Intermolecular and Intramolecular Solubilization: Collapse and Expansion of a Polymer Chain in Surfactant Solutions

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Solubilization and conformational transitions of a polymer in dilute surfactant solutions are studied by dynamic light scattering. The polymer, poly(*N*-isopropylacrylamide), aggregates in aqueous solution when heated above 34 °C. A small amount of surfactant, sodium dodecyl sulfate, prevents aggregation—intermolecular solubilization takes place. The polymer then forms a stable dispersion of isolated collapsed globules. A further increase of the surfactant concentration leads to an expansion from the globule to the coil state due to intramolecular solubilization.

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It is an everyday experience that the solubility of a substance in a given solvent depends on the temperature: Usually, a lowering of the temperature increases the tendency of clustering or aggregation of the solute. Eventually, cooperative effects will lead to a phase separation. A substance that is insoluble at given thermodynamic conditions can often be solubilized by a cosolute.[1] An example of great fundamental and technological importance is the solubilization of oil in water (or vice versa) by surfactants. Intense research on the phenomenon of surfactant-mediated solubilization has revealed a large variety of states of such ternary mixtures ranging from micelle dispersions to various types of thermodynamically stable microemulsions and to emulsions.[2] The rich phenomenology of dispersions becomes even more complex when the solute consists of flexible polymer chains. The forces acting between two solute particles are effective also within a single polymer molecule. A large macromolecule represents a macroscopic system in the statistical sense and the intramolecular segment aggregation can therefore result in a sharp conformational transition. In the case of a linear chain this can be a collapse from an extended, flexible conformation to a compact and rather stiff globular state. The term "coil-globule transition" was coined to describe such a behavior. Despite extensive theoretical and experimental research over more than two decades (see Refs. 3–5 for reviews of the topic), the nature of the coil-globule transition still remains rather controversial. This is primarily due to experimental problems arising from the double nature of a polymer solution: One wants to study the transition of a single macromolecule, but the sample is a dispersion of many interacting particles which may aggregate or undergo phase separations just as an ordinary solute. Even in the case of the drosophila of the field —high-molecular-weight polystyrene—there are still doubts concerning the practical attainability of a truly thermodynamically stable dispersion of isolated collapsed globules.[6]

We were confronted with this problem when attempting to investigate the coil-globule transition of poly(*N*-isopropylacrylamide) [poly(NIPAM)] in water. The system exhibits a lower consolute temperature T_c;[7] i.e., the polymer becomes insoluble when the temperature is increased above approximately 34 °C. Experiments on gels have indicated that the transition is accompanied by a reversible collapse of the chain.[8] In solutions, the coil-globule transition is masked by aggregation because the polymer is rather stiff.[9] As shown in Fig. 1, one can therefore observe a cloud point down to the extremely small concentration of 10 μg/ℓ. Despite this seemingly hopeless situation, two sets of light-scattering studies on the coil-globule transition of poly(NIPAM) in an aque-

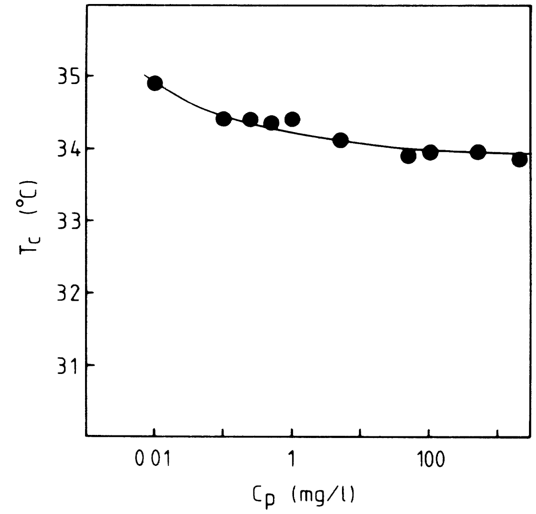

FIG. 1. Dependence of cloud-point temperature T_c on the polymer concentration c_p in water determined by photon counting of the scattered light at a 90° scattering angle. The heating rate was 0.3 K/h. Aggregation of the polymer can be observed down to the concentration of 10 μg/ℓ; at this concentration the polymer contributes only 0.2% of the background scattering below T_c, whereas above T_c the contribution rises to 7%.

ous solution have recently been reported.[10,11] Whereas Yamamoto, Iwasaki, and Hirotsu[10] suggest that their dynamic-light-scattering measurements above the cloud-point temperature should be regarded as heterodyne (the light scattered from large aggregates giving the local oscillator[12]), Fujishige, Kubota, and Ando[11] do not comment on how they obtained their data.

