

Longer time kinetics of collapse transition of polymer-surfactant complexes at interfaces near to collapse temperatures

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The later stages of the collapse transition kinetics of fractionated poly(*N*-isopropylacrylamide) (PNIPAM) chains at interfaces in the presence of the surfactant sodium dodecyl sulfate (SDS) were studied for molecular weights ranging from 4.5×10^5 to 1.6×10^6 . The interfacial PNIPAM-SDS complexes were quickly heated to the temperatures that were near to the collapse transition temperatures. The longer time collapse of the PNIPAM-SDS complexes at interfaces was found to proceed through two stages. The collapse kinetics at the later stages was interpreted in terms of a “globule growth” model. It was found that under the experimental conditions, the fast relaxation time was independent of the molecular weight, whereas the slow relaxation time was weakly dependent on the molecular weight.

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INTRODUCTION

The kinetics of the coil-to-globule transition in polymer systems has not been comprehensively understood [1,2]. de Gennes theoretically proposed a two-stage process to describe the kinetics of the coil-to-globule transition [3]. Polymer chains are first predicted to collapse to a “sausage”-shaped object wherein the subunits of the chains, the so-called “blobs,” tend to stick together. Then, in the second stage, the sausage-shaped chains transform with a hydrodynamic friction into their final spherical form. A more detailed outline of the two-stage kinetics of the coil-to-globule transition has been presented by Grosberg *et al.* [4]. It has been proposed that in the first stage of the transition, polymer chains collapse to form a so-called “crumpled globule,” which is formed through a self-similar process. This means that the crumpled globule manifests a fractal dimension. In the first stage, the density inside the blobs is close to the final globular density but the blobs are still spatially segregated. In the second stage, the crumpled globule continues to shrink to the final equilibrium state by slow knotting or topological relaxation of the blobs. The main difference between the crumpled and the equilibrium globules is that in the equilibrium globule, segments along the chains are more likely to be in contact whereas in the crumpled globule they are more likely to be neighbors in space. The first successful experimental demonstration of an apparent two-stage process for the coil-to-globule transition was reported by Chu and co-workers for a single polystyrene chain in cyclohexane [5,6]. In more recent developments, the kinetics of the coil-to-globule transition has been explored by computer simulations [7–12]. Especially important in this context is the work of Kuznetsov, Timoshenko, and Dawson (KTD) [10–12], which predicts a three-stage collapse model.

Since polymer chains also tend to undergo the phase separation under worse than θ conditions simultaneously as the

collapsed state is achieved, studies of the collapse transition of polymer chains have proven to be a difficult experimental challenge, especially for the collapse kinetics. Two ways have been proposed to prevent the aggregation of the polymer chains during the coil-to-globule transition: one is to add a small amount of surfactants [13–15] and the other is to tether the polymer chains to interfaces of latex particles that bear an electrostatic charge [16–18]. The present authors have studied some of the characteristics of the coil-to-globule type transition of poly(*N*-isopropylacrylamide) (PNIPAM) chains attached to charged polystyrene latex particles [16,17]. It has been known that at room temperature the PNIPAM chains dissolve in water to form a coil state that undergoes the chain collapse when the temperature is increased to between 31 and 34 °C [19,20]. The experimental data have demonstrated that if the surface charge density of the latex particles is sufficiently high, the aggregation of the latex particles can be totally prevented. This allows the collapse transition of interfacial chains to be observed by direct measurements of the hydrodynamic particle size using dynamic light scattering (DLS). It is worth noting that conformational transitions of interfacial polymer chains are believed to be different from those of free polymer chains. First, the degree of freedom of the polymer chains at surfaces is expected to be less than that in free solutions. Interfacial polymer chains exhibit strongly restricted orientations. Second, the collapse transition of interfacial chains may be more complex phenomenologically than implied by the concept of a coil-to-globule transition. For example, the collapse transition of interfacial polymer chains could be influenced by *n*-cluster formation proposed by de Gennes [21].

