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Kinetics of Coil−Globule Collapse in Poly(methyl methacrylate) in Dilute Solutions below Θ Temperatures

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ABSTRACT: The time dependence of coil−globule collapse in atactic poly(methyl methacrylate) samples having molecular weights 6.5×10^6 and 3.3×10^6 g/mol dissolved in isoamyl acetate and *n*-butyl chloride were studied by dynamic light scattering. For example, a dilute solution of PMMA (6.5×10^6 g/mol) in isoamyl acetate was quenched from 61 °C (Θ temperature) to 18.5 °C. As a result, the measured hydrodynamic radius ($\langle R_h \rangle$) was reduced from 42 ± 2 to 15 ± 2 nm. For the cells used in these DLS measurements the thermal equilibration time was found to be about 20 s. The transition from coil to globule in this cell was observed to take place in almost 35 s. We have found the coil-to-globule transition time to be inversely related to the depth of quench (ΔT) of the process. This transition time also increases with increase in molecular weight of the polymer chain.

Introduction

Dilute solutions of poly(methyl methacrylate) (PMMA) can show very slow aggregation and phase separation in various solvents even well below the respective Θ temperatures. Because of this behavior, the dimensions of a single PMMA chain can be studied reliably at such temperatures. Recently, static[1,2] and dynamic[3−5] light scattering and viscometric[3] studies of this polymer were carried out in several solvents at relatively deep quench temperatures.

Chu and co-workers reported two-stage kinetics in a single-chain collapse of polystyrene in cyclohexane.[6−9] A theoretical two-stage model of single-chain collapse had been proposed earlier.[10−12] This theory predicted a rather fast crumpling of the unknotted polymer chain (crumpled globule with “blobs”) and a subsequent slow rearrangement of the blobs of the collapsed polymer chain into a compact globule. The relaxation time of collapse of a single chain predicted from the above theory[10] ($\sim 10^{-3}$ s) is many orders of magnitude lower than is observed experimentally[8] ($\sim 10^2$ s). For a high molecular weight polystyrene sample ($M_w = 8.0 \times 10^6$ g/mol) the total relaxation time to a compact globule in cyclohexane (after quenching the sample from 35.0 (Θ) to 28.0 °C) is reported to be about 700 s.[8] However, the validity of the two-stage collapse concept was challenged by Allegra and co-workers.[13,14] They considered the possibility of chain clustering or aggregation during the second stage of collapse. It was found that clusters of two to five polystyrene chains have a smaller radius than a single globular polystyrene chain. Therefore, Allegra and co-workers concluded that the much smaller objects observed in the second stage of collapse reported as “compact globules” by Chu and co-workers[6−9] emerging with time are actually macromolecular clusters resulting from the aggregation of a small number of polystyrene chains. Consequently, it was argued that the initial collapse stage (with about 25% contraction) corresponds to the final pseudoequilibrium state for individual polystyrene macromolecules in cyclohexane.

Recently, we have studied the coil−globule transition of PMMA chains in a Θ solvent (*tert*-butyl alcohol + water) by viscometric measurements.[3] We have also carried out dynamic light scattering studies of this polymer in *n*-butyl chloride[4] and in isoamyl acetate.[5] Both of the PMMA solutions of these solvents exhibit UCST’s associated with liquid−liquid transitions.Their Θ temperatures are 38 and 61 °C, respectively. In the present work, the time dependence of the coil−globule chain collapse of PMMA in isoamyl acetate (iAac) and *n*-butyl chloride (nBuCl) were studied by dynamic light scattering.

Experimental Section

Materials. Two fractionated PMMA samples were used in this work. Unfractionated PMMA was prepared by thermal bulk polymerization of distilled methyl methacrylate. The polymerization was carried out at 30 °C for 50 days to high conversions. This polymer was fractionated by a standard precipitation technique at 25 °C, using toluene as solvent and methanol as nonsolvent.[3] In this process, 1 g of the atactic PMMA was dissolved in 0.1 w/w % toluene and 0.409 g of PMMA as the first (highest molecular weight) fraction was obtained. Some of this fraction (0.300 g) was redissolved in toluene to produce a 0.03 w/w % solution and further fractionated. The resulting material (0.110 g) was designated PMMA-1. The preparation and characterization of the other sample (PMMA-2) were described earlier.[5]

Characterization. A. Viscometry. The molecular weights of fractionated and unfractionated samples were determined by viscosity measurement using the following relationship.[15]

$$[\eta] = 1.91 \times 10^{-3} P^{0.80} \text{ (chloroform, 20 °C)} \qquad (1)$$

where P is the polymerization degree of PMMA and $[\eta]$ is in dL/g units. A precision capillary viscometer (Cannon 75 M-710) was used for the intrinsic viscosity measurements.