We sought to overcome the aggregation by solubilizing the polymer by means of small amounts of the surfactant sodium dodecyl sulfate (SDS). [Solubilization of a polymer by SDS has been reported for poly(vinyl acetate)[13] and has also been indicated for poly(NIPAM).[14]] This approach not only proved successful, but also revealed a very interesting manifestation of the double nature of the polymer solution in the phenomenon of solubilization: When a very small amount of surfactant is added to the polymer dispersion at a temperature beyond its cloud point, the dispersion clarifies. Increasing the concentration of surfactant inhibits and eventually prevents the formation of aggregates—the dispersion consists of isolated collapsed polymer globules. We call this effect *intermolecular solubilization.* Upon a further increase of surfactant concentration—still well below the critical micelle concentration—we observe a second solubilization step, the *intramolecular solubilization*, as a sharp transition from the globular state to the state of an extended coil.

The polymer was synthesized by radical polymerization.[15] The monomer, NIPAM, was purified by crystallization from a 50-wt% benzene-hexane mixture and the polymerization product by repeated precipitation through heating in an aqueous solution. The weight-average molecular weight M_w of 3.2×10^6 g/mol was determined by light scattering in water. The molecular-weight distribution is considerably broad. The theoretical result for the polydispersity (M_w/M_n) for radical polymerization is 1.5, but from size-exclusion chromatography (SEC) we estimate a higher value of 1.8. We found, however, in accordance with the results reported in Ref. 11, that the cloud-point temperature exhibits only a weak dependence on molecular weight. The samples with varying surfactant concentration c_s were prepared at room temperature by adding first the surfactant and subsequently a polymer stock solution to the water. The resulting polymer concentration was 100 mg/ℓ throughout, which is 10 times less than the c^* concentration, where the polymer chains begin to overlap. The concentration of the surfactant SDS was varied between 0 and 600 mg/ℓ, the critical micelle concentration of SDS in water being 2.3 g/ℓ.[16] The solutions can therefore be regarded as dilute with respect to both polymer and surfactant. Since the surfactant is ionic we controlled the ionic strength of the solution by adding $10^{-4}M$ NaCl. Such low ionic strength does not appreciably affect the critical micelle concentration of SDS in water.[16] The temperature of the solutions was controlled to 0.1 K. Our main investigation technique is dynamic light scattering.[12] The measurements were performed with a commercial light-scattering apparatus (ALV) at 90° scattering angle using the 514-nm argon line. The photon-count correlation function was obtained with a four-bit correlator (Brookhaven).

For a dilute solution of monodisperse, flexible macromolecules, we expect the normalized time autocorrelation function of the scattered intensity $g^{(2)}(\tau) = \langle I(0)I(\tau)\rangle/\langle I\rangle^2$ to obey the relation[12]

$$g^{(2)}(\tau)-1\approx[1+f(\tau)]e^{-\tau/\tau_c}, \qquad (1)$$

where the correlation time $\tau_c = 1/q^2D$ depends on the magnitude of the scattering vector q and the diffusion coefficient D of the scatterers. The exponential factor describes the translational movement of the solute molecules; polydispersity will cause a deviation from the single exponential. From D, the hydrodynamic radius can be calculated using the Stokes-Einstein relation. The function $f(\tau)$ describes internal motions or rotations of flexible or anisotropic scatterers and vanishes for rigid globules.[12] Indeed, we observe two distinct types of the correlation functions (Fig. 2): Curve a exhibits a behavior typical for flexible coils. After the fast initial relaxation resulting from internal motions, the decay becomes approximately exponential, reflecting the translational diffusion of the coils. The much faster decaying curve b is consistent with the picture of small, compact (but polydisperse) globules. The interpretation of the data would thus require two different models and would be ambiguous in the transition region close to T_c. We have instead chosen an apparent average hydrodynamic radius

