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NMR Study on the Effects of Sodium *n*-Dodecyl Sulfate on the Coil-to-Globule Transition of Poly(*N*-isopropylacrylamide) in Aqueous Solutions

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1. INTRODUCTION

Poly(*N*-isopropylacrylamide) (PNIPAM)[1−5] is a well-known thermosensitive polymer that exhibits a low critical solution temperature (LCST) at around 32 °C in aqueous solutions. The coil-to-globule transition of this polymer can be induced by a small temperature variation (1−2 K) accompanied by abrupt conformational changes. The LCST behavior of PNIPAM has been attracting research interests for several decades because of its implication in a number of living phenomena, especially on protein folding and DNA packing.[6−8] However, some additives in solutions,[9] such as various cosolvents,[10−12] electrolytes,[13,14] and surfactants,[15−17] may influence its LCST.

The anionic surfactant sodium *n*-dodecyl sulfate (SDS) has been receiving particular attention[15,16,18−24] because of the rise in the LCST of PNIPAM solutions in the presence of SDS resulting from their peculiar interactions. The surfactant effects on the conformational change of PNIPAM in water have been extensively studied using various techniques such as laser light scattering (LLS),[18,19] conductometric measurements,[20] nuclear magnetic resonance,[21,22] fluorescence spectroscopy,[23] and small-angle neutron scattering.[24] Two different SDS structures in PNIPAM aqueous solution were proposed[23] at the SDS concentration between the 0.23 mg/mL[1] critical aggregation concentration (CAC) and the 2.3 mg/mL[25] critical micelle concentration (CMC). One is the individual SDS in a free state, and the other is the SDS micelle bound to PNIPAM segments via hydrophobic interactions.[16,23,26]

However, the possible morphologies of PNIPAM and SDS in the compact globule state have remained ambiguous for decades. Walter et al.[23] thought that the surfactants form a surface layer with the polymer globule to prevent phase separation when the temperature increases up to the LCST. In our previous experiment, a collapsed, single-chain PNIPAM globule was obtained by the removal of the surfactant via dialysis above the LCST,[27] and its viscosity behavior was quantitatively determined.[28] Meanwhile, Wu and Zhou[18] proposed a PNIPAM−SDS complex structure above the LCST opposite from that of the PNIPAM microgel system obtained using LLS. When the temperature was increased, the polymer-bound SDS micelles gradually disintegrated into individual molecules and expelled from PNIPAM, followed by the collapse of the surfactant-free polymer network. Furthermore, they thought that very similar surfactant effects occur on the PNIPAM microgel particles and linear individual chains.

High-resolution NMR is a powerful technique of studying the structures of various materials as well as the molecular interactions among the components of a mixture under various conditions.[26,29,30] Spěváček[31−33] used NMR spectra, NMR relaxation times, and diffusion coefficients to systematically study the coil-to-globule transition of a number of thermosensitive polymers, copolymers, and chemically cross-linked hydrogels. In addition, two-dimensional nuclear Overhauser effect spectroscopy (2D NOESY)[34] can provide detailed information on the proximity in space of two different components. Tzeng and Hou[35] studied the interactions of poly(*N*-vinylformamide) (PNVF) with SDS and proposed a microstructure of PNVF-induced SDS aggregates. However, the effects of SDS on the coil-to-globule transition of PNIPAM have not been systematically studied using 2D NOESY NMR. In the current paper, a systematic investigation on the complex structures and interactions of a polymer and its surfactant in aqueous solutions during the coil-to-globule transition, focusing on the role of SDS below and above the LCST, was conducted using a combination of high-resolution ^{1}H, 2D NOESY, and pulsed-field gradient (PFG) NMR.

2. EXPERIMENTAL SECTION

2.1. Materials. *N*-Isopropylacrylamide (NIPAM) was purchased from Aldrich. The monomer was recrystallized three times in a benzene/hexane mixture before use. PNIPAM was prepared[36] in the laboratory via free radical polymerization in benzene, initiated by recrystallized azobis(isobutyronitrile) (AIBN). The resultant PNIPAM sample was carefully fractionated by successive dissolution−precipitation cycles in a mixture of extremely dried acetone and *n*-hexane at ambient temperature. The average molecular weight of the sample was 1.2×10^5 g/mol, and the ratio of the weight-average to the number-average molar mass was 1.77, as determined by size exclusion chromatography. SDS was