B. GPC. Gel permeation chromatography (GPC) was also used to determine the molecular weight of fractionated and unfractionated PMMA sample and its distribution with a Waters instrument (410 differential refractometer). Tetrahy-

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Table 1. Characterization of Fractionated and Unfractionated PMMA Samples

					contents of triads,[d] %		
sample	M_v (×10^6 g/mol)[a]	M_w (×10^6 g/mol)	M_n (×10^6 g/mol)	M_w/M_n	syndiotactic	atactic	isotactic
PMMA[e]	3.25	4.00[b]	2.33[b]	1.72			
PMMA-1	4.62	6.47[b]	4.62[b]	1.40	61.2	34.1	4.7
PMMA-2		3.30[c]	2.26[c]	1.46	60.2	33.9	5.9

[a] Molecular weight calculated using eq 1, via viscometry. [b] Using GPC. [c] Using LS/SEC (ref 5). [d] Using ^{1}H NMR. [e] Unfractionated.

drofuran (THF) served as eluent. The flow rate was 1 mL/min. A Waters styragel column HT6F was used, and molecular weight calibration was performed by using polystyrene standard samples. Characterization data for unfractionated and fractionated samples are presented in Table 1.

C. ^{1}H NMR. ^{1}H NMR spectra of the PMMA samples were obtained on a Bruker MX-500 spectrometer at 500 MHz. The spectra were taken in deuterated chloroform at 20 °C. The three peaks observed at 0.80, 1.00, and 1.20 ppm represent the resonances of syndiotactic, atactic, and isotactic methyl groups.[16] The area under each of these three peaks corresponds to the content of each triad present in the polymer chain.[16] The results are included in Table 1.

D. DLS Measurements. The preparation of dust-free solutions for dynamic light scattering (DLS) measurements was as follows. Stock solutions of PMMA with a concentration of $\sim 10^{-4}$ g/g were prepared in the Θ solvents isoamyl acetate and *n*-butyl chloride. The stock solutions were held in an oven at 80 and 55 °C, respectively, for complete dissolution. The stock solutions were then diluted to a concentration of 2.5×10^{-5} g/mL and filtered carefully into a dust-free light scattering cell using 0.2 μm Millipore filters.

DLS measurements were conducted by using a commercial DLS spectrometer (ALV/LSE 5000) operating at $\lambda = 514.5$ nm with an Ar laser. Thin-walled cylindrical Pyrex cells (0.38 mm wall thickness, 5 mm outer diameter, and 75 mm length) (Wilmad Glass, Buena, NJ) were used to shorten the thermal equilibration time.[8] Temperature was controlled to ±0.1 °C.

A given polymer solution was quenched to the selected temperature from the Θ temperature to induce the size change, which was determined by means of DLS in terms of the hydrodynamic radius ($\langle R_h \rangle$).

The raw output of a dynamic light scattering experiment is the autocorrelation function of the scattered light intensity, $G_2(\tau)$, typically plotted on a logarithmic time scale. DLS experiments were carried out at a small scattering angle, 33° ($qR_g \ll 1$), to avoid intensity fluctuation contributions from the internal motions of the polymer coil.[17] $G_2(\tau)$ is related to the normalized first-order electric field correlation function $g_1(\tau)$ by[18,19]

$$G_2(\tau) = A[1 + \beta |g_1(\tau)|^2] \tag{2}$$

where A is a baseline constant, β is a coherence parameter depending on the instrumental optics, and τ ($\equiv \Gamma^{-1}$) is the delay time. For polydisperse and concentrated systems, $g_1(\tau)$ is expressed by the distribution function $G(\Gamma)$ of the decay rate as Γ as

$$g_1(\tau) = \int G(\Gamma) \exp(-\Gamma\tau)\, d\Gamma \tag{3}$$

where $\int G(\Gamma)\, d\Gamma = 1$. That is, $g_1(\tau)$ is the Laplace transform of $G(\Gamma)$.