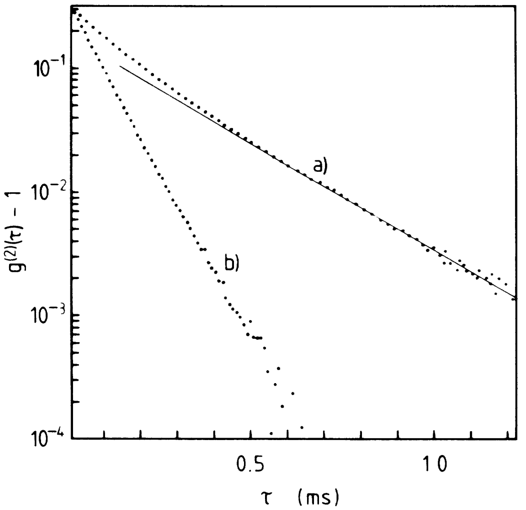

FIG. 2. Typical photon-count correlation function for (curve a) coils and (curve b) globules. The solid line indicates the exponential decay attributed to translational diffusion. ($T = 36\,°C$; the surfactant concentration c_s is 550 and 300 mg/ℓ, respectively.)

R_a to characterize the state of the polymer molecules: We approximate the correlation function by

$$g^{(2)}(\tau)-1\approx Ae^{-\tau/\tau_1}+Be^{-\tau/\tau_2}, \qquad (2)$$

and calculate R_a from the average relaxation time $\bar{\tau}_c=(A\tau_1+B\tau_2)/(A+B)$. Thereby we estimate the hydrodynamic radius of the coils by approximately 30% (see solid line in Fig. 2). Varying the two independent parameters c_s and T, a two-dimensional state diagram $R_a(c_s,T)$ can be constructed. In Fig. 3 we show two isotherms: For the data obtained at 25 °C, well below the transition temperature T_c of the surfactant-free polymer, the measured correlation functions are of the type *a* in Fig. 2, indicating the coil state of the polymer. The apparent radius R_a is essentially unaffected by the presence of the surfactant; we observe only a slight decrease of R_a at the highest surfactant concentrations. Concomitantly the scattering intensity decreases by one-third. The particle scattering factor is well described by Debye's model for Gaussian coils;[17] the radius of gyration amounts to 115 ± 5 nm ($c_s=300$ mg/ℓ). At 36 °C the c_s dependence of R_a is more interesting: For $c_s=0$ we observe large aggregates; the turbidity is clearly perceptible by eye. Already 10 mg/ℓ of the surfactant is sufficient to clarify the suspension and R_a drops below its value for extended coils. Upon a further increase of the surfactant concentration, both R_a and the scattering intensity decrease further to reach a plateau at $c_s\simeq150$ mg/ℓ. The correlation functions take the form *b*. The radius of gyration is correspondingly small, amounting to 17 ± 2 nm, the value being consistent with the picture of the scatterers as compact, homogeneous spheres. The scattering intensity (extrapolated to zero scattering angle) is 30% larger than at 25 °C; it is not clear whether this reflects the association of the surfactant to the polymer or whether there is some residual aggregation. Furthermore, the polydispersity of the globules, estimated from cumulant analysis, agrees well with the value obtained from SEC. From the hydrodynamic radius, we estimate[18] the packing density of the polymer material in the globules to 0.25 ± 0.01 g/cm^3. This value compares favorably with the maximum packing density of 0.4 g/cm^3 we were able to realize with a space-filling model of the polymer, especially if one takes into account that there is presumably some surfactant associated with the polymer. We conclude that in this regime the intermolecular solubilization is completed—the polymer is dispersed in the form of compact monomolecular globules.

At $c_s=400$ mg/ℓ we observe the intramolecular solubilization as a drastic increase of the apparent radius. It finally approaches the value obtained at temperatures below T_c while the correlation functions transform into the form *a* of Fig. 2, which is characteristic for flexible coils. The picture of the globules expanding to the coil state is confirmed by a fivefold *decrease* of the scattering intensity, also reaching exactly the value obtained at 25 °C for the same surfactant concentration. The intramoleculary solubilized polymer retains its ability to collapse into globules: As shown in the $R_a(T)$ diagram (Fig. 4), the transition is merely shifted towards a higher temperature with increasing c_s. All its features, including the steepness, the extent of the change of R_a, and the increase of the scattering intensity upon collapse, remain unaffected by the surfactant concentration, providing of course, that c_s is high enough to prevent aggregation.

