

Coil to globule transition behaviour of poly(methyl methacrylate) in isoamyl acetate

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Abstract

The coil–globule transition behaviour of poly(methyl methacrylate) has been studied in isoamyl acetate by using the dynamic light scattering technique. The dimensions of the polymer show smooth and continuous contraction below θ temperature (61.0°C). The hydrodynamic size of PMMA in isoamyl acetate ($M_w = 3.3 \times 10^6 \text{ g mol}^{-1}$) decreases to 41% in an unperturbed state at 18.4°C. The temperature dependence of a chain contraction can be represented by a master curve in $\alpha_h^3 |\tau| M_w^{1/2}$ vs $|\tau| M_w^{1/2}$ plot, where $\alpha_h = R_h/R_{h,\theta}$ and $\tau = (T - \theta)/\theta$. A high-chain density value implies that the highly collapsed globule contains 56% isoamyl acetate in its hydrodynamic volume. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Dynamic light scattering; Coil–globule collapse; Poly(methyl methacrylate)

1. Introduction

In 1960, Stockmayer [1] first predicted that “even atactic chain molecules must collapse to a rather dense form if the net attraction between their parts becomes sufficiently large”. Since then, the transition of macromolecular chains from a random-coil behaviour in the theta state to a globular compact form in the collapsed state, has been the subject of extensive studies. This change in the state of a polymer chain from the open coil to the globular particles is called the coil–globule transition. A summary of contributions made by the end of 1970 was presented by Williams et al. [2], and a more recent review has been presented by Fujita [3] in 1992. The interest in this coil-to-globule transition is not only due to its importance in polymer solution dynamics, but also due to its implications in many biological systems, such as protein folding [4], DNA packing [5,6] and the nature of the collapse of a network gel [7].

Various experimental methods such as static and dynamic light scattering, small-angle neutron scattering, ultracentrifugation and viscosimetric measurements were used for the determination of linear polymer dimensions. The expansion of a random coil and the temperature dependence of the expansion factor α can be obtained from the classical Flory equation given for the excluded volume effect [8].

The contraction of the polymeric chain is considered using both mean-field theories and other new approaches over a wide range of temperature [9–12]. For the contracted coil, Birshtein and Pryamitsin derived the following equation for the expansion factor α as

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

where N represents the number of Kuhn segments in the chain, B and C are parameters that do not depend on molecular weight M or temperature T , but rather on chain stiffness, $\tau = (T - \theta)/\theta$ is the reduced temperature and C is caused by the third virial coefficient [14].

Most of the coil–globule transition experiments were carried out for polystyrene solutions at extremely low concentrations [13,15–18]. Recently, Chu and co-workers reported a two-stage kinetics of a single-chain collapse for polystyrene in cyclohexane [19–21]. A theoretical two-stage kinetics of a single chain collapse was proposed earlier [22,23]. However, the possibility of chain clustering during the second stage of collapse was taken into consideration by Raos and Allegra [24]. It was found that the clusters of two to five polystyrene chains have a smaller radius than a single chain. Raos and Allegra [24] concluded that the much smaller objects observed in the second stage of collapse, reported as “compact globules” by Chu and co-workers [23], under kinetic conditions are actually macromolecular clusters

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Table 1
The characterization of the fractionated and unfractionated PMMA sample

Sample	[η] ^a	M^b ($\times 10^{-6}$ g mol ⁻¹)	M_w ($\times 10^{-6}$ g mol ⁻¹)	M_n ($\times 10^{-6}$ g mol ⁻¹)	M_w/M_n	Contents of triads ^c (%)		
						Syndiotactic	Atactic	Isotactic
PMMA (unfractionated)	4.134	1.48	1.74 ^d	0.90 ^d	1.92	—	—	—
PMMA (fractionated)	—	—	3.30 ^e	2.26 ^e	1.46	60.2	33.9	5.9

^a Intrinsic viscosity in chloroform at 25°C.

^b Molecular weight calculated using Eq. (2), via viscometry.

^c Via ¹H NMR.

^d Via GPC.

^e Via LS/SEC.

resulting from the aggregation of a small number of polymer chains. Consequently, the initial collapse stage (about 25% contraction) corresponds to the final equilibrium state for the polystyrene in cyclohexane.

Considering contradictory experimental data and a limited contraction observed for the polystyrene–cyclohexane system, we have studied the collapse behavior of poly (*o*-chlorostyrene) and poly (*p*-chlorostyrene) under poor solvent conditions [25]. For these polymers, we have not observed a two-stage kinetics. Although α values for these chains exceed the contraction reported for polystyrene in cyclohexane, they are still not satisfactory for a single globule formation.

Nakata carried out detailed static light scattering experiments using various poly(methyl methacrylate) (PMMA) samples in the mixed solvent *tert*-butyl alcohol + water [26] and in isoamyl acetate [27]. Since the phase separation occurred very slowly for this system, the mean square radius of gyration $\langle s^2 \rangle$ and the second virial coefficient A_2 were determined reliably even far below the phase separation temperature.