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

$$\langle R_h \rangle = k_B T / 6\pi\eta D \tag{4}$$

where k_B is the Boltzmann constant, η is the solvent viscosity and T is the absolute temperature. The respective viscosities of the solvents *n*-butyl chloride[4] and isoamyl acetate[5] were calculated by using the following equations:

$$\log \eta(T) = -1.7545 + 410.28/T \tag{5}$$

$$\log \eta(T) = -1.7374 + 490.40/T \tag{6}$$

where η is the solvent viscosity in cP and T is the temperature in K. Data analysis of the electric field time correlation curve was performed by using the method of cumulants[8] and the CONTIN method.[20]

Results and Discussion

In our previous discussion of the coil-to-globule transition behavior of poly(methyl methacrylate) in isoamyl acetate, we had also reported preliminary results for the time dependence of the polymer collapse process.[5] As we have already indicated, the time for a polymer solution to reach a newly specified temperature in a quenching process is highly relevant to the study the kinetics of chain collapse.[5] The time necessary to reach a given quenched temperature using the cells described was of the order of 20 s.

Two sets of experiments were carried out to study the kinetics of the collapse. In the first set of experiments (procedure 1), dilute solutions of PMMA that had been held at their respective Θ temperatures for >100 h were filtered into light scattering cells. The solutions that were kept at the Θ temperatures in an oven were transferred into the vat of the DLS spectrometer. The temperature of the vat was fixed at the desired quench temperature. The reduction of hydrodynamic radius ($\langle R_h \rangle$) was measured as a function of time. After each measurement the cell was transferred back to the oven at the Θ temperature and remained there for a further 1 h. The dimensions of this sample did not recover to the original value. In fact, even if the same sample was kept in the oven at the Θ temperature (61 °C) for a period of 3 days, recovery to the original equilibrium dimension was not observed. The experiments were then repeated by quenching the same solution to a lower temperature. In the second set of experiments (procedure 2) a fresh solution was quenched each time from the Θ temperature to a selected low temperatures, and the reduction of hydrodynamic radius was again measured as a function of time.

Figure 1 shows the equilibrium hydrodynamic radius ($\langle R_h \rangle$) of PMMA-1 chains in dilute solutions of isoamyl acetate and *n*-butyl chloride as a function of temperature. The $\langle R_h \rangle$ values shown were determined from the DLS correlation function measurements by using procedure 1 described above. The average hydrodynamic radius of the polymeric chain was calculated from eq 4 as 42 ± 2 nm at 61.0 °C in iAac and 42 ± 2 nm at 38.0 °C in nBuCl. The variances are $\mu_2/\bar{\Gamma}^2 = 0.0356$ and 0.0320 for these solvents, respectively. M_z/M_w values were found to be 1.143 and 1.128 for PMMA-1 in iAac and nBuCl, respectively, by using the following relation:[21] $M_z/M_w = 1 + 4(\mu_2/\bar{\Gamma}^2)$. For PMMA-1 in iAac a gradual contraction in equilibrium values was

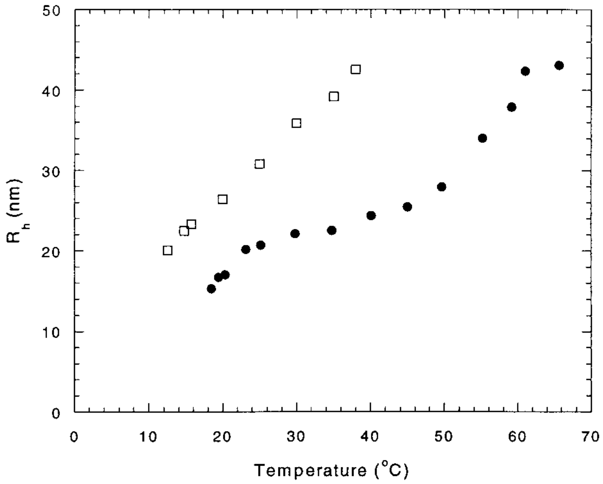

Figure 1. Hydrodynamic radius, ⟨R_h⟩, vs temperature for PMMA-1 in isoamyl acetate (●) and in *n*-butyl chloride (□), procedure 1 (see text).