The kinetics of later stages of the temperature-induced collapse transition of interfacial PNIPAM in the presence of the surfactant sodium dodecyl sulfate (SDS) has recently been studied [22]. The longer time collapse processes were interpreted in terms of the “globule growth” model [10–12]. The relaxation times of the collapse transition were determined from the longer time kinetics and were found to decrease with increasing quench temperature above the transition temperature. Since there is a cooperative binding of surfactant molecules onto interfacial polymer chains, the

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neutral PNIPAM chains at interfaces are converted into partial polyelectrolyte complexes as the surfactant concentration is higher than the critical association concentration (CAC) above which the individual surfactant molecules form aggregates bound to the polymer chains in good solvency domain. In this paper, we report on the molecular weight dependence of the longer time kinetics of the collapse transition of the interfacial PNIPAM-SDS complexes.

EXPERIMENTAL DETAILS

N-isopropylacrylamide (NIPAM) (Monomer-Polymer) was purified by recrystallization from a 65/35 mixture of hexane and benzene. Styrene (AJAX chemicals) was distilled at 55 °C under reduced pressure. Azobisisobutyronitrile (AIBN) (Fluka) was recrystallized from methanol. Potassium peroxydisulfate (KPS) (Britain Drug House chemicals), sodium metabisulfite (Merck), and SDS were used as received. All solvents were analytical grade. Water was Millipore Milli-Q grade.

The PNIPAM was prepared by the solution polymerization of NIPAM following the procedure described in the literature [23]. NIPAM (5 g) was polymerized for about 20 h at 65 °C in a 70/30 benzene/acetone mixture (100 ml) using AIBN (0.5%) as the initiator under a positive nitrogen pressure. The solvents were then evaporated in a vacuum at room temperature. The PNIPAM obtained was fractionated by dissolution of the dried solid in dry acetone, followed by the careful addition of dry *n*-hexane [24]. The weight-average molecular weights were determined by static light scattering at 25.0 ± 0.1 °C to be ~1.6 × 10⁶, ~1.0 × 10⁶, ~6.3 × 10⁵, and ~4.5 × 10⁵, respectively. The polydispersity ratios of the PNIPAM were estimated from the dynamic light-scattering measurement in the sodium dodecyl sulfate solution of 120 mg/L, following the procedure of Meewes *et al.* [13]. They were found to be ~1.4 for 1.6 × 10⁶, ~1.2 for 1.0 × 10⁶, and ~1.8 for 6.3 × 10⁵ and 4.5 × 10⁵.

Graft polymerization of styrene onto PNIPAM (1.5 g) in water (80 cm³) was accomplished by the slow addition (about 40 min) of styrene (0.3 g) in the presence of redox initiator potassium peroxydisulfate (1 × 10⁻³ g)/sodium metabisulfite (4 × 10⁻⁴ g) to yield a clear solution. To generate a latex, styrene (1.2 g) was then added quickly, along with additional potassium peroxydisulfate (1.9 × 10⁻² g) and sodium metabisulfite (7.6 × 10⁻³ g), to a final volume of 100 cm³ water. After about 20 h, the resultant latex was filtered and then dialyzed by repeated changes of fresh Millipore Milli-Q water for about three days. Nongrafted PNIPAM was removed by centrifugation and decantation of the supernatant. The latex particles were redispersed in Millipore Milli-Q water and filtered using a 0.8 μm Millipore filter.

Dynamic light-scattering measurements of the average latex size were performed at a particle concentration of about 5 × 10⁻⁵ (g/g) with an argon ion laser operating at a scattering angle of Θ = 90° and a wavelength of λ = 488 nm at a power of 50 mW. The intensity autocorrelation function $G^{(2)}(\tau) = \langle I(\tau)I(0) \rangle$ was measured using a Malvern 4700c correlator and has a form

$$G^2(\tau) = A[1 + \beta |g^{(1)}(\tau)|^2], \quad (1)$$

where A is the experimental base line, β is a spatial coherence factor, and $g^{(1)}(\tau)$ is the electric-field autocorrelation function. For a polydisperse system, $g^{(1)}(\tau)$ consists of a sum of a single exponential:

$$g^{(1)}(\tau) = \int_0^\infty G(\Gamma) \exp(-\Gamma \tau) d\Gamma, \quad (2)$$