Recently, we have studied the coil–globule transition of PMMA by an intrinsic viscosity [28] and by dynamic light scattering [29] in dilute theta solutions. In this work, we report dynamic light scattering results in isoamyl acetate. The data analyzed in terms of the temperature dependence of the hydrodynamic radius (R_h) and the segment volume fraction (ϕ) in the globular state. The results were compared with previously reported values of expansion factors based on static light scattering [26,27] viscosity measurements [28], and dynamic light scattering [29] for PMMA in various theta solvents. We have observed much shorter collapse time for PMMA in isoamyl acetate in comparison with the collapse time reported for polystyrene in cyclohexane as about 800 s [21].

2. Experimental

2.1. Materials

Poly(methyl methacrylate) (PMMA) sample with weight-average molecular weight M_w of 2.3×10^6 g mol⁻¹ was

purchased from Polysciences Inc. This was fractionated by the fractional precipitation technique at 25.0°C, using toluene as solvent and methanol as non-solvent [30]. In our process, 1 g of PMMA was dissolved in 0.1 w/w % toluene and 0.310 g PMMA as the first (highest molecular weight) fraction was obtained. This highest fraction (0.150 g) was dissolved in toluene to produce 0.027 w/w % solution and further fractionated. The resulting product was 0.040 g PMMA.

2.2. Characterization

2.2.1. Viscometry

The molecular weight of unfractionated sample was determined by the viscosity measurement using the following relationship [31].

$$[\eta] = 1.91 \times 10^{-3} P^{0.80} \text{ (chloroform, 25}^\circ\text{C)} \quad (2)$$

where P is the polymerization degree of PMMA.

2.2.2. Gel permeation chromatography

Gel permeation chromatography (GPC) was used to determine the molecular weight of unfractionated PMMA sample and its distribution with a Waters instrument (410 Differential Refractometer). Tetrahydrofuran (THF) served as an eluent. The flow rate was 1 ml min⁻¹. Waters styragel column HT6F was used and molecular weight calibration was performed by using polystyrene standard samples.

2.2.3. Light scattering/size exclusion chromatography

Light scattering/size exclusion chromatography (LS/SEC) measurements were carried out to characterize the fraction of PMMA using the PMMA standard samples. The sample was dissolved in THF and filtered through a 0.5 μ m Teflon disposable filter. It was then run in THF at a flow rate of 1.0 ml min⁻¹ using a Jordi Gel DVB Mixed Bed column, 50 cm \times 10 mm (ID), at a column oven temperature of 35°C. The sample injection size was 200 μ l of an approximately 0.1 w/v % solution. The sample was monitored at a sensitivity of $8 \times$ and a scale factor of 20 on a Waters Model 410 DRI fitted with a Precision Detectors Model PD2000. The detector wavelength was 685 nm.

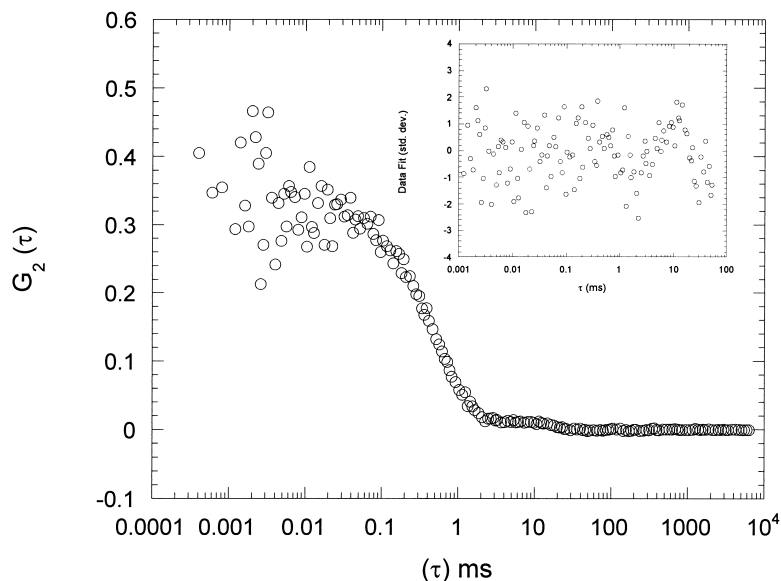


Fig. 1. The intensity autocorrelation function $G_2(\tau)$ of PMMA in isoamyl acetate solution ($C = 3.45 \times 10^{-5} \text{ g ml}^{-1}$) at 61.0°C (θ temperature). The inset shows the deviation plot based on the second-order cumulants fit.

Molecular weight characterization of unfractionated and fractionated samples are presented in Table 1.