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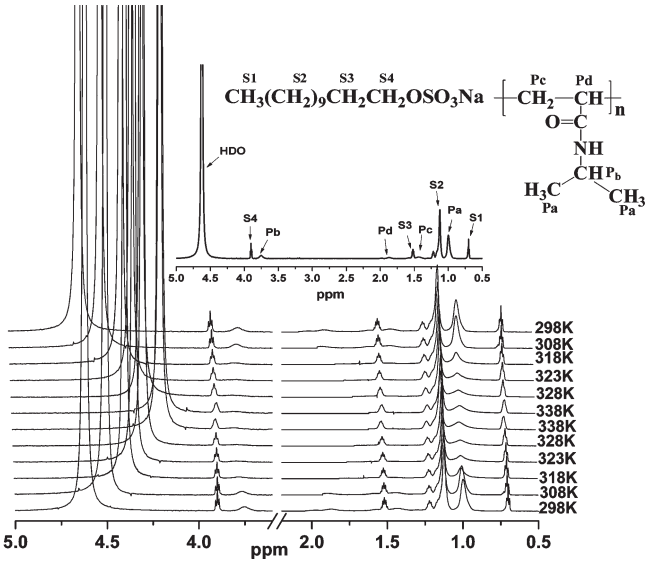

Figure 1. ^{1}H NMR spectra of the PNIPAM/SDS/D_2O solution at various temperatures during the heating and cooling processes. The inset shows the chemical shift in the ^{1}H NMR spectrum of the PNIPAM/SDS/D_2O solution at 298 K.

recrystallized three times from methanol before use. Deuterium oxide (D_2O) was purchased from Cambridge Isotopes Laboratories.

2.2. Preparation of PNIPAM/SDS/D_2O Solution. PNIPAM/SDS/D_2O solution was carefully prepared to obtain an accurate concentration using 0.25 mg/mL PNIPAM and 0.3 mg/mL SDS; the SDS concentration is higher than the 0.23 mg/mL[1] CAC, which is the onset concentration at which the polymer-bound SDS micelles start to form.

2.3. NMR Measurements. The NMR experiments were performed using a Varian 700 MHz spectrometer equipped with a 5 mm standard probe and a 70 G/cm maximum available gradient pulse field. ^{1}H NMR spectra were acquired gradually at 298, 308, 318, 323, 328, and 338 K, with 10 min of thermostatic time and 5 s recycle time before each acquisition. The temperature was reduced 10 min after the temperature increase.

NOESY 2D experiments were conducted at 298, 323, and 338 K with 400 ms mixing time. PFG NMR was used to measure the self-diffusion coefficient. The PSTE pulse sequence[37] included a 2 ms offset-independent adiabatic inversion pulse along with a 7.26 G/cm gradient pulse for the selective excitation of an ~0.65 cm central sample region. Using these parameters, the molecular diffusion coefficient was quantitatively determined. The recycle time was set at 10 s, and the gradient pulse duration was 2 ms. The diffusion time was 200 ms. The gradient pulses were calibrated on a water sample (10% D_2O and 90% H_2O) under the experimental conditions used in the PNIPAM/SDS/D_2O system.

3. RESULTS AND DISCUSSION

3.1. ^{1}H NMR Spectra at Various Temperatures. Figure 1 shows the various ^{1}H NMR spectra of the PNIPAM/SDS/D_2O solution at different temperatures during the heating and cooling processes. The assignments of the characteristic peaks are given in the inset of Figure 1. The proton signal of the external standard tetramethylsilane (TMS) was used as the reference resonance. The signals of the methyl (Pa) and methylene (Pb) protons on the isopropyl group of PNIPAM are at 1.0 and 3.75 ppm, respectively, whereas those of the methylene protons (Pc and Pd) on the main chain are at 1.44 and 1.88 ppm, respectively. The SDS peaks at 3.9, 1.52, and 0.7 ppm correspond to the protons of the α-alkyl group (S4), β-alkyl group (S3), and end alkyl group

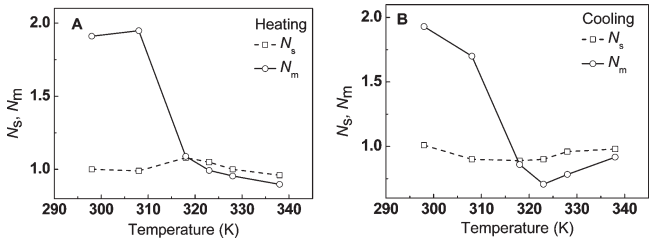

Figure 2. Normalized number of SDS (N_s) (□) and repeated unit of PNIPAM (N_m) (○) at various temperatures during the heating (A) and cooling (B) processes, as calculated from the integrated intensities of Pa and S1 according to Figure 1, respectively. The integrated intensity of S1 at 298 K is set as the reference.

