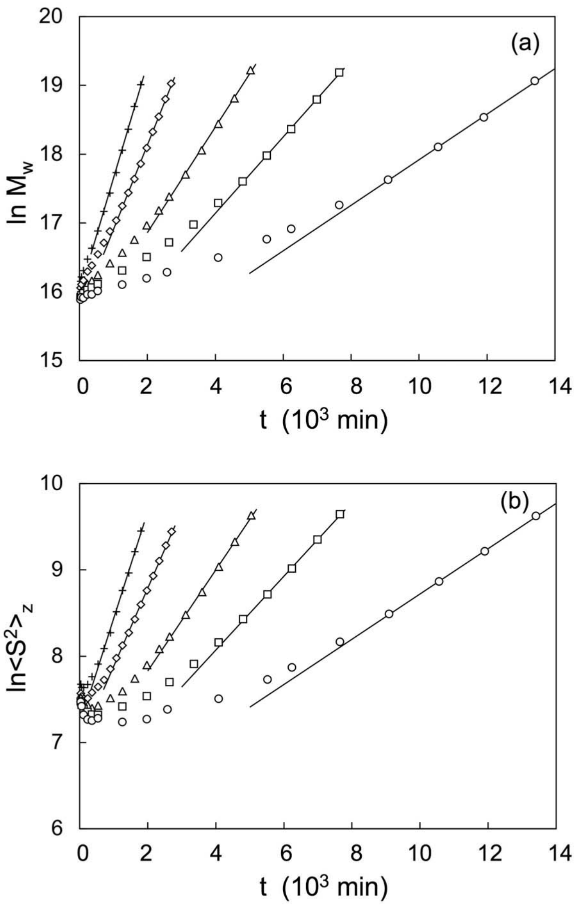

FIG. 3. Time evolution of the weight-average molecular weight M_w (g/mol) (a) and z-average square radius of gyration $\langle S^2\rangle_z$ (nm^2) (b) for clusters of PMMA chains in AcN at 15.0 °C. Plots of $\ln M_w$ and $\ln\langle S^2\rangle_z$ vs t were obtained at the concentrations c (10^{-4} g/cm^3)$=1.28$ (circles), 1.91 (squares), 2.58 (triangles), 3.90 (diamonds), and 5.20 (crosses).

As described in the Introduction, the chain collapse of PMMA in AcN+water (10 vol %) has been found to occur much faster than that in AcN [9]. The ratio γ of the rate of chain collapse in AcN+water to that in AcN was determined to be 12 and 9.5 for $m_w=11.4\times10^6$ and 6.4×10^6, respectively. On account of experimental errors, the ratio seems to be independent of the molecular weight and would be given by the average value $\gamma=11$, which is close to the present value $\sigma=9$ for chain aggregation. The close ratio of γ and σ suggests that a specific nature of solvent affects the rates of chain collapse and chain aggregation through a similar mechanism. The large value of the ratios indicates that the rates of the chain collapse and chain aggregation depend strongly on the solvent species. Furthermore, recent analyses of experimental data suggest that the rates of chain collapse and chain aggregation have the same molecular weight dependence of m_w^{-3} [9,11]. These results are compatible with the experimental observation on dilute PMMA solutions: The chain collapse finishes before the chain aggregation develops

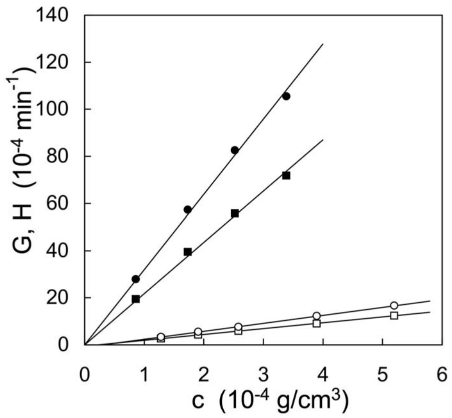

FIG. 4. Rates G (circles) and H (squares) of chain aggregation as a function of the concentration c. The closed symbols and open symbols represent the data for PMMA in AcN+water (10 vol %) at 32.0 °C and in pure AcN at 15.0 °C, respectively.

effectively, irrespective, of the molecular weight and solvent species

According to phenomenological theories [15,16], the chain collapse occurs at two stages: At the first stage polymer chains collapse by crumpling, and at the second stage the crumpled globules contract to equilibrium globules forming knots due to reptationlike motion. The characteristic times at the first and the second stage depend on the solvent viscosity η and the molecular weight m as ηm^2 and ηm^3, respectively. The chain collapse process, which was measured for PMMA solutions of large m_w at the later stage, was found to accompany a knot formation [17]. This observation at the later stage and the observed molecular weight dependence m_w^{-3} of the chain-collapse rate correspond to the second stage predicted by the phenomenological theories. However, the characteristic times of chain collapse at the first and the second stage are estimated roughly as millisecond and second for usual solutions of $m_w \sim 10^7$, respectively. These times are much smaller than experimental times of minutes to weeks for chain collapse of PMMA and also that of 10 min for polystyrene of $m_w = 8.0\times 10^6$ in cyclohexane [18]. It has been argued that the solvent viscosity in compact globules should be redefined as an effective viscosity [15,18]. To explain the observed chain-collapse rate, the effective viscosity should change largely depending on the solvent-polymer system.