2.2.4. ^1H nuclear magnetic resonance

^1H NMR spectrum of PMMA sample was recorded on a Bruker-AC 200L spectrometer at 200 MHz. The spectrum was taken in deuterated chloroform at room temperature ($23 \pm 0.1^\circ\text{C}$). The three peaks observed at 0.85, 1.00 and 1.25 ppm represent the resonance of syndiotactic, atactic and isotactic methyl groups [32]. The area under each of these three peaks corresponds to the content of each triad present in the polymer chain [32]. The calculated results are included in Table 1.

2.2.5. Dynamic light scattering measurements

The preparation of dust-free solutions for dynamic light scattering (DLS) measurements was as follows. A stock solution with a concentration of $\sim 10^{-4} \text{ g g}^{-1}$ was prepared for PMMA in its theta solvent isoamyl acetate. The stock solution was kept in an oven at 80°C for complete dissolution. The stock solution was diluted to the concentration of $3.45 \times 10^{-5} \text{ g ml}^{-1}$. The solution was filtered carefully into a dust-free light scattering cell with $0.2 \mu\text{m}$ Millipore filters.

DLS measurements were conducted by using a commercial DLS spectrometer (ALV/LSE 5000) operating at $\lambda = 514.5 \text{ nm}$ with an Ar laser. Thin-walled cylindrical cells (0.3048 mm wall thickness, 10 mm outer diameter and 75 mm length) were used to shorten the thermal equilibration time [21]. The borosilicate flat bottom cells were purchased from Wilmad Glass, NJ, USA. Temperature was controlled to $\pm 0.01^\circ\text{C}$.

The polymer solution was quenched to the selected temperature from the θ temperature in order to induce the

size change, which was determined by means of DLS in terms of the hydrodynamic radius (R_h).

The raw output of a DLS experiment is the autocorrelation function of the scattered light intensity, $G_2(\tau)$, typically plotted with a logarithmic time. The correlation functions were measured at a scattering angle of 33° . $G_2(\tau)$ is related to the normalized first-order electric field correlation function $g_{(1)}(\tau)$ as [33,34]

$$G_2(\tau) = A[1 + \beta |g_{(1)}(\tau)|^2] \quad (3)$$

where A is the baseline, β the coherence parameter depending on the instrumental optics and $\tau (\equiv \Gamma^{-1})$ the delay time. For polydisperse and concentrated systems, $g_{(1)}(\tau)$ is expressed by the distribution function $G(\Gamma)$ of the decay rate Γ as

$$g_{(1)}(\tau) = \int G(\Gamma) \exp(-\Gamma\tau) d\Gamma \quad (4)$$

where $\int G(\Gamma) d\Gamma = 1$. That is, $g_{(1)}(\tau)$ is the Laplace transform of $G(\Gamma)$.

For a diffusive relaxation, Γ can be further related to the average translational diffusive coefficient D by $D = (\Gamma/q^2)_{q \rightarrow 0}$, where $q = 4\pi n/\lambda(\sin \theta/2)$, $\lambda = 514.5 \text{ nm}$, $n =$ refractive index of solvent and $\theta =$ scattering angle. By using the Stokes–Einstein equation, the hydrodynamic radius, R_h , may be evaluated from the diffusion coefficient

$$R_h = k_B T / 6\pi\eta D \quad (5)$$

where k_B is the Boltzmann constant, η the solvent viscosity and T the absolute temperature. Viscosity (η) of the solvent isoamyl acetate was measured by a precision capillary viscometer (Cannon-Ubbelohde 50 B-313). The viscometer constant is the same at all temperatures and its value is $0.004178 \text{ cS s}^{-1}$. The solvent viscosity, η , in centipoise

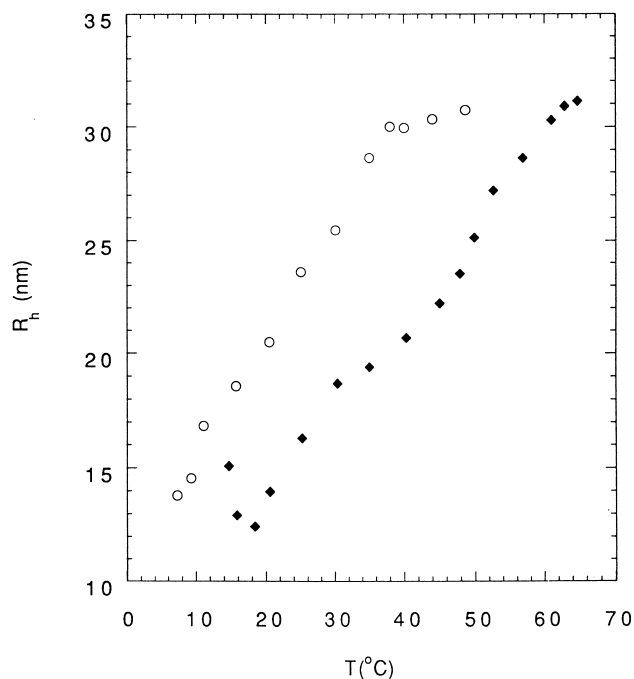


Fig. 2. The plot of hydrodynamic radius (R_h) vs temperature for PMMA in isoamyl acetate (\blacklozenge). For comparison, R_h values obtained from Ref. [29] were included (\diamond).