(S1), respectively, whereas the signals of the other methylene protons (S2) on the SDS alkyl chain are superposed at 1.12−1.22 ppm. The broad signal corresponding to water is at ~4.62 ppm.

As shown in Figure 1, the chemical shifts of the PNIPAM and SDS signals are nearly constant, whereas the NMR signal of water shifts toward smaller chemical shifts and then recovers during the heating and cooling processes. The PNIPAM (Pa−Pd) signals undergo apparent broadening with increasing temperature; i.e., the spin−spin relaxation times T_2 of the respective protons become short because of the reduction in the mobility of most of the PNIPAM units. However, all PNIPAM signals are restored after the temperature is decreased. Moreover, the fine triplets corresponding to S1, S3, and S4 of SDS in the low temperature range gradually transform into broad singlets with increasing temperature. The fine splitting of the triplets is attributed to the *J*-coupling with the adjacent methylene protons, whereas the merging of the triplets is due to the fast T_2 relaxation resulting from enhanced hydration effects of the SDS alkyl chain upon heating.[21] Interestingly, the fine triplets are also reproduced during the cooling process. The recovery of the signal intensity of PNIPAM as well as the reappearance of the triplets of SDS suggests a reversible conformational transition of the thermosensitive polymer in solution.

Furthermore, the normalized number of SDS (N_s) and repeated unit of PNIPAM (N_m) at various temperatures during the heating and cooling processes are calculated based on the integrated intensities of S1 and Pa from Figure 1; the results are shown in Figure 2. The integrated intensity of S1 at 298 K is set as the reference. According to Spďváček's theory,[31] the integrated intensities should decrease with reciprocal absolute temperature as $1/T$ when integrated intensities took value at low temperature. The normalized number of SDS, based on S1, is almost kept constant at around 1.0 as shown in Figure 2, indicating a temperature independence during both the heating and cooling processes. The normalized number of repeated PNIPAM units generally decreases during the heating process and recover in the cooling process, indicating the reversibility of the coil-to-globule transition. Interestingly, the molar ratio of SDS to the repeated PNIPAM unit is roughly 1:2 at 298 K, as shown in Figure 2. This ratio is coincidentally equal to the original stoichiometric ratio of the solution preparation, in which the concentrations of PNIPAM and SDS were approximately 0.25 and 0.3 mg/mL, respectively. This observation indicates that all SDS and PNIPAM protons are detectable by ^{1}H NMR at low temperatures, and the polymer chain shows an extended random-coil conformation in solution. When the temperature increases, the polymer chain collapses. The normalized number of the repeated

