Surfactant-assisted entanglement of interfacial polymer chains

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The temperature-induced conformational transitions of neutral poly(*N*-isopropylacrylamide) chains at interfaces are studied in the presence of a surfactant, sodium dodecyl sulfate in an aqueous solution. The results obtained from the collapse-to-swelling transition show that the polymer dimension in good solvency is smaller after collapse transition than that before the transition. Such a dimension difference due to the conformational changes becomes significant with increasing the surfactant concentration and final collapse temperature. The polymer-surfactant complexes, the ion pair, and the multiplet structure are believed to play roles in inducing the entanglement of interfacial chains in the poor solvency domain.

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INTRODUCTION

Macromolecules can exist in principle in a large number of different conformations [1,2]. In a good solvent, the segmental pair interactions of a polymer are repulsive and tend to expand the random coil conformation. When a polymer is in a poor solvent under worse than θ conditions, the mean force acting between segments becomes attractive. This attraction can ultimately lead to the collapse of a single polymer coil to the space filling globular conformation. As the solvency is changed, a polymer chain may undergo a coil-to-globule or a globule-to-coil transition. The continuing interest in the conformational transitions arises not just from their importance in understanding the fundamental properties of polymers but also from important biological implications, being analogous to the transitions involved in protein folding and DNA packing [3,4].

Since the addition of surfactants can significantly change the hydrophobic-hydrophilic balance of macromolecular groups, the surfactant effect on the conformational changes of polymer chains has attracted current interest. In the study of the coil-to-globule transition of poly(*N*-isopropylacrylamide) (PNIPAM) in an aqueous solution, a small amount of ionic surfactant, sodium dodecyl sulfate (SDS), was added to prevent aggregation of the polymer chains [5,6]. Under better than θ conditions, the dimension of PNIPAM chains increases with increasing SDS concentration [5–8]. The cooperative binding of surfactant SDS to free PNIPAM chains results in an expansion of chains due to the repulsive electrostatic interactions between the firmly adsorbed amphiphiles [5–10]. As the solvent quality is changed from good to poor, the collapse transition of the PNIPAM-surfactant complex shifts to higher temperatures with increasing the surfactant concentration. The collapse transition of PNIPAM chains can be assumed to result from changes in the hydrogen bonding and the hydrophobic interactions that occur both within and between the segments of the PNIPAM chains and the solvent water molecules. The structure of free PNIPAM-SDS complexes at low and high temperatures is considered to be ''necklaces,'' where each PNIPAM chain has collected a set of SDS micelles [9].

The present authors have studied the temperature-induced coil-to-globule type transition of interfacial PNIPAM chains [11–13]. The PNIPAM chains are chemically bound to electrosterically stabilized polystyrene latex particles. The experimental data indicates that if the surface charge density of the latex particles is sufficiently high, the aggregation of the latex particles can be prevented without surfactants. This allows the coil-to-globule type transition of interfacial PNIPAM chains to be observed as compared to free polymer system. In the presence of surfactant SDS, three types of collapse transition curves of the PNIPAM and PNIPAM-surfactant complex at interfaces are observed with SDS concentration [13]. At lower SDS concentrations ($<\sim$150 mg/L), most of the interfacial PNIPAM chains collapse to their globule state in much the same fashion as in the absence of surfactant. The conformational change under such an intermolecular solubilization is consistent with that of surfactant-free system. As the SDS concentration is increased ($>\sim$150 mg/L), PNIPAM chains are swollen by SDS molecules and the magnitude of the chain shrinkage under better than θ-solvency conditions is reduced continuously and finally eliminated. At higher SDS concentrations ($>\sim$800 mg/L), an interesting feature is that the interfacial chains proceed through a weak transition and then collapse in a sharp way at the corresponding transition temperature. Note that previous studies were focused on effects of surfactants on the collapse transition of PNIPAM.

Recently, we have studied the collapse-to-swelling transition of interfacial PNIPAM, an opposite process of the collapse transition, in the presence of SDS. We here use the terminology ''collapse to swelling'' for the conformational changes of polymer-surfactant complexes, distinguishing them from the coil-to-globule transition for pure polymers. The aim of this work was to study the universal features, if in existence, of the surfactant effects on the conformational changes (the swelling to collapse and the collapse to swelling) of PNIPAM and PNIPAM-surfactant complexes at interfaces. In spite of the fact that the interactions between polymer segments and surfactant molecules are complicated and the exact nature of these interactions is still open to debate [10], it seems natural to speculate that in the presence of surfactant molecules, a compact conformation of PNIPAM at a poor solvency would transform to an expanded conformation at a good solvency, being analogous to the free

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polymers in the presence of surfactant under a good solvency condition. However, unexpectedly, the results obtained from the collapse-to-swelling transition show that even in a good solvency domain the existence of the surfactant molecules results in a smaller polymer dimension than that in surfactant-free solutions. Such a phenomenon was not found for neutral polymers in a good solvency domain and is considered as the formation of entanglement of interfacial polymer during conformational transitions. In this paper, we report on the surfactant-assisted entanglement of neutral polymer at interfaces during conformational changes as studied by dynamic light scattering.