(cP) was obtained by multiplying the efflux time in seconds by the viscometer constant and the density of the solvent in g cm^{-3} . The temperature dependence of solvent viscosity is given in the following equation.

$$\log \eta(T) = -1.7374 + 490.4/T \quad (6)$$

where η is the isoamyl acetate viscosity (cP) and T is the temperature (K). Data analysis of the electric field time correlation curve was performed by using the method of cumulants [21] and the CONTIN method [35].

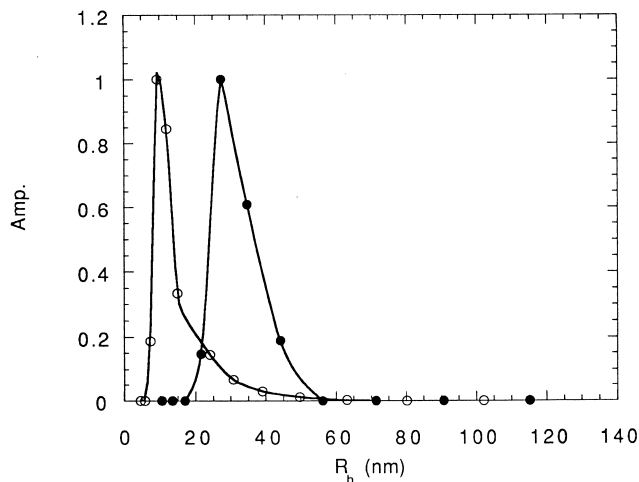


Fig. 3. A typical hydrodynamic size distribution of PMMA in isoamyl acetate at theta conditions (\bullet : $T = 61.0^\circ\text{C}$, $R_h = 30.3$ nm) and poor solvent conditions (\circ : $T = 18.4^\circ\text{C}$, $R_h = 12.44$ nm).

3. Results and discussion

For the PMMA–isoamyl acetate system, θ temperature is reported to be 57.5 [36] and 61.0°C [27]. For the determination of θ , a second virial coefficient A_2 was measured at several temperatures and the temperature at which A_2 vanished was reported as the θ temperature [27].

Fig. 1 shows the intensity autocorrelation function $G_2(\tau)$ of the dilute (3.45×10^{-5} g/ml) PMMA solution with an average decay rate, $\bar{\Gamma} = 1.27 \text{ ms}^{-1}$ and the variance, $\mu_2/\bar{\Gamma}^2 = 0.038$ at a θ temperature of 61.0°C and a scattering angle of 33° . M_z/M_w was found to be 1.15 for this sample by using the relation [37] $M_z/M_w \cong 1 + (\mu_2/\bar{\Gamma}^2)$. The average hydrodynamic radius R_h of the polymer is calculated from Eq. (5) as 30.3 nm at 61.0°C . In Fig. 2, the hydrodynamic radius determined from the correlation function measurements is shown as a function of temperature for the dilute PMMA solution in isoamyl acetate. The PMMA solution was brought from θ temperature (61.0°C) to the designated temperature. DLS measurements at each temperature was conducted after the equilibrium was reached. The contraction can be seen in Fig. 2. For comparison, our previous data for the same sample of PMMA in *n*-butyl chloride ($\theta = 38^\circ\text{C}$) was also included in this figure [29]. The overall trend for the contraction of the PMMA chain in isoamyl acetate is similar to that of the *n*-butyl chloride system. A gradual contraction was observed for PMMA in isoamyl acetate up to 18.4°C ($\alpha_h = 0.41$). The system was thermodynamically stable and the reported hydrodynamic radius values were independent of time down to 18.4°C . The hydrodynamic size (R_h) of the PMMA chain at 18.4°C was reduced to 41% of its θ state dimension. The contraction value for PMMA observed in this work is slightly higher than the reported value ($\alpha_h = 0.44$) for the PMMA–*n*-butyl chloride system [29].

A typical hydrodynamic size distribution of PMMA in isoamyl acetate at θ temperature ($\theta = 61.0^\circ\text{C}$) and poor solvent condition ($T = 18.4^\circ\text{C}$) are given in Fig. 3. In this figure, the data for the distribution plot was taken 12 min after the PMMA–isoamyl acetate solution was quenched from above θ to 18.4°C . Although the shape of R_h distribution still obeyed a single modal distribution, the polydispersity of R_h distribution (M_z/M_w) increased from 1.15 to 2.61, where the symmetrical shape of the curve began to be distorted, with the larger size end of the distribution curve being stretched out. The experimental observation could imply that, the polymer coil was stable in the contracted state for a time period of about 17 min, and DLS could not yet resolve the bimodal distribution. However, with a further increase of time to 18 min, the aggregation effect among the higher molecular weight fractions of the polymer chains due to the intermolecular interactions began to be observable (Fig. 4). The intensity time correlation function was no longer close to a single exponential and the size distribution began to become bimodal. In Fig. 4, the inset shows the R_h distribution of the large-size aggregates. The