where $G(\Gamma)$ is the normalized distribution function of the decay rates and $\Gamma = D_z q^2$ is at a very dilute solution concentration. Here D_z is the z -average translational diffusion coefficient and $q = (4\pi n_0/\lambda) \sin(\Theta/2)$ the magnitude of the scattering vector. The analysis of the electric-field autocorrelation function was made using the method of cumulants [25]. Hydrodynamic diameters d_h were calculated from the translational diffusion coefficients using the Stokes-Einstein equation, $d_h = k_B T / (3\pi\eta D_z)$, with k_B being the Boltzmann constant, T the temperature (K), and η the solvent viscosity. The light-scattering cell had a diameter of 10 mm and a wall thickness of 0.5 mm. The average diameters of the dried core of the latex particles were determined by transmission electron microscopy (TEM).

The collapse transition was studied as follows. The latex dispersions containing a SDS concentration $C_s = 1023$ mg/L were quickly heated to the requisite temperatures, which were close to the transition temperatures. The time dependence of latex diameters was then monitored by dynamic light scattering. The temperature was controlled with the precision of ±0.1 °C. When the latex dispersions were heated from the region of the interfacial swollen chains to the region of the interfacial globular chains, it was important that the times required for the latexes to reach the requisite temperatures were as short as possible. To shorten the thermal equilibration times, the empty sample cells were first immersed in the water bath of DLS apparatus at the requisite temperatures for at least a half hour prior to the samples being injected into the cells. A thermocouple was inserted into the empty sample cell. The water was injected for a simulation of the temperature change. The time required for the samples to reach the designated temperatures was found to be about 110 sec. Unfortunately, it is not yet possible to obtain reliable measurements of the initial stages of the collapse transition due to the uncertainties associated with thermal equilibration after heating. We started DLS measurements about 25 sec after heating but only the data collected after about 130 sec were used to manipulate the collapse kinetics for the present system; i.e. here we only studied the later stages of the collapse transition of PNIPAM-SDS complexes at interfaces. For each sample, the heated experiments were repeated twice and the data presented here are their average values. In measurements of latex particle diameters at different temperatures, the samples were kept at the temperatures for at least 15 min before the data collection.

RESULTS AND DISCUSSION

Figure 1 shows the temperature-induced collapse transition of the interfacial PNIPAM chains in water in the presence of surfactant molecules. The SDS concentration $C_s = 1023$ mg/L is much higher than the CAC (~230 mg/L) [13,14] but much smaller than the critical micellar concen-