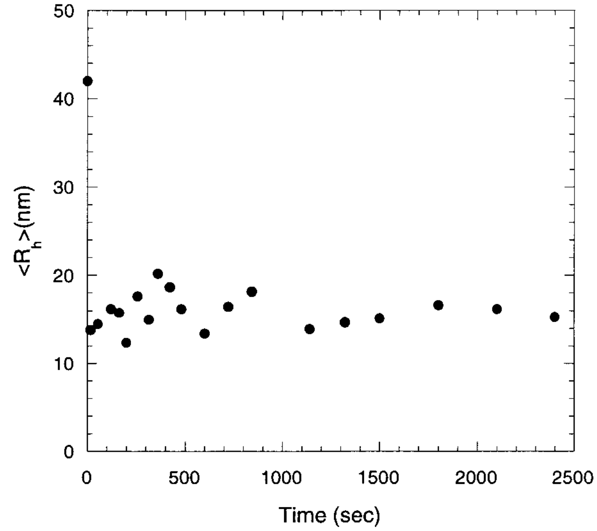

Figure 2. ⟨R_h⟩ versus time for PMMA-1 chain in isoamyl acetate at 18.5 °C, procedure 1.

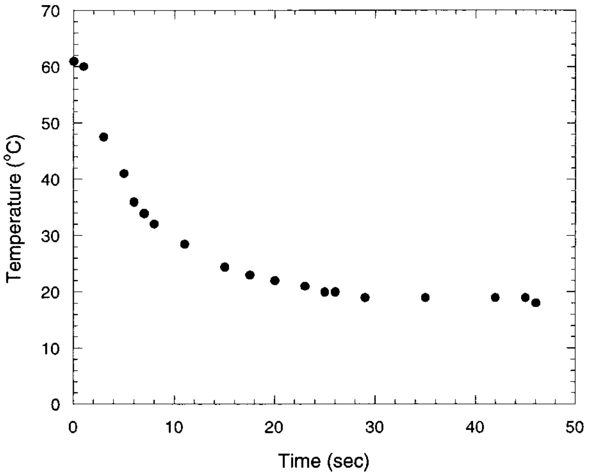

Figure 3. Temperature−time curve of an isoamyl acetate filled DLS cell on quenching from 61 to 18.5 °C.

Table 2. Equilibration Times as a Function of Quench Temperature (Procedure2)

	t_e (sec)					
	PMMA-1				PMMA-2	
ΔT (°C)[a]	iAac	(⟨R_h⟩, nm)	nBuCl	(⟨R_h⟩, nm)	iAac	(⟨R_h⟩, nm)
21.0	200	(29 ± 2)				
24.2			150	(22 ± 2)		
31.0	170	(25 ± 2)				
41.0	35	(22 ± 3)			15[b]	(15 ± 3)
42.0	35	(22 ± 2)				

[a] Quench depth. [b] Close to thermal equilibrium time of pure solvent.

observed for successive quenches down to a quench temperature of 18.5 °C (α_h = 0.36). The segmental volume fraction (ϕ) in the globule at 18.5 °C is calculated as 0.60. The details of calculations and discussion of ϕ were given in our earlier work on the same system.[5] The contraction for the same polymeric sample in nBuCl could be followed down to 12.5 °C. Both systems were thermodynamically stable at these temperatures, and no scattering intensity increase was observed with time.

We now discuss the results of the stepwise cooling (procedure 1) of PMMA-1 in iAac, particularly with respect to the final quench to 18.5 °C. In Figure 2, the contraction of the hydrodynamic radius in this experiment from the Θ temperature to 18.5 °C is shown as a function of time. The transition from the coil to globule in this cell was already observed at 35 s as judged from Figure 2. By measuring the temperature profile of a typical DLS cell quenched from 61 to 18.5 °C (Figure 3), it can be seen that the time to reach thermal equilibrium (t_e) is about 20 s. For this measurement, a thermocouple read by a digital thermometer (Omega Engineering, Inc., model 115 KC) was inserted into the center of the cell filled with iAac for simulation of the temperature changes in the quenching process. The hydrodynamic radius ⟨R_h⟩ at 18.5 °C was 15 ± 2 nm and was constant for at least a further 40 min.