The coil-globule transition temperatures for the present solutions are estimated to be 24.3 °C in AcN and 39.8 °C in AcN+water from the transition points $\tau m_w^{1/2} = -168$ and -82.4, respectively [8,9]. Since the present experimental temperatures were much lower than the transition ones, compact globules of collapsed chains aggregated to form clusters. Light-scattering data at the initial stage were analyzed by using the Zimm plot and the size of collapsed chains was determined as $\langle s^2\rangle_z = 1.02\times 10^{-11}$ cm^2 in AcN and $\langle s^2\rangle_z = 0.84\times 10^{-11}$ cm^2 in AcN+water. On the other hand, as seen in Figs. 2(a) and 3(a), the chain-aggregation process was measured up to $\ln M_w \sim 19$, which gives $M_w/m_w \sim 30$. Thus the present study was made for clusters of small size.

The phase separation has been discussed to develop via different mechanisms above and below the spinodal, that is, nucleation and growth in the metastable region and spinodal decomposition in the unstable region [19,20]. For dilute solutions of small molecules, the phase separation occurs rapidly when quenched below the binodal, and the spinodal far below the binodal cannot be located experimentally. Raos and Allegra made theoretical studies on the collapse and aggregation of polymer chains under poor-solvent conditions [21,22]. According to their argument on cluster formation, the concentration within a collapsed chain would become comparable with that in a polymer-rich phase when quenched below the coil-globule transition temperature, and consequently the phase separation would start without the free energy barrier for cluster formation. This means that the compact globule of the collapsed chain would behave as a critical nucleus, and the spinodal practically coincides with the binodal. For dilute PMMA solutions, the phase separation has been observed to occur without an incubation time and the average size of clusters increased continuously from that of a single collapsed chain [3,5,11]. This observation is in accord with the above argument by Raos and Allegra. Furthermore, they showed that the volume of a small cluster

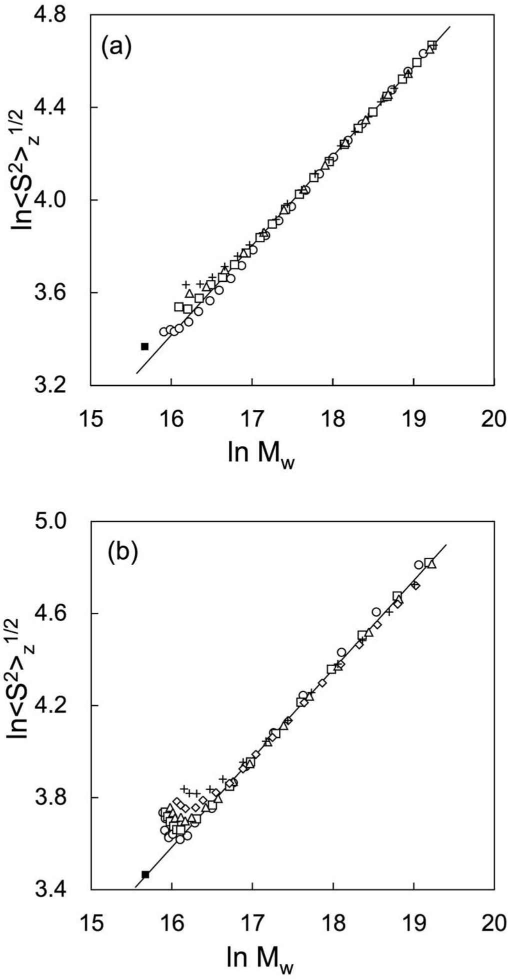

FIG. 5. Double-logarithmic plot of $\langle S^2\rangle_z^{1/2}$ (nm) vs M_w (g/mol) for PMMA in AcN+water (10 vol %) at 32.0 °C (a) and in AcN at 15.0 °C (b). The symbols in (a) and (b) are the same as those in Figs. 2 and 3, respectively. The closed squares represent data for a single collapsed chain.