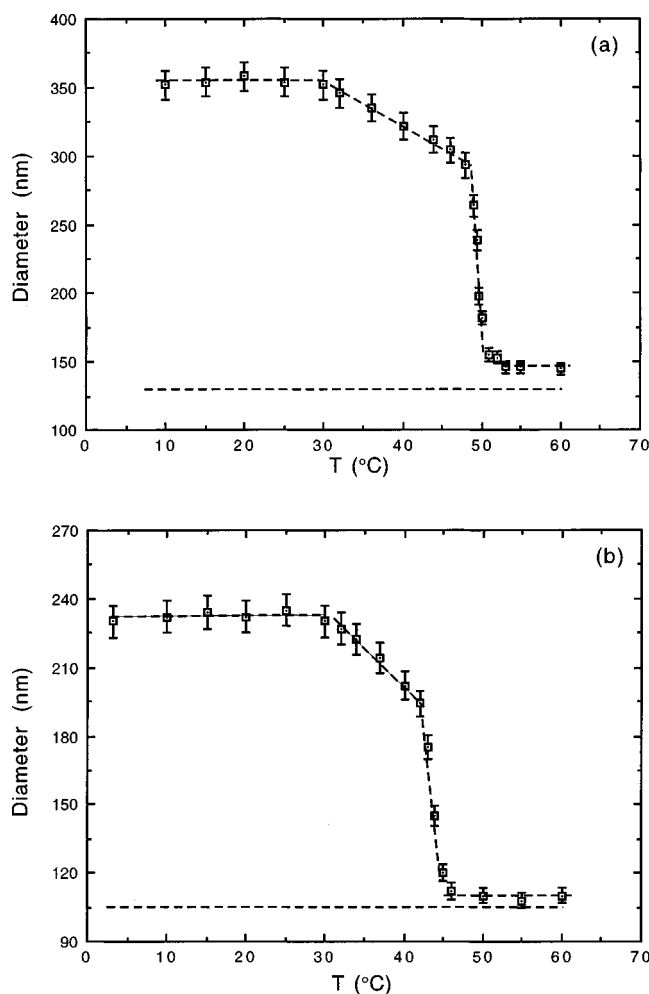


FIG. 1. Plots of the temperature dependence of the hydrodynamic diameter of the latex particles coated by PNIPAM at a SDS concentration $C_s = 1023$ mg/L. Molecular weights are (a) 1.6×10^6 and (b) 6.3×10^5 . Dot lines are the core diameters of polystyrene latex particles.

tration (CMC) (~ 2300 mg/L) of a salt-free solution [26]. The cooperative binding through hydrophobic interactions of SDS aggregates with the polymer segments of the interfacial PNIPAM layers is expected to occur. This results in locally swollen chains at interfaces as a consequence of the repulsive electrostatic interactions between the firmly adsorbed amphiphiles. The collapse transition at this SDS concentration proceeded through a relatively weak transition before the onset of a much sharper collapse, which occurred upon an increase in the temperature, as has been reported previously [27,28]. This weak transition has been interpreted as involving the formation of ion pairs between the charges on the PNIPAM-SDS complexes and their counterions [27,28]. The formation of the multiplet structure of ion-pair aggregates is taken into account [27,28]. The interesting finding presented in Fig. 1 is that the collapse transition temperature of the interfacial PNIPAM-SDS complexes is elevated with increasing the molecular weight. It is worth noting that studies of the molecular weight dependence of lower critical solution temperatures (LCST) for free PNIPAM chains in aqueous solutions are controversial [23,24,29]. The longer time collapse kinetics of the interfacial PNIPAM-SDS complexes was then studied at the designated temperatures close

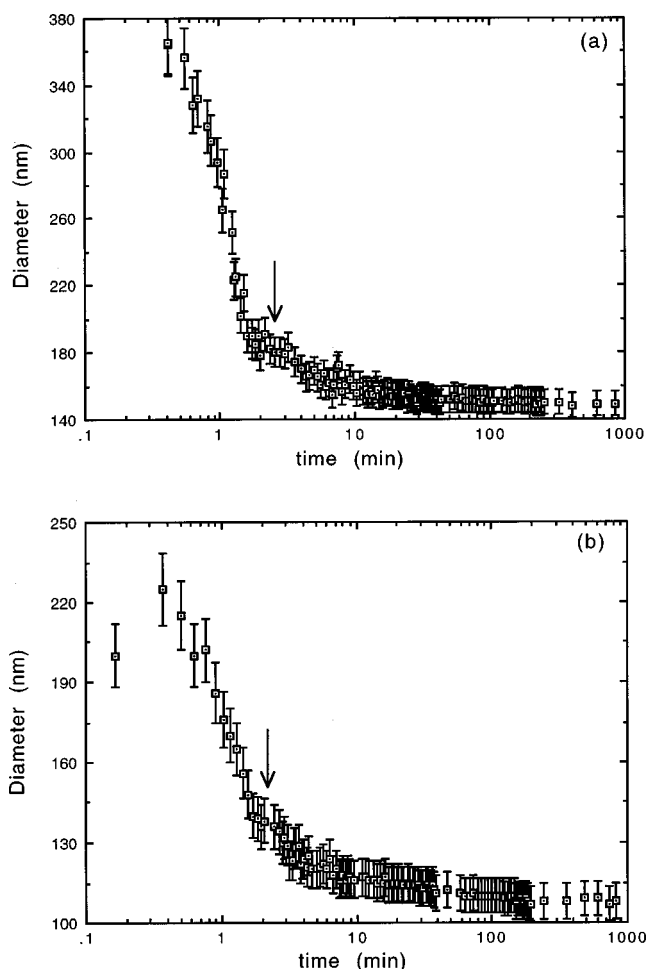


FIG. 2. Plots of the time dependence of the hydrodynamic diameter of the latex particles coated by PNIPAM at a SDS concentration $C_s = 1023$ mg/L. Molecular weights are (a) 1.6×10^6 and (b) 6.3×10^5 . The latex particles were quickly heated to the temperatures (a) 51.1°C and (b) 44°C .