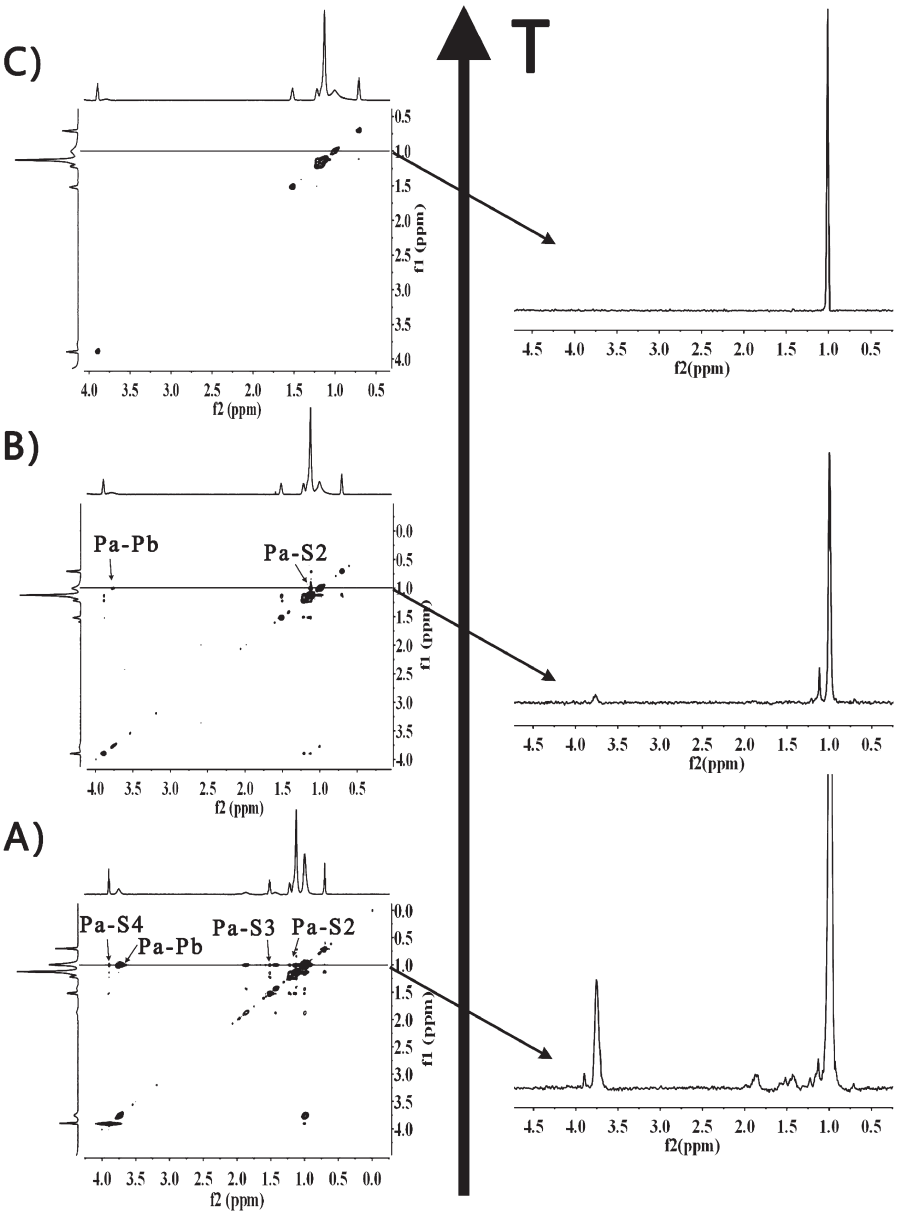

Figure 3. Left: $^{1}H-^{1}H$ 2D NOESY spectra at various temperatures: 298 K (A), 323 K (B), and 338 K (C). Right: 1D spectra extracted from the underlined slices in the left spectra.

PNIPAM unit decreases because a portion of the PNIPAM segment is enwrapped and restricted in the collapsed chains upon heating. On the basis of the abrupt decrease in N_m, the current LCST is roughly estimated at 312 K, which is highly consistent with the previous report by Walter et al.[23] Above the LCST, nearly half of the PNIPAM segments have been restricted and immobile. Similar phenomena were also observed by Chiu et al.,[21] wherein the detectable fraction of the methyl protons of the PNIPAM grafts continuously decreases above 308 K as a result of the progressive transformation of PNIPAM.

However, for SDS, the constant number detected during both the heating and cooling processes suggests that SDS mobility has not been restricted by the collapsed polymer chains during the coil-to-globule transition, making the exact role of SDS during the conformational transition process quite interesting. The detailed structural information on SDS below and above the LCST was determined using 2D NOESY NMR spectroscopy and diffusion coefficient analysis and discussed in the subsequent sections.

3.2. 2D NOESY Spectroscopy. 2D NOESY spectroscopy is often used to monitor the spatial correlation between different spins. By choosing a suitable time window (the mixing time), the magnetization may transfer between the dipolar, coupled spin pair, giving rise to the cross-peaks in the spectrum. Figure 3 shows the 2D NOESY spectra of the PNIPAM/SDS/D_2O solution at 298, 323, and 338 K, all with a mixing time of 0.4 s. At 298 K, strong positive cross-peaks between PNIPAM and SDS appear between the Pa−S4, Pa−S2, Pa−S3, and Pb−S2 proton pairs. This result indicates that the SDS alkyl protons are in close proximity (<0.5 nm) to the polymer side chains.