below the coil-globule transition temperature depended linearly on the total number of chain segments in the cluster. This relation, which is expressed by Eq. (4) with $D=3$ for monodisperse clusters, seems to be reasonable for compact clusters containing a large number of chain segments. Hence the observed value $D=2.59$ smaller than 3 would be attributed to the cluster size distribution. Accordingly, the volume fraction ϕ of chain segment in a cluster may be constant independent of the cluster size, though the volume fraction estimated from $\phi=\frac{M_w/\rho}{(4\pi/3)N_A[(5/3)\langle S^2\rangle_z]^{3/2}}$ decreases with increasing M_w due to $D=2.59$ with ρ being the density of PMMA in the liquid state. Thus the volume fraction in a cluster would be represented by that in a collapsed chain, which is estimated as 0.030 in AcN and 0.040 in the mixed solvent AcN+water with $\rho=1.2\ \mathrm{g/cm^3}$. In Fig. 5 the data of single collapsed chains are given by the closed squares which are very close to the straight lines for the chain aggregation process. In the present experimental range of $M_w/m_w<30$, the property of clusters would be similar to that of a single collapsed chain. In light of the large amount of solvent in the globule, the collapsed chain could change its conformation rapidly. On account of the smooth completion of chain collapse shown in Figs. 2(b) and 3(b), the collapsed chains would be fairly deformable and far from the glass state. Correspondingly, clusters with the same concentration as the collapsed chain would be soft and deformable.

The chain aggregation in dilute PMMA solutions is very slow and depends strongly on the solvent species. This characteristic behavior of chain aggregation cannot be interpreted as a diffusion controlled process. According to Smoluchowski [23], a characteristic time for the diffusion limited cluster aggregation (DLCA) is given by $3\eta m/4N_AkTc$, where k is the Boltzmann constant. For the present solutions at $c\sim 2\times 10^{-4}\ \mathrm{g/cm^3}$ the characteristic time is estimated roughly to be 10^{-2} s, which is several orders of magnitude smaller than the experimental time scale. The exponential growth expressed by Eqs. (2) and (3) as well as the slow growth of clusters is characteristic to the reaction limited cluster aggregation (RLCA) [10]. Particular attention was paid to slow aggregations in dilute polymer solutions [18,24]. Tanaka observed an unusual behavior of small droplets in a phase-separation process of poly(vinyl methyl ether) in water [24]. In a restricted region of concentration and temperature, the droplets did not undergo coalescence and appeared to be stable. For dilute polymer solutions, a coalescence of two clusters was considered to be brought about by a chain which migrates between the clusters forming a bridge during a contact. This idea was substantiated by introducing the two characteristic times, that is, the chain diffusion time τ_r and contact time τ_c [24]. For $\tau_r/\tau_c\gg 1$ chains could hardly bridge two clusters during a contact and the aggregation would occur due to RLCA. For $\tau_r/\tau_c\ll 1$, a coalescence of two clusters would occur at each collision and the aggregation would develop due to DLCA.

In order to elucidate the stable droplets in the phase-separation process, Tanaka roughly estimated the ratio τ_r/τ_c by using $\tau_r\sim a^2N^3\phi^{3/2}/D_1$ for reptation of a chain in a dense polymer matrix [25] and $\tau_c\sim r_0^2/D_R$ for the diffusion time of a droplet, where a is the length of a unit monomer, N is the degree of polymerization, ϕ is the volume fraction of a polymer, r_0 is the range of interaction, and D_1 and D_R are the diffusion constants of a monomer and a droplet, respectively. The ratio τ_r/τ_c was found to have a value of several orders of magnitude and to be consistent with the observed stable droplet. A similar estimation for the clusters of PMMA chains yielded a ratio τ_r/τ_c of several orders of magnitude [11]. This is also the case of the present solutions. Chu *et al.* were puzzled about the fact that chain aggregation of polystyrene in cyclohexane occurred much slower than that predicted by DLCA [18] because the experimental observation was straightforward and the Smoluchowski equation had been derived with only plausible assumptions. Chuang *et al.* were interested in the slow chain aggregation indicated by Chu *et al.* and argued the coalescence of polymer chains in a different way [12]. They demonstrated an existence of an entanglement force acting between two approaching polymer globules in poor solvent by a molecular dynamics simulation. This force was shown to be strong enough to slow down the aggregation of polymer globules and consequently indicated $\tau_r/\tau_c\gg 1$. This argument for two approaching polymer globules is suggestive to the present slow formation of small clusters.