to the transition temperatures. In order to compare the collapse transition of interfacial PNIPAM-SDS complexes with different PNIPAM molecular weights, the designated temperature of each molecular weight was chosen to be about one degree higher than the one at which the particle diameters started to be temperature independent. These temperatures are 55.1 , 45 , 44 , and $42.9 \pm 0.1^\circ\text{C}$ for the molecular weights 1.6×10^6 , 1.0×10^6 , 6.3×10^5 , and 4.5×10^5 , respectively.

Figure 2 shows the typical time dependence of the hydrodynamic diameter of the latex particles coated by the PNIPAM chains in water. Since the interparticle aggregation was totally prevented and the latex core diameter did not change with temperature, the time dependence of the hydrodynamic diameter represents a time dependence of the layer of thickness of the swollen PNIPAM chains at interfaces in the course of the collapse transition. Since the time required for the samples to reach a thermal equilibrium state was about 110 sec on heating, the kinetic behavior of the collapse transition was meaningfully studied when the experimental time was longer than about 130 sec. The longer time collapse transition is shown in Fig. 3. It can be seen from Fig. 3 that after the abrupt temperature change the hydrodynamic diam-

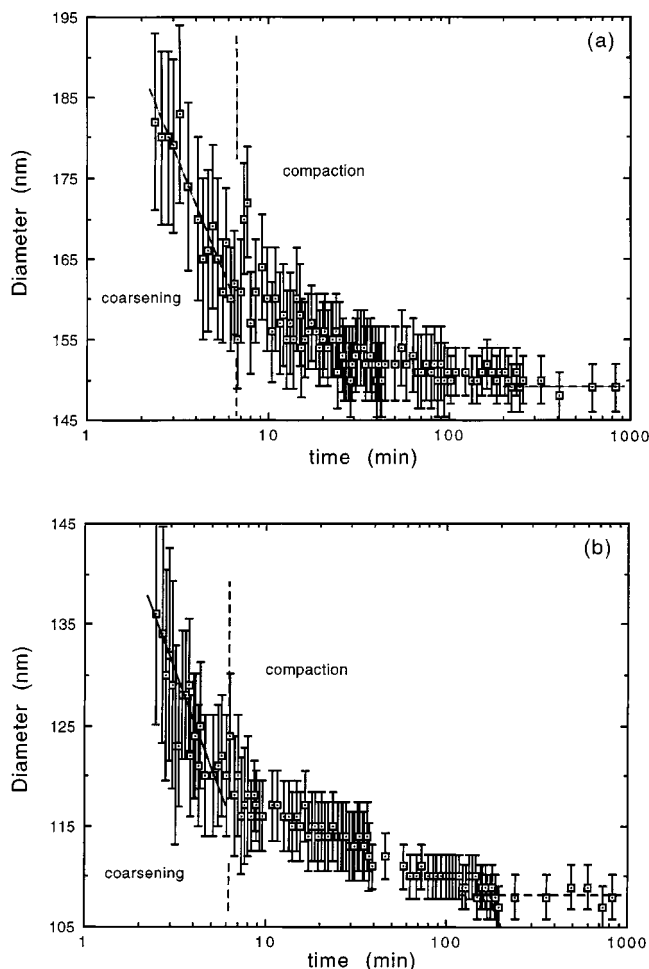


FIG. 3. Plots of the longer time dependence of the hydrodynamic diameter data shown in Fig. 2.

eter decreased rapidly at short times and then converged slowly to a stable limit at much longer times. Accordingly, the longer time kinetics of the collapse transition can be classified as two stages. The minimum size that the latex particles could reach became somewhat larger as the molecular weight increased. It has been found [22] that the swollen interfacial PNIPAM chains can reach similar levels of collapse as normal interfacial chains. The polymer dimension in the final collapse state is essentially independent of the SDS concentration [22]. It is believed that during the collapse transition the surfactant molecules are excluded from the domains inside the globules and adsorbed on the globule surfaces.