A PNIPAM and SDS complex structure formed through the hydrophobic interactions between the SDS alkyl chain and

Table 1. Diffusion Coefficients of SDS and PNIPAM in the PNIPAM/SDS/D_2O Solution at Various Temperatures

	SDS								
	individual SDS				polymer-bound SDS			PNIPAM	
temp (K)	f_{free}^{SDS}	$f_{free\text{-}error}^{SDS}$	D_{free}^{SDS}	$D_{free\text{-}error}^{SDS}$	f_{bound}^{SDS}	D_{bound}^{SDS}	$D_{bound\text{-}error}^{SDS}$	D^{PNIPAM}	D_{erros}^{PNIPAM}
298	0.84	±0.04	6.90×10^{-10}	$\pm 0.70 \times 10^{-10}$	0.16	0.58×10^{-10}	$\pm 0.38 \times 10^{-10}$	1.13×10^{-10}	$\pm 0.01 \times 10^{-10}$
323	1.0	±0.1	8.23×10^{-9}	$\pm 0.71 \times 10^{-9}$	0			1.01×10^{-9}	$\pm 0.58 \times 10^{-9}$
338	1.0	±0.2	9.43×10^{-8}	$\pm 2.20 \times 10^{-8}$	0			3.71×10^{-8}	$\pm 0.71 \times 10^{-8}$

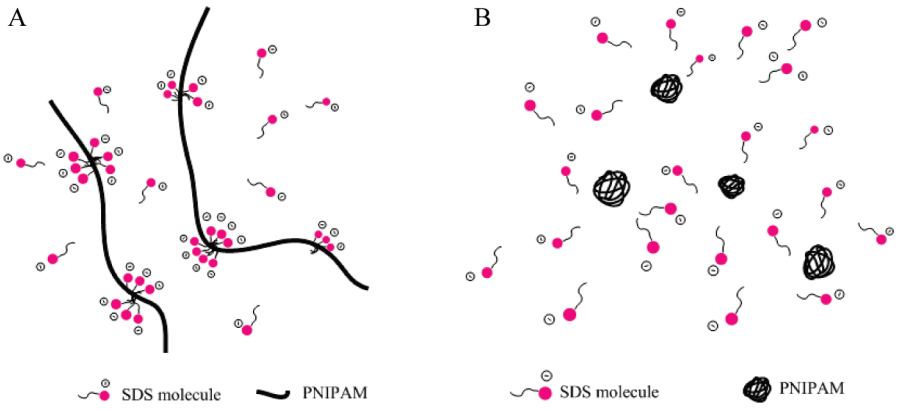

Figure 4. Possible morphologies of the PNIPAM and SDS complexes below (A) and above (B) the LCST.

PNIPAM isopropyl groups can thus be obtained. This complex model is consistent with the previously proposed pearl necklace-like polymer−surfactant complex structure.[16,23] The anionic SDS is firmly associated with the polymer chain; thus, the PNIPAM and SDS complexes bear the characteristics of a polyelectrolyte.[22] Therefore, the hydrodynamic sizes of the individual linear chain[19] and microgel particle[18] of PNIPAM in the presence of SDS are both increased because of intrachain electrostatic repulsion effects compared with those in surfactant-free solutions. The polyelectrolyte-like complexes of PNIPAM and SDS greatly affect the coil-to-globule transition of PNIPAM in an aqueous solution. The electrostatic repulsions of the charged chains resist the hydrophobic interactions between the polymer chain segments when heating induces the solvent to turn bad, which results in the retardation of the PNIPAM chain collapse and an increase in the LCST level. On the other hand, the interchain electrostatic repulsions inhibit the interchain aggregation so that the PNIPAM single-chain compact globule can be obtained.[27,28]

However, the noticeable change in the 2D NOESY spectra in Figure 3 shows the decrease in the signal intensity of the cross-peaks between PNIPAM and SDS with increasing temperature, although nearly half of the PNIPAM units are undetected in the NMR spectra above the LCST. Slice 1D spectra were extracted from the 2D NOESY spectra and are shown in the right list of Figure 3. Compared with the extracted slice spectra, the signal intensities of the cross-peaks at the Pa−S4, Pa−S2, and Pa−S3 proton pairs are clearly reduced with increasing temperature, and almost no cross-peak is observed between PNIPAM and SDS above the LCST. This temperature dependence of the cross-peak indicates a disassociation between the polymers and SDS molecules. At high temperatures, most of the original polymer-bound SDS are assumed to be expelled from PNIPAM. This expulsion is ascribed to the electrostatic repulsions and steric hindrance effects accompanying the continuous collapse of the polymer chain. This phenomenon also provides a plausible explanation for our previous observation[27,28] that the removal of SDS from the PNIPAM/SDS aqueous solution by dialysis under an electrostatic field above the LCST in the preparation of a single-chain compact PNIPAM globule is easily achieved, given that most of the SDS are already dissociated from the polymer at that time.