In Figure 4a−d, the effect of quench depth (ΔT) on the transition time of the coil-to-globule conformation of the PMMA-1 chain can be seen. For this purpose, fresh dilute polymer solutions were quenched to the selected temperatures (procedure 2) from the Θ temperature (61.0 °C). As the quench depth (ΔT) increases, the time required to reach to the new equilibrium size decreases. In Table 2 the effect of quench depth on the time dependence of thermal equilibrium is given. We can see that larger quench depths give faster transitions. Also, the collapse time of the chains having high molecular weight exceeds that of the lower molecular weight chains.

In Figure 5, the time dependence of scattering light intensity (I) (θ = 33°) at 61.0 °C of PMMA-1 and at quenching temperatures of 40, 30, 20, and 19 °C is shown. There is no noticeable increase in intensity with the time at any temperatures except for the run observed at 19 °C. For this quenching experiment, the scattering intensity increases with time, which indicates some interchain aggregation. It should be noted that R_h is not very sensitive to a slight degree of aggregation. Therefore, it was possible to measure ⟨R_h⟩ values at 19 °C prior to complete aggregation, which starts after about 1200 s.

The time dependence of the hydrodynamic radius of PMMA-2 in iAac after cooling from the Θ temperature (procedure 2) is shown in Figure 6. The lowered average radius value is ⟨R_h⟩ = 15 ± 3 nm at 20 °C. The equilibrium is attained after 15 s. For about 2.5 h, although the shape of R_h distribution still obeyed single-