The aggregation of polystyrene in cyclohexane was shown to grow exponentially and to occur a few hundred times faster than that of PMMA in AcN [8]. Nevertheless, the rate of the chain aggregation of polystyrene is several orders of magnitude smaller than that by DLCA and might be dominated by a similar mechanism as that of PMMA in AcN. Tanaka as well as Chuang *et al.* conjectured the relation $\tau_r/\tau_c\gg 1$ on the basis of the chain entanglement [12,24]. In view of a universal nature of the chain entanglement, RLCA would be a common phenomenon in dilute polymer solutions as demonstrated by the solutions of PMMA and polystyrene. However, it is not explained by the arguments due to Tanaka and Chuang *et al.* that the observed rate of chain aggregation depends strongly on the polymer-solvent system. It should be mentioned that the characteristic time τ_r due to reptation in a dense polymer matrix can be related to the solvent viscosity by $D_1\sim kT/\eta a$. It is conceivable that the solvent viscosity for reptation might be redefined as an effective viscosity as in the case of the characteristic time of chain collapse [15,18]. As seen from the values of σ and γ obtained for the present solutions, the rates of chain collapse and chain aggregation depend largely on the solvent and the dependences are nearly the same. The effective viscosity could be an important factor for this behavior of the rates because it could vary with the polymer-solvent system and is involved in both the rates of chain collapse and chain aggregation. At present the mechanism of the effective viscosity is not clear, though a hint may be obtained from the solutions of PMMA in the mixed solvent AcN+water and in TBA +water. The rates of chain collapse and chain aggregation of PMMA in TBA decrease by an addition of water, while the rates in AcN increase. The effective viscosity can be investigated systematically by varying the content of water. Furthermore, it is advantageous for a comparative study that water affects the effective viscosity in an opposite way in these PMMA solutions. The solution of the mixed solvent may give rise to an additional effect due to the preferential adsorption. Since the refractive index of AcN is very close to that of water as mentioned in Sec. II, the effect of the preferential adsorption cannot be deduced from the static light-scattering data. According to the above argument, the preferential adsorption would affect the rates of chain collapse and chain aggregation similarly through the effective viscosity. However, the preferential adsorption would not be of primary importance for the effective viscosity because the rates of chain collapse of PMMA in pure TBA and in pure AcN are found to be very different [7,8].

[1] M. Nakata and T. Nakagawa, J. Chem. Phys. **110**, 2703 (1999).
[2] M. Nakata, T. Nakagawa, Y. Nakamura, and S. Wakatsuki, J. Chem. Phys. **110**, 2711 (1999).
[3] Y. Nakamura, T. Nakagawa, N. Sasaki, A. Yamagishi, and M. Nakata, Macromolecules **34**, 5984 (2001).
[4] Y. Nakamura, N. Sasaki, and M. Nakata, Macromolecules **34**, 5992 (2001).
[5] T. Nakagawa, Y. Nakamura, N. Sasaki, and M. Nakata, Phys. Rev. E **63**, 031803 (2001).
[6] Y. Nakamura, N. Sasaki, and M. Nakata, Macromolecules **35**, 1365 (2002).
[7] Y. Nakamura, N. Sasaki, and M. Nakata, J. Chem. Phys. **118**, 3861 (2003).
[8] Y. Maki, N. Sasaki, and M. Nakata, Macromolecules **37**, 5703 (2004).
[9] Y. Maki, T. Dobashi, and M. Nakata, J. Chem. Phys. **126**, 134901 (2007).
[10] T. Vicsek, *Fractal Growth Phenomena* (World Scientific, Singapore, 1989).
[11] M. Nakata, Y. Nakamura, N. Sasaki, and Y. Maki, Phys. Rev. E **76**, 041805 (2007).
[12] J. Chuang, A. Yu. Grosberg, and T. Tanaka, J. Chem. Phys. **112**, 6434 (2000).
[13] M. B. Huglin, S. J. O'Donohue, and M. A. Radwan, Eur. Polym. J. **25**, 543 (1989).
[14] M. Nakata, Polymer **38**, 9 (1997).
[15] P. G. de Gennes, J. Phys. (France) Lett. **46**, L–639 (1985).
[16] A. Yu. Grosberg, S. K. Nechaev, and E. I. Shakhnovich, J. Phys. (France) **49**, 2095 (1988).
[17] M. Nakata, Y. Nakamura, Y. Maki, and N. Sasaki, Macromolecules **37**, 4917 (2004).
[18] B. Chu, Q. Ying, and A. Yu. Grosberg, Macromolecules **28**, 180 (1995).
[19] K. Binder and D. Stauffer, Adv. Phys. **25**, 343 (1976).
[20] J. W. Cahn, Trans. Metall. Soc. AIME **242**, 166 (1968).
[21] G. Raos and G. Allegra, J. Chem. Phys. **104**, 1626 (1996).
[22] G. Raos and G. Allegra, J. Chem. Phys. **107**, 6479 (1997).
[23] M. von Smoluchowski, Phys. Z. **17**, 585 (1916); Z. Phys. Chem., Stoechiom. Verwandtschaftsl. **92**, 129 (1917).
[24] H. Tanaka, Macromolecules **25**, 6377 (1992); Phys. Rev. Lett. **71**, 3158 (1993).
[25] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, New York, 1979).