EXPERIMENT

N-isopropylacrylamide was purified by recrystallization from a 65/35 mixture of hexane and benzene. Styrene was distilled at 55 °C under reduced pressure. Potassium peroxydisulfate, sodium metabisulfite, and sodium dodecyl sulfate (SDS) were used as received. Azobis(isobutyronitrile) was recrystallized from alcohol. All solvents were of analytical grade. Water was Millipore Milli-Q grade.

The PNIPAM was prepared following the prodedure described by the literature [8]. The PNIPAM that was obtained was fractionated by the careful addition of dried solid in dry acetone, followed by the dissolution of dry *n*-hexane. The samples were dried by a vacuum and dissolved in Millipore Milli-Q water. The samples were filtered through a 0.45-μm filter and then recovered by free drying. The highest weight-average molecular weight fraction was used for the study. The weight-average molecular weight and radius of gyration were determined by static light scattering at 25 °C, using the Zimm plot procedure, to be 1.6×10^6 and 58 nm, respectively. The polydispersity ratio of the PNIPAM was estimated from the dynamic light scattering measurement in the SDS solution of 120 mg/L, following the procedure of Meewes *et al.* [6] and was found to be about 1.4

Graft polymerization of styrene onto PNIPAM (1.5 g) in water (80 mL) was accomplished by the slow addition (approximately 40 min) of styrene (0.3 g) in the presence of the redox initiator potassium peroxydisulfate $(1\times10^{-3}\,\mathrm{g})$/sodium metabisulfite $(4\times10^{-4}\,\mathrm{g})$ to yield a clear solution [13]. To generate a latex, styrene (1.2 g) was then added quickly, along with additional potassium peroxydisulfate (0.019 g) and sodium metabisulfite (0.0076 g) to a final volume of 100 mL water. After about 20 h, the resultant latex was filtered and then dialyzed by repeated changes of freshly Millipore Milli-Q water for about 3 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 $\theta=90°$ and a wavelength of $\lambda=488$ nm at a power of 50 mW. The analysis of the electric field autocorrelation function was made using the method of cumulants. Hydrodynamic diameters d_h were calculated from the translational diffusion coefficients using the Stokes-Einstein equation, $d_h=k_BT/(3\pi\eta D_z)$, with k_B being the Boltzmann constant, T the temperature, and η the solvent viscosity. The average diameter of the core polystyrene latex particles coated by PNIPAM was determined by transmission electron microscopy to be 130 nm. The data were collected about 45 min after the measurement temperature was reached. In the collapse-to-swelling transition experiments, the samples were kept at 50 and 60 °C for 40 min before the temperature was lowered.

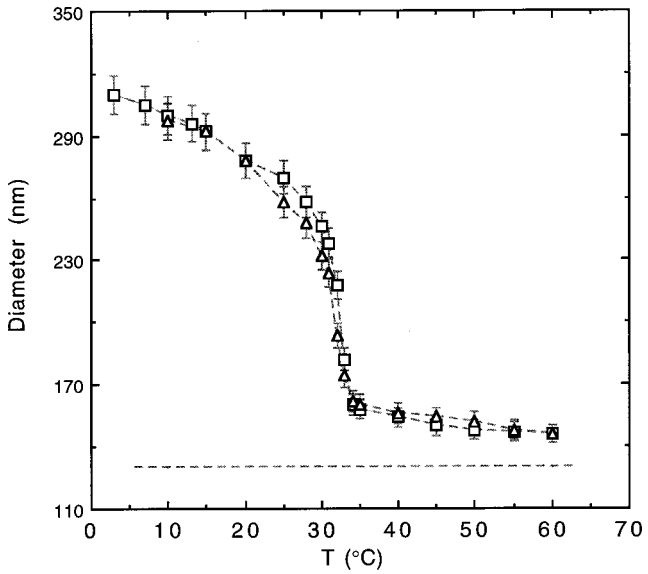

FIG. 1. The temperature dependence of the average hydrodynamic diameter of latex particles chemically bound by PNIPAM in the coil-to-globule transition (squares) and in the globule-to-coil transition (triangles) in the absence of SDS. The dotted line represents the data of the average hydrodynamic diameter of polystyrene latex particles.