The recent computer simulations of the KTD model [11,12] for the kinetics of the collapse transition of homopolymers can be used, as a first approximation, to describe the collapse transition of the present system. According to the KTD model, the kinetics of the collapse transition consists essentially of three stages. First, localized dense clusters are formed along the chain. In this stage, many small collapsed clusters quickly form and grow. These small collapsed clusters are randomly distributed along the polymer chains at relatively low densities (a “necklace” structure). The polymer segments between the small collapsed clusters are expected to still be flexible. The size distribution of the small collapsed clusters along a single chain could be quite

broad. In the next coarsening stage, neighboring small collapsed clusters aggregate to form larger collapsed clusters. The density of the collapsed clusters tends to be high as a result of internal rearrangements, but does not reach that of the completely compacted state. The polymer segments linking these collapsed clusters are relatively short and quite stiff. At this stage, some of polymer chains are predicted to have collapsed to only an approximate spherical form. The final stage of collapse is thus described as a compaction process of these collapsed globules to form the optimal spherical shape.

The collapse mechanism of the postulated PNIPAM chains bears some resemblance to the globule growth model of KTD [30,31]. It has been found that when the molecular weight of the PNIPAM chains is sufficiently large, the coil-to-globule transition of the PNIPAM chains is not a so-called *all-or-nothing* process; i.e., single PNIPAM chains do not undergo coil-to-globule transitions as a whole [30,31]. The collapse transition of the PNIPAM chains presumably proceeds through a set of intermediates consisting of a number of the so-called “cooperative units” or “domains.” Such behavior was first reported for the folding transition of larger proteins [32,33]. The main difference between proteins and PNIPAM in the transitions is that the folding transition of proteins involves two or more different structural domains whereas the collapse transition of the homopolymer PNIPAM only involves an identical structural domain.

The KTD simulations predict quantitatively that the intermediate coarsening process in the collapse transition can be described by a relaxation equation [11,12]

$$R_g^2(t) = R_g^2(\infty) + A_1 \exp(-t/\tau), \quad (3)$$

where R_g is the radius of gyration of the polymer chain and τ is the characteristic relaxation time of the coarsening stage. Since the radius of gyration is proportional to the hydrodynamic radius for a coil, a similar equation can be utilized if the radius of gyration is replaced by the hydrodynamic diameter. Note that for a real system it is strictly not possible to differentiate between the coarsening stages of the chain collapse and their ultimate compaction stages [12]. Nonetheless, according to the KTD model, the kinetic behavior at longer times, including the coarsening and compaction processes, can be described by a two-exponential relaxation law:

$$R_g^2(t) = R_g^2(\infty) + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2). \quad (4)$$

The fast relaxation time τ_1 could theoretically be considered as a characteristic time for the coarsening stage [11,12], being equivalent to the τ in Eq. (3), although strictly τ_1 may also be somewhat associated with the compaction process. The slow relaxation time τ_2 is a characteristic time for the compaction stage. Note that any transition from one equilibrium state to another due to changes in thermodynamic variables may generally be considered as a relaxation process.

The experiments in the present work do not exactly satisfy the assumptions made in the KTD simulations in that surfactant molecules were present in the experimental systems. It is assumed that the presence of the SDS molecules does not qualitatively alter the processing aspects of the collapse transition; i.e., the collapse transition of the PNIPAM-SDS complexes still proceeds through a set of intermediate