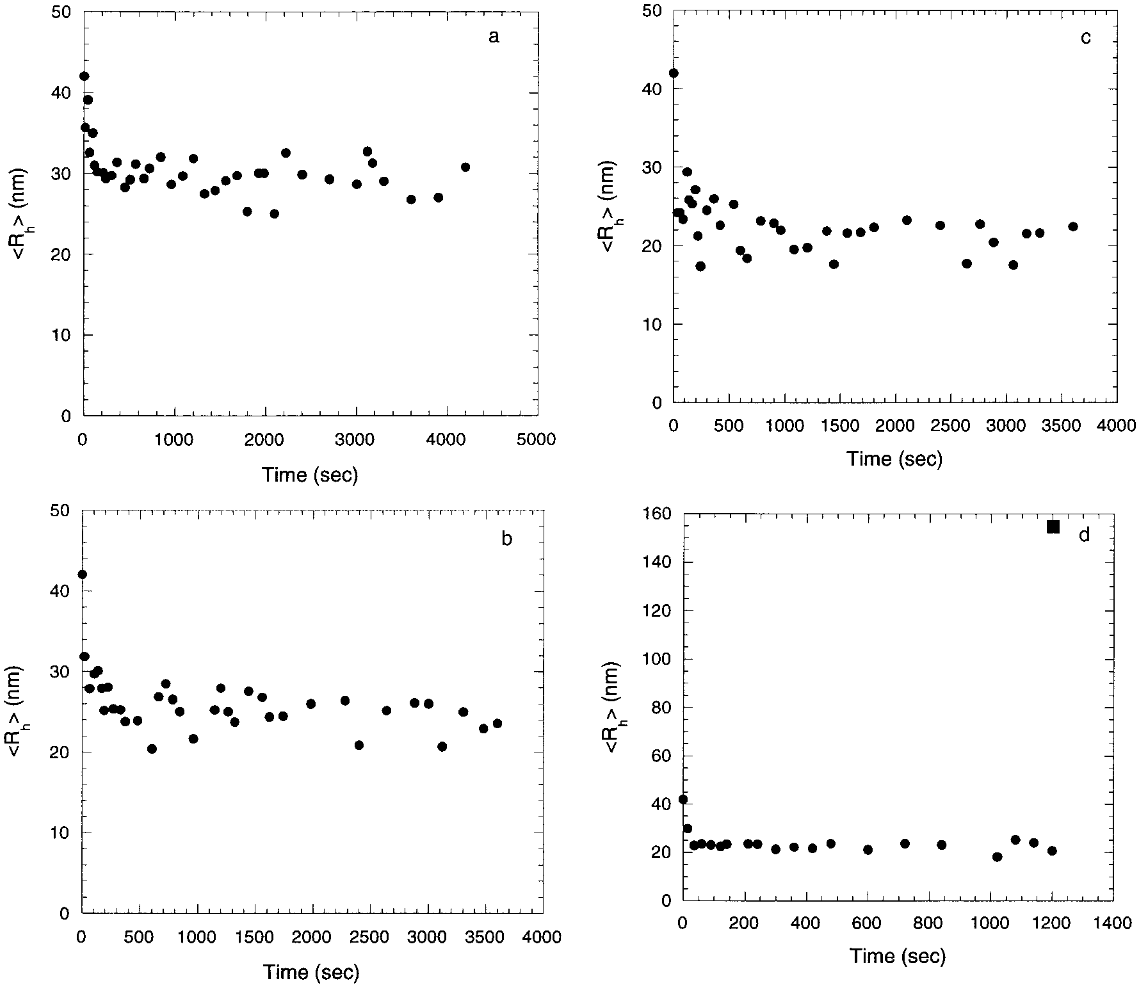

Figure 4. (a−d) $\langle R_h \rangle$ of PMMA-1 chain in iAac as a function of time. The quench depths (procedure 2, see text), ΔT, are 21.0, 31.0, 41.0, and 42.0 °C for parts a, b, c, and d, respectively. In (d), ■ corresponds to aggregation appearing after 1200 s.

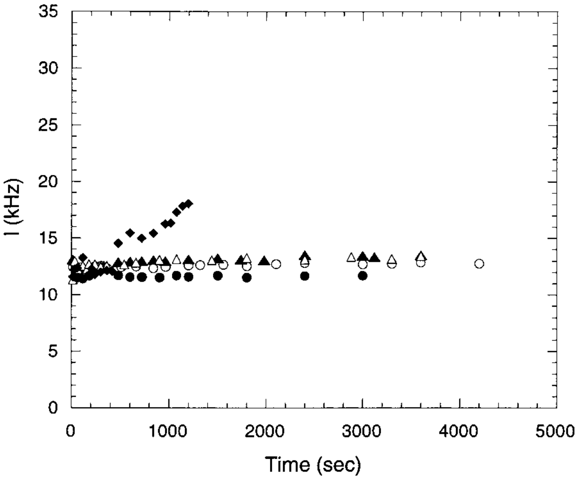

Figure 5. Time dependence of scattered light intensity (I) of PMMA-1 sample in iAac at 61 (●), 40 (○), 30 (△), 20 (▲), and 19 °C (♦), procedure 2.

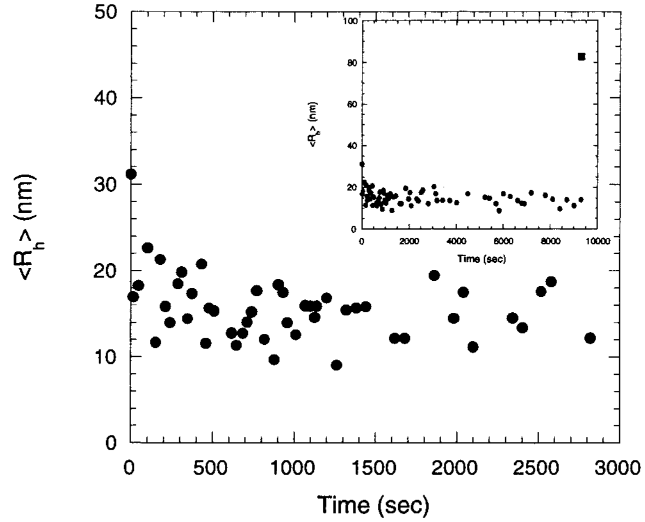

Figure 6. Hydrodynamic radius versus time for PMMA-2 in isoamyl acetate at quenched to 20 °C from the Θ temperature. The inset shows the appearance of the aggregates.

mode behavior, the polydispersity of the R_h distribution (M_z/M_w) increased from 1.25 to 1.64 at which point the symmetrical shape of the curve began to be distorted, with the larger end of the distribution curve becoming stretched out. However, after 2.5 h, the formation of aggregated chains can be seen in this experiment. The intensity−time correlation function was no longer fitted to a single exponential, and the size distribution began to become bimodal. The smaller size globules had an average size of $R_h \cong 14$ nm and $M_z/M_w = 1.14$. The average size of the large size aggregates obtained from CONTIN analysis was 83 nm with $M_z/M_w = 1.41$.