The intrinsic colloid stability of the latex particles in the presence of lower concentrations of SDS was checked over a period of about 3 days by repeated measurements of the average hydrodynamic diameter at scattering angles of both 90° and 45° at 20 °C. The average sizes were found to be constant, implying that no aggregation was occurring in the samples studied.

RESULTS AND DISCUSSION

Figure 1 shows the temperature-induced conformational transitions of the interfacial PNIPAM chains in the absence of SDS. The interfacial PNIPAM chains undergo a continuous conformation change with a variation of the temperature. In the collapse transition, the interfacial chains have significantly collapsed (~90 nm) before the collapse temperature is achieved. A gradual weakening of hydrogen bonding between PNIPAM chains and water molecules is attributed to the polymer collapse under better than θ-solvency conditions. The formation of *n* clusters [14] in the inner dense layer of the PNIPAM through the hydrophobic interaction could be taken as an attractive force inducing the conformational transition in better than θ solvency. In the swelling transition, the polymer dimension is found to be slightly smaller between 25 and 31 °C. Such a reduction of polymer dimension can be explained as the formation of transit networks inside the chains during the collapse transition. The

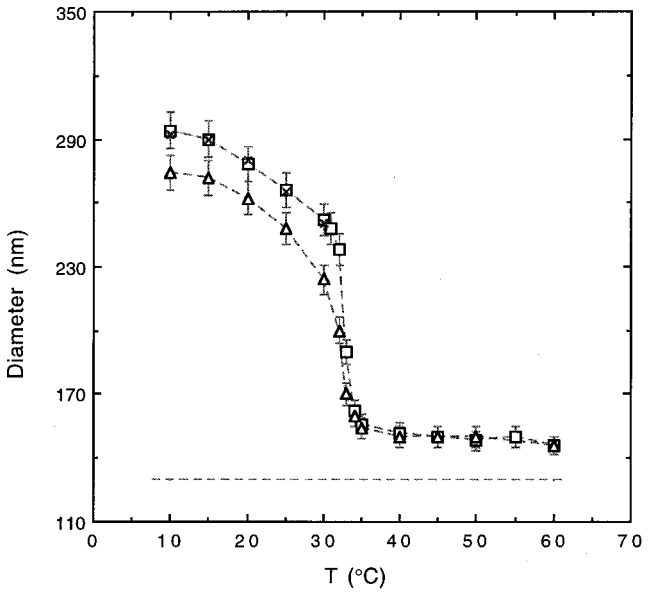

FIG. 2. The temperature dependence of the average hydrodynamic diameter of latex particles chemically bound by PNIPAM in the coil-to-globule transition (squares) and in the globule-to-coil transition (triangles) at the SDS concentration $C_s = 158$ mg/L. Crosses are the data for the sample which was first heated from 10 to 30 °C and then cooled to 10 °C. The dotted line represents the data of the average hydrodynamic diameter of polystyrene latex particles.

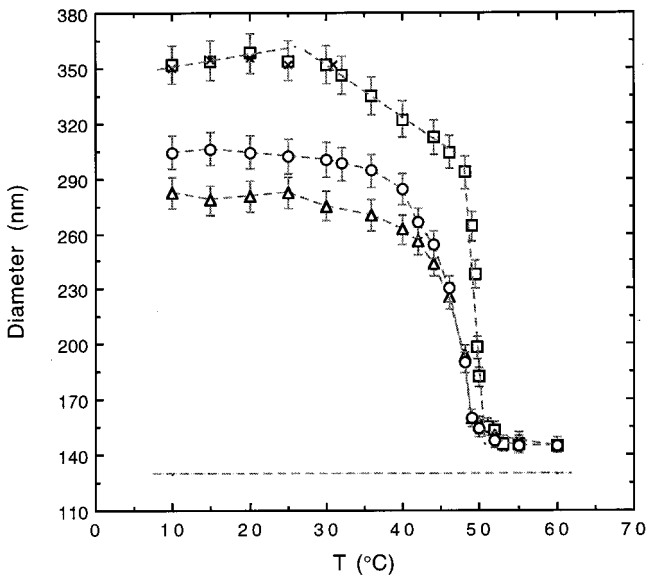

FIG. 3. The temperature dependence of the average hydrodynamic diameter of latex particles chemically bound by PNIPAM in the coil-to-globule transition (squares) and in the globule-to-coil transition (triangles and circles represent the final collapse temperatures 60 and 50 °C, respectively) at the SDS concentration $C_s = 1023$ mg/L. Crosses are the data for the sample which was first heated from 10 to 31 °C and then cooled to 10 °C. The dotted line represents the data of the average hydrodynamic diameter of polystyrene latex particles.