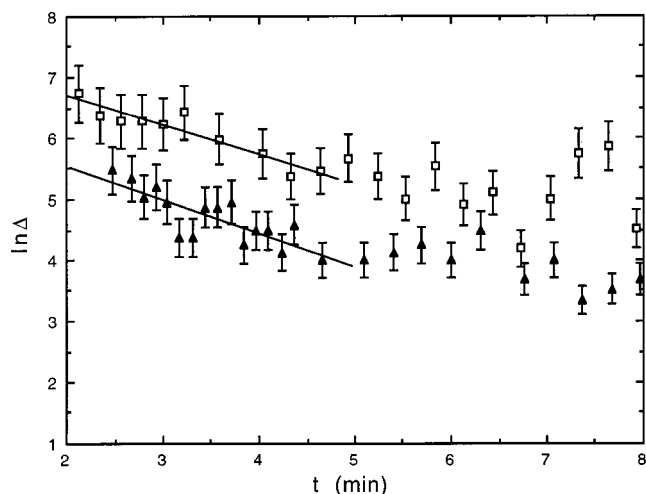


FIG. 4. Semilogarithmic plots of the longer time dependence of the squared layer thickness of interfacial PNIPAM-SDS complexes at a SDS concentration $C_s = 1023$ mg/L. The polystyrene core size was subtracted from the total measured sizes. Empty squares and filled triangles are the data of molecular weights 1.6×10^6 and 6.3×10^5 , respectively. The latex particles were quickly heated to the temperatures (a) 51.1°C and (b) 44°C . In the plots, $\ln \Delta \equiv \log[(\text{layer thickness})^2(t) - (\text{layer thickness})^2(\infty)]$.

stages, although the mechanism of the collapse transition could be changed. This assumption is likely to be correct since the results presented in Fig. 3 indicate that the collapse transition proceeds through two stages at longer times. Since the experiments were conducted at surfactant concentrations well below the CMC, the relaxation times for the rearrangement of the surfactant molecules, either singly or in small groups, are likely to be of the order of milliseconds whereas the relaxation times for the collapse processes may be of the order of several hundred seconds. The relaxation times that relate to the collapse transition of the PNIPAM-SDS complexes could not be influenced by the free SDS molecules and unadsorbed SDS aggregates if they exist. However, since the exact nature of the collapse transition of the PNIPAM-SDS complexes is not clear, the longer time collapse kinetics in the present system is phenomenologically treated as multiple relaxation processes, which are approximated by Eqs. (3) and (4). If the terminologies in the KTD model are to be used for the present system, the observed collapse data can be referred to as the coarsening and compaction processes in the course of the collapse transition.

Figure 4 shows semilogarithmic plots of the squared layer thickness of the interfacial PNIPAM-SDS complexes as a function of the experimental time as implied by Eq. (3). In the plots, the average core diameters were subtracted from the total measured values to give twice the effective hydrodynamic diameters of the interfacial PNIPAM chains. The diameters of the interfacial PNIPAM chains at infinite times were estimated from the plateaus in Fig. 3. It can be seen from the plots that the data collected at the earlier time deviate from the behavior observed at the longer time. It is postulated that the linear ranges observed in Fig. 4 represent the coarsening stage of the later times predicted by the globule growth mechanism of collapse transition. The relaxation time τ was found to be about 2 min, irrespective of the molecular weight under the experimental conditions.

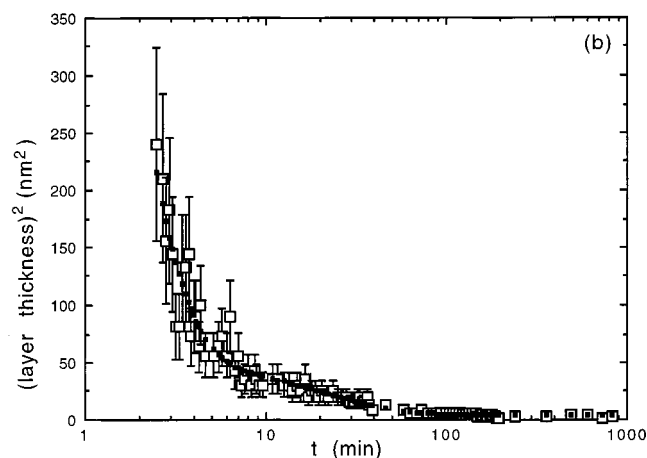
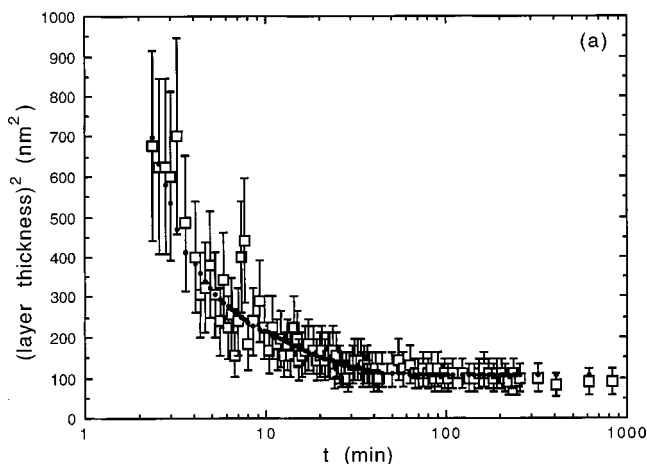