3.3. Diffusion Coefficient Analysis. PFG NMR analyses of the PNIPAM/SDS/D_2O solutions were also synchronously conducted. The diffusion coefficients of PNIPAM and SDS at various temperatures were calculated based on the analysis of their integrated intensities. Moreover, based on the previous reports[16,23] and the aforementioned discussions, two types of SDS, namely, the polymer-bound and free SDS, exist in the PNIPAM aqueous solution at the 0.3 mg/mL SDS concentration. Therefore, a minimal[38] or two-site model[39] was employed to further analyze the diffusion coefficients of SDS. Consequently, according to the Stejskal−Tanner equation,[40] the SDS diffusion data are calculated using eq 1

$$\frac{I}{I_0} = f \exp(-(g^2 D_{free}^{SDS})) + (1-f) \exp(-(g^2 D_{bound}^{SDS})) + A \quad (1)$$

where the polymer-bound and free SDS diffusion coefficients are expressed as D_{bound}^{SDS} and D_{free}^{SDS}, f is the molar fraction of the polymer-free surfactant in solution, I/I_0 is the ratio of the signal intensity to the outset value, g is the gradient pulse field, and A is a constant.

The diffusion coefficients of SDS and PNIPAM at various temperatures were analyzed based on eq 1 and are summarized in Table 1. At 298 K, which is lower than the LCST, SDS clearly exists as two components, most of which is in the individual state

but roughly 16% is bound to the PNIPAM chain and forms polymer-bound SDS micelles. The diffusion coefficient of the polymer-bound SDS is lower than that of individual ones by one order of magnitude but approaches that of PNIPAM. When the temperature is increased to a value above LCST, only one component of SDS is observed at 323 and 338 K. In addition, the normalized number of SDS is almost kept constant at around 1.0 (Figure 2), and all SDS are detected in the NMR spectra during both the heating and cooling processes. Thus, all SDS at the elevated temperatures are uniform and correspond to only one component. The diffusion coefficients of SDS are much higher than those of PNIPAM, which is due to the conversion of all SDS moieties into the free individual ones above the LCST. The 2D NOESY spectra shown in Figure 3 confirms the dissociation and expulsion of a portion of the original polymer-bound SDS from PNIPAM above the LCST, possibly because of electrostatic repulsions and steric hindrance effects during the continuous collapse of the polymer chain.

In addition, the diffusion coefficients of SDS and PNIPAM (Table 1) both increase with increasing temperature for the improved movement of the surfactant and the polymer. However, based on Figure 2, only half of the PNIPAM units are detected in the NMR spectra at elevated temperatures, indicating that two components in the polymer exist above the LCST. One component is the mobile PNIPAM segments outside the complex, and the other is the immobile one restricted in the compacted globule.

4. CONCLUSION

The role of SDS below and above the LCST in the PNIPAM/SDS aqueous solution has been fully discussed, and the different morphologies of the complexes are illustrated in Figure 4. SDS exists in two different forms, namely, the polymer-bound and free surfactants, at SDS concentrations above the CAC and temperatures below the LCST, as shown in Figure 4A. Approximately 16% of SDS binding to polymer chain greatly affects the conformational changes of the polymers, which exhibit the characteristics of a polyelectrolyte. The electrostatic repulsions result in the increase in the LCST level and the inhibition of interchain aggregations. The disappearance of the cross-peaks between PNIPAM and SDS in the 2D NOESY spectra above the LCST gives direct evidence that most of the polymer-bound surfactants do not coat on the surface of the polymer globule but are dissociated and expelled from the polymer chain because of electrostatic repulsions and steric hindrance effects, as shown in Figure 4B, when the PNIPAM chain transforms into a compact globule.

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