expansion of the compact conformation during the swelling transition is hindered by these networks in the temperature range 25–31 °C. It should be noted, however, that with a further decrease in temperature, for example at 15 °C, the interfacial PNIPAM can expand to the same dimension as that before the collapse transition. No dimension difference between the collapse and swelling transitions clearly indicates that no entanglement is formed within the interfacial layers during conformational changes. The hysteresis observed in the temperature range 25–31 °C may not reach a thermodynamical equilibrium. The results obtained from the absence of surfactant are then comprehensively compared with those from the presence of surfactant.

Figure 2 shows the temperature-induced conformational changes of the interfacial chains at the surfactant concentration $C_s = 158$ mg/L. This surfactant concentration is smaller than the critical association concentration CAC (~230 mg/L) above which individual surfactant molecules form aggregates bound to the polymer chains in the good solvency domain [8]. The collapse transition of the interfacial PNIPAM at this SDS concentration exhibits a similar behavior to that in the surfactant-free sample. It is found from the swelling transition, however, that the dimension of interfacial PNIPAM chains is reduced over the whole range of good solvency domain. In comparison to the surfactant-free sample at 15 °C, the polymer thickness obtained from the swelling transition is found to be only about 89% of that before the collapse transition. Since there is no influence of the addition of surfactant on the polymer chains in the good solvency domain, the surfactant molecules should play a role in the collapse transition process and in the formation of the equilibrium globules as well. It is assumed that additional interchain and intrachain interactions inside the polymer layers are promoted by the presence of surfactant molecules in poor solvency domain. Note that the polymer dimension is not changed when the temperature is lower than 30 °C. Apparently, the shrinking of the interfacial chains in a good solvency domain cannot be explained as a consequence of conformational hysteresis due to the formation of transit networks in poor solvency domain. It is suggested that during the conformational transitions the entanglement has been induced by surfactant aggregates in poor solvency domain.

The effect of surfactant molecules on the interfacial chains becomes more significant as the surfactant concentration is further increased. Figure 3 shows the temperature-induced conformational transitions at $C_s = 1023$ mg/L. This SDS concentration is higher than CAC but lower than the critical micelle concentration of a salt-free SDS solution (~2300 mg/L) [15]. The cooperative binding through hydrophobic interactions of SDS aggregates with the polymer segments in the interfacial PNIPAM layers is expected to occur. This could result in locally swollen coils in good solvency domain, as a consequence of the repulsive electrostatic interactions between the firmly adsorbed amphiphiles, as well as perhaps some effects of steric hindrance. In the collapse transition, the collapse of PNIPAM-SDS complexes proceeds through a relatively weak transition at ~31 °C before the onset of a sharper collapse at ~49 °C. The collapse-to-swelling transition shows that the higher surfactant concentration leads to the smaller dimension of the interfacial chains in good solvency domain. At 15 °C, for example, the polymer thickness is reduced to 66% of that of swollen chains. The results imply that at higher surfactant concentra-

tions the chain interpenetration at interfaces is effectively enhanced by surfactant aggregates in poor solvency domain and the entanglement structure remains thermodynamically stable in good solvency domain. It can also be seen from Fig. 3 that the dimension of the interfacial PNIPAM chains is smaller if the final collapse temperature is higher.