FIG. 5. Semilogarithmic plots of the time dependence of the squared layer thickness of interfacial PNIPAM-SDS complexes at a SDS concentration $C_s = 1023$ mg/L. The polystyrene core size was subtracted from the total measured sizes. Molecular weights are (a) 1.6×10^6 and (b) 6.3×10^5 . The latex particles were quickly heated to the temperatures (a) 51.1°C and (b) 44°C . Filled squares are the data of the best fits of experimental results using Eq. (4).

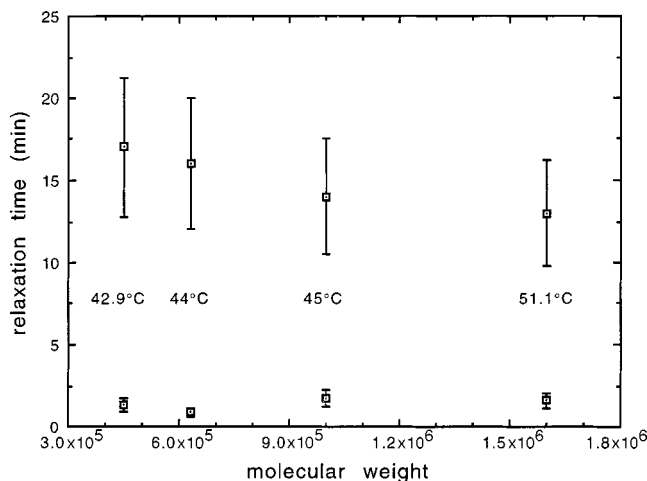


FIG. 6. Relaxation times are plotted versus the molecular weight under the experimental conditions seen in the text.

The longer time kinetics of the collapse transition was also fitted by Eq. (4). The fitting covered the whole range of experimental times studied. The experimental and calculated data are presented in Fig. 5. The relaxation times obtained are shown in Fig. 6. It is found that the fast relaxation times τ_1 are about 1–1.7 min, being in good agreement with those determined from Fig. 4. The slow relaxation time τ_2 appears to have a weak molecular weight dependence under the experimental conditions, which may be associated with the stiffness of the short segments during the compaction process. The results indicate that under the experimental conditions, the compaction process is much slower than the coarsening.

CONCLUSIONS

The kinetics of the collapse transition of the PNIPAM-SDS complexes at interfaces in aqueous solution was studied using dynamic light scattering. The interfacial PNIPAM-SDS complexes with different PNIPAM molecular weights were quickly heated to the requisite temperatures. These temperatures were chosen to be about one degree higher than

the temperatures at which the dimensions of the interfacial chains collapsed completely to minimum values. The longer time stages of the kinetic behavior of the PNIPAM-SDS complexes were interpreted in terms of the ‘globule growth’ model of KTD. In terms of this model, the growth of the localized collapsed globules and the compaction of these collapsed globules were described by the observed relaxation processes. Under the experimental conditions, the relaxation time of the coarsening stage was found to be independent of the molecular weight whereas the relaxation time of the compaction stage was weakly dependent on the molecular weight. The kinetics of the collapse transition of PNIPAM-SDS complexes at interfaces could be a model for studying the kinetics of the collapse transition of weak polyelectrolytes at interfaces.

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