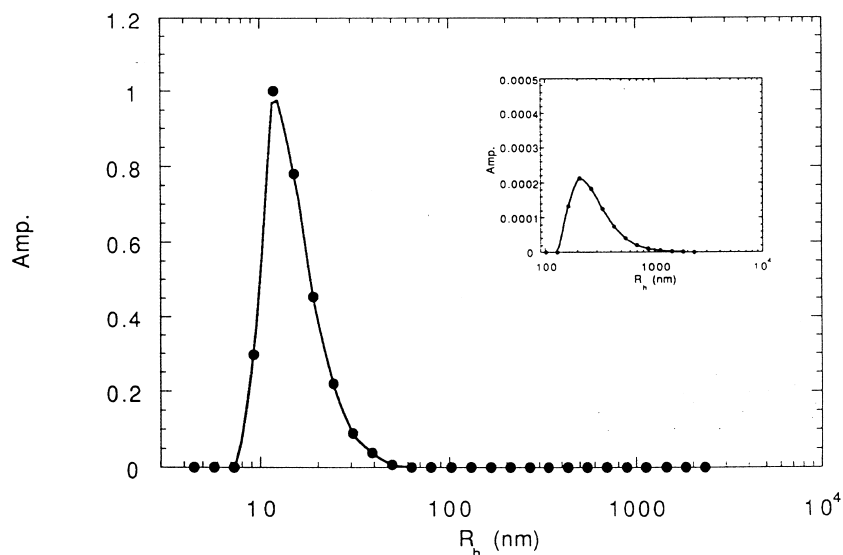


Fig. 4. A typical hydrodynamic radius distribution of the PMMA–isoamyl acetate solution, determined at 18 min, after the sample was quenched from 61.0 (θ temperature) to 18.4°C. The inset shows the R_h distribution of the large size aggregates.

smallest size globules had an average size of $R_h \cong 14.6$ nm and $M_z/M_w = 1.67$. The average size of the large aggregates obtained from CONTIN analysis was 276 nm with $M_z/M_w = 2.89$. These made up to 0.1% of the total sample.

It was possible to measure R_h value after the PMMA–isoamyl acetate system was quenched from 61.0 to 15.8°C (for a period of 9 min). At 14.7°C, the above period will be reduced to 4 min. However, at these temperatures the system is not stable and the scattered intensity increases gradually, confirming that the aggregation of PMMA chains is in progress. At 11.0°C, the process of aggregation was too fast to obtain reliable data.

Fig. 5 shows the temperature dependence of the mean-squared linear expansion of PMMA in isoamyl acetate. In order to make a comparison, static light scattering data reported by Nakata were also included in this figure [27]. Experimental data based on the static and dynamic light scattering measurements exhibit a continuous rather than a discrete transition. The phase separation temperature for PMMA with $M_n = 65\,000$ g mol⁻¹ and concentration $c = 1 \times 10^{-2}$ g cm⁻³ was previously reported to be 0°C [38]. It will be seen from Fig. 5 that, Nakata et al. observed a gradual contraction down to 0°C for the PMMA–isoamyl acetate system by static light scattering measurements [27]. They also reported that very slow phase separation did not prevent the determination of M_w and $\langle s^2 \rangle$. However, in the present work, the lowest accessible temperature was 18.4°C, and we could observe satisfactory chain collapse at this temperature ($\alpha_h = 0.41$) before the system reached thermodynamically unstable regime, i.e. phase separation and aggregation.

In order to compare the observed behaviour of α with Eq. (1), $(\alpha^3 - \alpha)/(1 - \alpha^{-3})$ values were plotted against $|\tau| N^{1/2}/(1 - \alpha^{-3})$ for $\alpha < 1$ in Fig. 6. The data points adequately fit the linear dependence. From the slope and

the intercept of the straight lines *B* and *C*, values were evaluated for the PMMA–isoamyl acetate and the PMMA–*n*-butyl chloride systems and are given in Table 2. This table also contains *B* and *C* values obtained from data [26,27] and the values calculated from viscosity results [28]. *B* and *C* are parameters that do not depend on molecular weight, but depend on the chain stiffness. As can be seen from Table 2, all *C* values are very close to each other. On the other hand, the values of *B* differ for the PMMA