In a good solvency condition, there is no or a very limited interaction between the interfacial PNIPAM chains and free surfactant molecules at $C_s = 158$ mg/L. This is evidenced by the observation that the curve shape of the collapse transition in the presence of SDS is similar to that in the absence of SDS and that no change in the collapse transition temperature is detectable. The cooperative binding through the hydrophobic interaction of SDS aggregates with the PNIPAM occurs only in poor solvency condition. Since the collapse transition of PNIPAM chains is not an all-or-nothing process and the random coil should pass sequentially through the crumpled coil and the molten globule before the compact globule is reached [16,17], the surfactant molecules and their aggregates can interact randomly and sequentially with these collapse states by hydrophobic interaction as soon as the temperature is increased to generate the poor solvency domain. The interactions results in the polymer-surfactant complex on the globule surfaces or near its surfaces if it is assumed that the interactions between the surfactant aggregates and the crumpled coils or the molten globules are dominant. The structure of PNIPAM-SDS complexes at interfaces cannot be predicted as ''necklaces'' in a poor solvency condition. The multichains must come in to play. The optimum structure of PNIPAM-SDS complexes at interfaces in the poor solvency domain is one in which a SDS aggregate can be shared by different portions of a polymer chain and most likely, by different polymer chains. The surfactant aggregates act like physical cross-linkers for the collapse segments. The most important feature corresponding to the present system is that the entanglement takes place locally at the possible sites where the PNIPAM-SDS complex forms in the poor solvency domain [18,19].

At the higher SDS concentration, $C_s = 1023$ mg/L, the SDS molecules start to interact with the PNIPAM chains in good solvency domain. Since the neutral PNIPAM chains at interfaces convert into partial polyelectrolyte complexes as a consequence of PNIPAM-SDS interactions, the density of the interfacial PNIPAM layers is decreased and the intramolecular interactions within the layers effectively inhibited. The structure of PNIPAM-SDS complexes at interfaces may be considered as ''necklaces'' in a good solvency domain.

Conformational changes of charged polymers or polyelectrolytes are much less understood than those of neutral polymers. In earlier studies, the effect of counterions on conformational changes of charged polymers were not taken into account. Recently, interest has grown in understanding the counterion-condensation-induced collapse of polyelectrolytes [20–23]. This interest derives from the fact that in a realistic system a finite concentration of charged polymers should correspond to a finite number of counterions. Although the effects of counterion on the collapse of charged polymers are complicated, it is generally recognized that the interaction between polyelectrolytes and their counterions can be neglected in good solvency. As the solvent quality is changed toward a bad solvency domain, the counterions begin to interact strongly with oppositely charged polymer chains. Such a counterion condensation results in a screening of electrostatic repulsion and finally induces the collapse of charged polymers.

In the present system, the free counterions at higher SDS concentrations are considered to be trapped and form ion pairs with the polymer chains when the temperature is higher than the collapse temperature of pure PNIPAM chains. The formation of ion pairs inside polymer layers can lead to a dipole-dipole attractive interaction and to a decrease in the osmotic pressure. The weak transition starting at 31 °C (the θ temperature of pure PNIPAM) is explained as the formation of ion pairs between the charges on the PNIPAM-SDS complexes and the sodium counterions. When the temperature exceeds the critical temperature at which the sharp transition occurs, the polymer volume fraction is significantly increased and the effective dielectric constant of polymers is lower than that of pure water. Note that the jump amplitude of the collapse transition is a feature of polyelectrolytes. As a result, the attractive interaction between the charges on the interfacial PNIPAM-SDS complexes and the counterions is progressively strengthened with increasing temperature. The ion pairs formed are expected to aggregate and to organize into a well-defined multiplet structure [20,21]. The distribution of the ion pairs and multiplet structure in the interfacial PNIPAM chains is not clear but they could be mainly located in the inner layer of the interfacial chains. At higher surfactant concentrations, the polymer entanglement is effectively promoted by the formation of the ion pairs and multiplets in the poor solvency domain.

CONCLUSIONS

The present study experimentally reveals the surfactant-assisted entanglement of the interfacial PNIPAM chains during conformational changes. The formation of thermodynamically stable entanglement is observed from the collapse-to-swelling transition by dynamic light scattering. It is found that the magnitude of the entanglement strikingly depends on the surfactant concentration and the final collapse temperature. At higher surfactant concentration and higher collapse temperature, the dimension of PNIPAM and PNIPAM-SDS complexes at interfaces, depending on the SDS concentration, is smaller after the collapse transition than that before the collapse transition. The polymer-surfactant complexes formed in poor solvency condition are believed to play a role in inducing the polymer entanglement at lower surfactant concentrations. The formation of the ion pairs and the subsequent formation of the multiplet structure at higher surfactant concentrations act like additional cross-linkers. The higher surfactant concentration produces a greater number of physical cross-linkers while the higher collapse temperature results in a greater compaction of chains. In a poor solvency condition the structure of PNIPAM-SDS complexes at interfaces is essentially different from that of free PNIPAM-SDS complexes. It is suggested that a SDS aggregate can be shared by different portions of a polymer chain and different chains as well. It is even possible that several necklaces can aggregate through the counterion-mediated manner.

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