In Figure 7, the time dependence of the hydrodynamic radius of PMMA-1 in nBuCl after cooling from the respective Θ temperature by procedure 2 is shown. The average value of the lowered radius is $\langle R_h \rangle = 22 \pm 2$

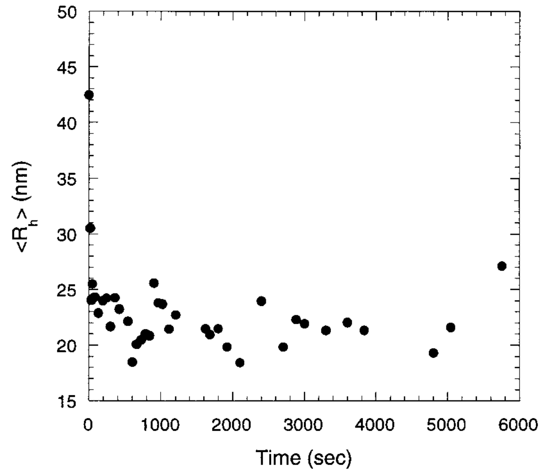

Figure 7. Hydrodynamic radius versus time for PMMA-1 chain in *n*-butyl chloride quenched to 13.8 °C from the Θ temperature.

nm at 13.8 °C. Here again after about 100 min the formation of aggregated chains is observed at 13.8 °C.

Conclusions

Dynamic light scattering experiments were performed for very dilute PMMA solutions in isoamyl acetate and *n*-butyl chloride. We have now studied the temperature dependence of the dimension of PMMA chains in three solvent systems: *tert*-butyl alcohol + water,[3] *n*-butyl chloride,[4] and isoamyl acetate.[5] The contraction of a PMMA-1 chain from a coil at 61.0 °C to a globule at 18.5 °C in iAac is $\alpha_h = 0.36$. The calculated volume fraction in the globule is $\phi = 0.60$, indicating that the density in the polymer domain of the globule is by no means dilute. However, there is a difference between the two sets of collapse experiments described herein. Using the stepwise procedure (1) to reach the globular chain, a lower temperatures can be attained before observation of aggregation. Moreover, in these experiments the globule radius after equilibrium is smaller than the radius observed in the straight quenched (procedure 2). These differences imply that there is a kind of "conditioning" of the chain during the stepwise cooling and heating process of the solution.

Our kinetic experiments also reveal the following results:

(1) The relaxation time of coil-to-globule transition of a high molecular weight PMMA chain (6.5×10^6 g/mol) is inversely related to the depth of shock-cooling. This observation is in contradiction to the earlier theoretical prediction.[10] However, the results of simulation calculations reported by Allegra and co-workers[22] show similar relaxation time dependence as described in this work.

(2) The relaxation time for a given quench depth increases with the molecular weight of the chains. This experimental observation is in agreement with the theoretical predictions.[10,11]

(3) The coil-to-globule transition time of a high-molecular-weight chain rapidly cooled from the Θ state to the lowest temperature attainable without complete aggregation is of the order of the thermal equilibration time (about 20 s) of the solution.

(4) By using the DLS technique, there is no indication of a two-stage kinetic process as proposed in earlier theoretical work.[10−12]

The kinetics of coil-to-globule transition of PMMA in isoamyl acetate was recently studied by static light scattering measurements by Nakata and co-workers.[23,24] These authors started to observe the dimensions of the collapsing chains 30 min after quenching. Since at that time the PMMA coil was already collapsed to a globular form, we believe they measured only the kinetics of aggregation. This contraction of aggregated molecules has been reported earlier by Allegra and co-workers.[13,14]

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