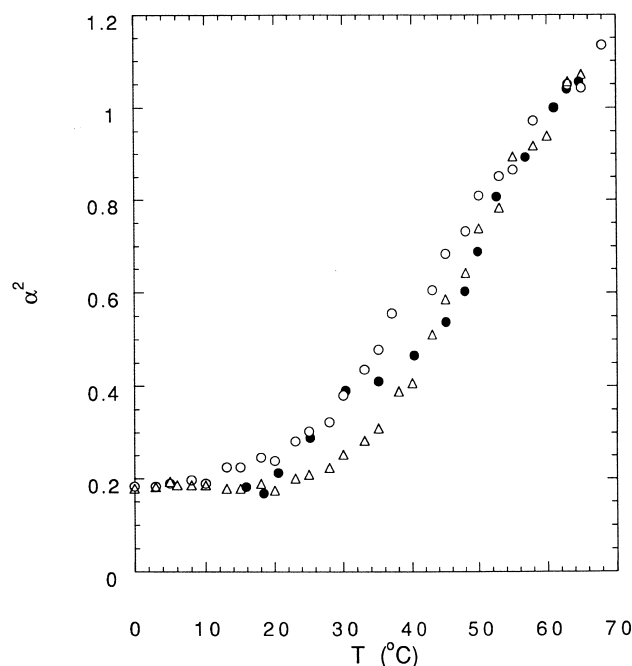


Fig. 5. The plot of expansion factor, α_h^2 , vs temperature for PMMA in isoamyl acetate, (●: $M_w = 3.3 \times 10^6$ g mol⁻¹). For comparison, α_s^2 values obtained from Ref. [27] were included (○: $M_w = 2.35 \times 10^6$ g mol⁻¹; △: $M_w = 4.4 \times 10^6$ g mol⁻¹).

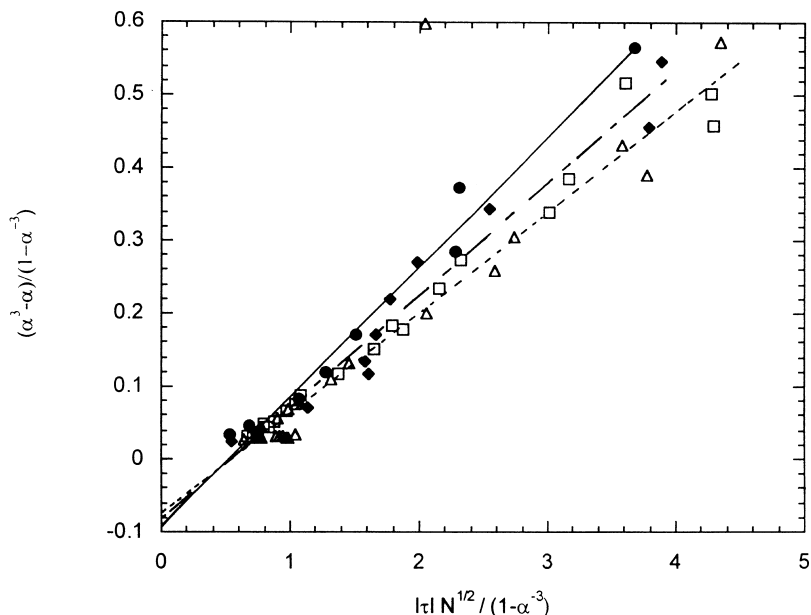


Fig. 6. The plot of $(\alpha^3 - \alpha)/(1 - \alpha^{-3})$ vs $N^{1/2} |\tau| / (1 - \alpha^{-3})$ for the random coil–globule transition of PMMA. (◆: PMMA–isoamyl acetate; ●: PMMA–*n*-butyl chloride Ref. [29]; □,△: PMMA–isoamyl acetate Ref. [27].

samples in various solvents. The observed differences are probably related to the effect of the finite size of solvent molecules on the second virial coefficient of the unit interaction in solution [14].

Fig. 7 shows a master curve of a scaled expansion factor of the hydrodynamic size $\alpha_h^3 |\tau| M_w^{1/2}$ vs $|\tau| M_w^{1/2}$ where $\alpha_h = R_h/R_{h,\theta}$ and $\tau = (T - \theta)/\theta$ for the PMMA–isoamyl acetate system. A well established plateau region was observed for the PMMA–isoamyl acetate system at $\alpha_h^3 |\tau| M_w^{1/2} \cong 34 \text{ g}^{1/2} \text{ mol}^{-1/2}$. The cross-over point was calculated for the PMMA–isoamyl acetate system from Eq. (1) by considering $(d^2(\alpha^2)/dT^2)^{-1} = 0$. For this system, α_h^2 was estimated to be 0.64 and the corresponding $|\tau| M_w^{1/2}$ value was 74.5 at the cross-over point as can be seen in Fig. 7. For the PMMA–*n*-butyl chloride system, $\alpha_h^2 = 0.65$ and $|\tau| M_w^{1/2} = 63.5$. It was observed that the $\alpha_h^3 |\tau| M_w^{1/2}$ drops at higher $|\tau| M_w^{1/2}$ for both PMMA–isoamyl acetate and PMMA–*n*-butyl chloride systems. This observation can

be reasonable for the highly collapsed globule where the attractive interaction between different segments should be much stronger than in the extended coil conformation [39]. The helical nature of the atactic PMMA chain also increases the segment interaction, and can be the reason for the decrease followed by a plateau [40].