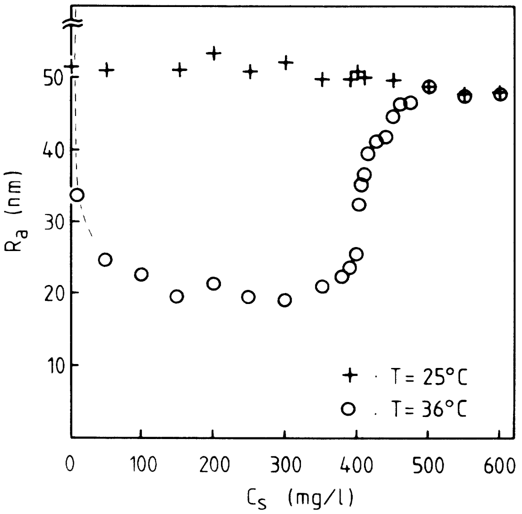

FIG. 3. Apparent hydrodynamic size R_a as a function of surfactant concentration c_s. The dashed line marks the onset of aggregation; the value of R_a for $c_s=0$ at $T=36$ °C could not be determined accurately because of the turbidity of the solution.

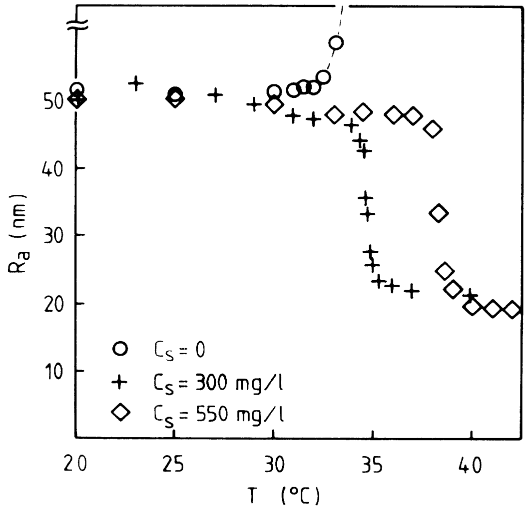

FIG. 4. Apparent hydrodynamic size R_a as a function of temperature. As in Fig. 3, the dashed line for $c_s=0$ marks the onset of aggregation.

All transitions are reversible: Upon cooling, the original coil state is attained with a reproducibility better than 5%. The waiting times to reach the equilibrium ranged from one hour to several days depending on the closeness to the transition region. The time necessary to collect the data for a curve in Fig. 3 or Fig. 4 was two to three weeks. On this time scale the dispersions were stable in both coil and globule state.

At the present stage of the investigation we can only speculate about the microscopic causes of the observed phenomena. The intermolecular solubilization can perhaps be understood in analogy to the solubilization of oil in microemulsion droplets. This picture would suggest aggregates of condensed polymer molecules coated with a surfactant layer. Just as the size of microemulsion droplets decreases with an increasing amount of surfactant,[2,19] the aggregation number of the particles would decrease in order to maintain a favorable surface-to-volume ratio. This analogy breaks down when the intermolecular solubilization is completed, i.e., when the polymer is dispersed in the form of monomolecular globules: In the microemulsion picture one would now expect a continuous deformation of the globules providing the increase of surface necessary to accommodate the increasing amount of surfactant. Instead, we observe the sharp transition into the coil state. There is a certain resemblance between our intramolecular solubilization and the surfactant-induced conformational changes known to occur in polypeptides.[20-22] Although the effects are somewhat similar, the mechanism is probably very different: In proteins, the charged residuals of the peptide backbone have been shown to be important[22,23] whereas our polymer is nonionic. The surfactant probably adheres to the polymer due to a hydrophobic interaction of its hydrocarbon tail with the isopropyl groups of the polymer.

In conclusion, we have shown that solubilization of poly(NIPAM) proceeds in two distinct steps. The *intermolecular solubilization* inhibits aggregation of the polymer molecules and makes it possible to study a stable solution of isolated collapsed globules at a temperature beyond the transition point. Increase of the amount of surfactant leads to *intramolecular solubilization*, and by varying the surfactant concentration we are able to control the temperature at which the coil-globule transition takes place.

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