The solid curves in Fig. 7, give the calculation due to Eq. (1) by using the corresponding *B* and *C* values. The horizontal lines at the right indicate the asymptotic globule state, i.e. $\alpha_h^3 |\tau| M_w^{1/2} = C/B = 16.49$ for the system of isoamyl acetate and 15.18 for the system of *n*-butyl chloride.

The segment volume fraction ϕ in the globule may be given by

$$\phi = (M_w/\rho)/\{4\pi/3\}\kappa\langle s^2 \rangle^{3/2} N_A \quad (7)$$

where $\rho = 1.2 \text{ g ml}^{-1}$ is the density of PMMA in the liquid state, M_w is the molecular weight of PMMA and N_A is the Avogadro number. (It should be noticed that, for a DLS value of radius R_h^3 , $\kappa = 1$.) The value of the segment volume fractions (ϕ) show variations depending on the technique used, such as DLS, SLS and viscometry are listed in Table 3. In this work, the segment volume fraction is estimated as $\phi = 0.56$ in isoamyl acetate. This means that density in the polymer domain of the globule is not dilute. However, the estimated value of the segment volume fraction of polymer domain is rather low for the PMMA–isoamyl acetate system by using static light scattering experiments. ($\phi = 0.07$ if $\kappa = (5/3)^{3/2}$ is taking into account in Eq. (7).) Segment volume fraction calculated by viscosity of the suspension of globular spheres is also low ($\phi = 0.061$) for the PMMA–*tert*-butyl alcohol + water system. It will be seen in Table 3, that only for the PMMA–isoamyl acetate system, the

Table 2
The values of parameters of *B* and *C* for PMMA obtained at $\tau < 0$

System	$M_w \times 10^{-6} \text{ (g mol}^{-1}\text{)}$	<i>B</i>	<i>C</i>
PMMA–isoamyl acetate ^a	3.3	0.154	0.080
PMMA– <i>n</i> -butyl chloride ^a	3.3	0.177	0.085
PMMA–isoamyl acetate ^b	2.35 and 4.4	0.130	0.073
PMMA– <i>tert</i> -BuOH + H ₂ O mixture	2.38 ^b	0.506	0.044
	2.5 ^c	0.377	0.110
	4.7 ^c	0.295	0.085

^a DLS.

^b SLS, Refs. [26,27].

^c Viscometry, Ref. [28].

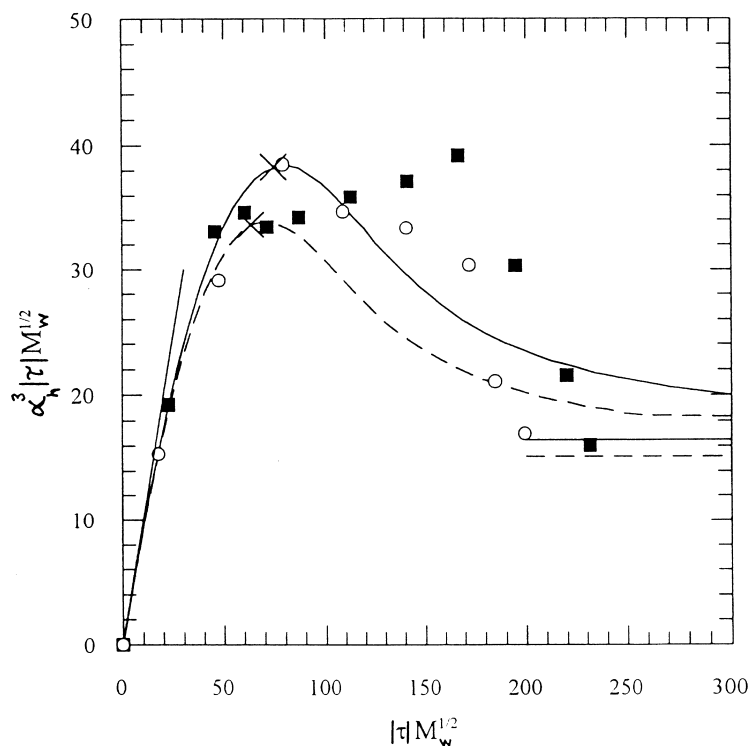


Fig. 7. The plot of scaled hydrodynamic expansion factor $\alpha_h^3 |\tau| M_w^{1/2}$ as a function of the reduced temperature $|\tau| M_w^{1/2}$ for PMMA–isoamyl acetate (■). Empty circles denote the results in Ref. [29]. The solid and dashed lines are due to Eq. (1) for PMMA–isoamyl acetate and PMMA–*n*-butyl chloride, respectively. The horizontal lines indicate the asymptotic limit, C/B . The crosses are cross-over points.

segment volume fraction values were evaluated by using both the DLS and SLS techniques. For this system, the value of κ has to be considered as 0.25 instead of $(5/3)^{3/2}$ in order to find segment fraction values as $\phi = 0.56$.

3.1. Time dependence of coil-to-globule transition

A two-stage kinetics of a single chain collapse was proposed theoretically [22,23]. The theory predicted a rather fast crumpling of the unknotted polymer chain (crumpled globule) and a subsequent slow knotting [23] of the rearrangement of thermal blobs [1] of the collapsed

polymer chain (compact globule). Recently, detailed experimental and theoretical descriptions of two-stage kinetics of polystyrene in cyclohexane system were published by Chu and coworkers [19–21]. However, as the two-stage kinetics theory was seriously challenged by Raos and Allegra [24], we will not refer further to polystyrene–cyclohexane system. The time for a polymer solution to reach the newly specified temperature in a quenching process is an important point to study the kinetics of chain collapse. In Table 4, the variation of the hydrodynamic radius of a single PMMA chain in isoamyl acetate with time is shown. It will be seen that R_h of this sample (PMMA, $M_w = 3.3 \times 10^6$) was

Table 3
The polymer segment volume fractions of PMMA chains in the globule in various solvents

M_w (g mol ⁻¹)	θ solvent	θ temperature (°C)	The lowest temperature (°C)	ϕ	κ	References
3.3×10^6	Isoamyl acetate ^a	61	18.4	0.56	—	—
4.4×10^6	Isoamyl acetate ^b	61	25	0.14	1	[27]
				0.07	$(5/3)^{3/2} = 2.15$	[27]
2.55×10^6	<i>n</i> -Butyl chloride ^a	38	13.0	0.19	—	[29]
3.3×10^6	<i>n</i> -Butyl chloride ^a	38	7.25	0.47	—	[29]
1.2×10^6	<i>n</i> -Butyl chloride ^a	35	9.0	0.24	—	[29]
4.73×10^6	<i>tert</i> -Butyl alcohol + H ₂ O ^c	41.5	20	0.06	—	[28]
2.38×10^6	<i>tert</i> -Butyl alcohol + H ₂ O ^b	41.5	25	0.36	1	[26]
				0.17	$(5/3)^{3/2} = 2.15$	[26]

^a DLS.

^b SLS.

^c Viscometry.

Table 4

Time dependence of the average hydrodynamic radius of a single PMMA chain ($M_w = 3.3 \times 10^6$) in isoamyl acetate

Time (min)	R_h (nm)
0 ^a	30.30 (the radius at θ temperature $\theta = 61^\circ\text{C}$)
The sample quenched from θ temperature to 18.4°C	
3.0	12.92
5.0	11.62
8.0	11.74
10.0	12.11
11.0	11.80
12.0	12.44
14.0	12.18
15.0	13.88
16.0	12.79
17.0	11.26
(Average value) 12.28 ± 0.78	

^a The sample was prepared in the light scattering cell at 61°C . The cell was transferred into the vat of the DLS spectrometer. First measurements were performed after 3.0 min.

reduced to a constant value within the experimental error, following quenching the solution from 61 (θ temperature) to 18.4°C . There is no indication of a two-stage transition. The collapsed globular state was observed for a period of 17 min. The aggregation of PMMA molecules was observed at the 18th minute after the quenching process. Temperature–time curves for various light scattering cells were reported earlier [21]. For the cell used in this work (10 mm in diameter and 0.3 mm wall thickness), the necessary time to reach a quenched temperature is about 120 s. The constant values of hydrodynamic radii after reaching the collapsed globular state show that the collapse time of a single PMMA molecule is less than 180 s. The upper limit of collapse time could be further reduced to the evaluation period of our DLS machine (30 s), if a cell having a smaller wall thickness (0.1 mm) can be used.

4. Conclusion

Dynamic light scattering experiments were performed for very dilute PMMA solutions in isoamyl acetate. The temperature dependence of the dimension of PMMA chains below the theta temperatures shows similar behaviour for the following three solvent systems: *tert*-BuOH + water [26,28], *n*-butyl chloride [29] and isoamyl acetate [27]. In contrast to mixed solvent system, the transition in isoamyl acetate occurs in a much wider temperature range. However, in each of these solvent systems a gradual contraction of PMMA chains was observed and the chain size was reduced to about 40% of its θ -state dimensions. The segment volume fraction is estimated as $\phi = 0.56$. This indicates that density in the polymer domain of the globule is not dilute. Preliminary results on the kinetics of chain collapse of PMMA in isoamyl acetate show that the collapse time of a single

macromolecule is less than 180 s. The very slow phase separation of dilute solutions of PMMA in isoamyl acetate provides the opportunity to study the kinetics of the collapse in short time periods after quenching the solution to globular state of single macromolecules. This work is currently in progress by using a cell having a smaller wall thickness.

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