J. MACROMOL. SCI.—PHYS., B36(3), 417–422 (1997)

NMR Evidence of the Formation of Surfactant Micelles Inside Spherical Poly(*N*-isopropylacrylamide) Microgels

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INTRODUCTION

In recent years, water-soluble polymers, or hydrogels, with a lower critical solution temperature (LCST) have been intensively studied. One typical example is poly(*N*-isopropylacrylamide) (PNIPAM) and its gel. The influence of both the surfactant type and concentration on the volume phase transition of the PNIPAM/water system has been investigated by various methods, such as static and dynamic laser light scattering [1–3 swelling equilibrium [4–6], UV [6], cloud point [6], conductivity [5] and electrophoretic mobility [2], to name but a few. These studies show that the PNIPAM chain or gel network can swell more in the presence of anionic surfactants, and that its volume phase transition temperature increases. The binding of the hydrophobic tail to the PNIPAM chain or gel is believed to be responsible for the additional swelling, but this cannot satisfactorily explain why cationic surfactants with a similar hydrophobic tail have much less effect on swelling whereas nonionic surfactants cause no observable additional swelling over a very wide range of surfactant concentrations. Thus, the detailed structure of the PNIPAM/surfactant complex remains unknown and the insight into this problem is important, as noted by Khokhlov [7], who recently stated: "The theoretical explanation of this pronounced capacity to form self-assemblies in such a complex system is at present lacking; however, it is clear that this fact can have far-reaching technological and biological importance."

In this study, we intentionally chose two different kinds of surfactants which have an identical hydrophobic tail, but with two different hydrophilic heads:

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namely, sodium dodecyl sulfate (SDS, anionic) and dodecyl pyridinium bromide (DPB, cationic). Dynamic laser light scattering (LLS) was used to monitor the additional swelling of spherical PNIPAM microgel particles (radius ~ 100–200 nm) in the presence of different amounts of these surfactants. Correspondingly, nuclear magnetic resonance (NMR) was used to measure the spin-lattice relaxation times of protons ($T_{1,H}$) on both SDS and DPB in order to reveal the status of these surfactants inside the PNIPAM microgel networks, particularly when the surfactant concentration is lower than its critical micelle concentration (CMC).

High-quality SDS (from BDH) and DPB (from Beijing University) were used without further purification. The distilled and deionized water from a Millipore Milli-Q water purification system was used as solvent in LLS. Deuterium oxide (D_2O, 99.5 D%, from Aldrich) was used as solvent in NMR experiments. Nearly monodisperse spherical PNIPAM microgel particles were prepared by free-radical polymerization in water at 70°C. The details of the preparation have been reported earlier [8]. The PNIPAM microgel concentration for dynamic LLS was very dilute at $\sim 10^{-6}$ g/mL. The hydrodynamic radius distributions $f(R_h)$ of the PNIPAM microgel particles in the presence of different amounts of SDS or DPB were determined using a modified commercial ALV/SP-150 LLS spectrometer equipped with an ALV-5000 digital time correlator and an ADLAS DPY425II solid-state laser (output power ~ 400 mW at $\lambda = 532$ nm) as the light source. With a proper modification [9], the spectrometer is capable of doing both static and dynamic LLS measurements continuously in a wide angular range of 6°–154°. In order to avoid the interference of the internal motions, the accessible small angular range of 6°–15° is particularly useful in measuring larger microgel particles. The long-term temperature stability inside the LLS sample holder is approx. ±0.02°C.

Figure 1 shows the surfactant concentration dependence of the hydrodynamic radius distribution $f(R_h)$ of the PNIPAM microgels at 30°C. It should be stated that at 30°C water is reasonably good solvent for PNIPAM, so that the PNIPAM microgels are swollen under this condition. Previously, we have shown that when temperature is higher than the volume phase transition temperature, the PNIPAM microgel particle can reach its collapsing limit, and its hydrodynamic size then becomes independent of the type or amount of the surfactant added in the solution [3]. This result is believed to indicate that at its collapsing limit, all surfactant molecules are excluded from the microgel network. Therefore, in this study, we concentrated on the status of the surfactant inside the swollen PNIPAM microgel networks.

Figure 1(a) shows that a small amount of added SDS (well below its CMC ~ 8 mM) can swell the PNIPAM microgel particles and the degree of swelling increases with the SDS concentration. It is clear that the SDS molecules have moved into the PNIPAM microgel networks, otherwise we would not observe the swelling of the PNIPAM microgels. This can be attributed to two driving forces: (1) the osmotic pressure and (2) the relatively more hydrophobic environment inside the microgel in comparison with the water outside the microgel network. When $C_{SDS} > \sim 4$ mM, further addition of SDS has no effect on the swelling, which indicates that the microgel network has been fully stretched. On the other hand, Fig. 1(b), the effect of adding DPB on the swelling is quite different. When C_{DPB} is lower than its critical micelle concentration (~ 12 mM), the microgel particles show a slightly shrinking instead of swelling as shown in the case of adding SDS. This difference in the

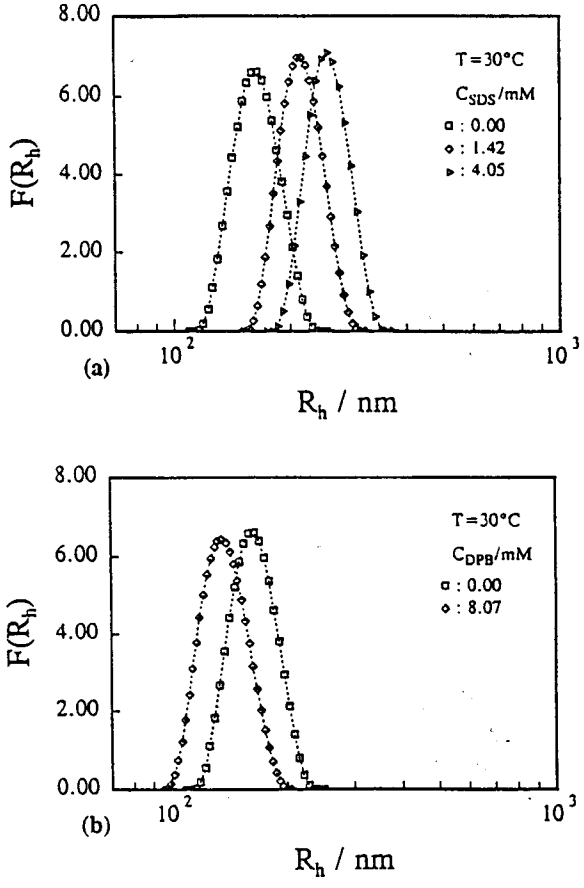

FIG. 1. Surfactant concentration dependence of the hydrodynamic radius distribution $f(R_h)$ of spheric poly(*N*-isopropylacrylamide) microgel particles at 30°C. (a) Anionic surfactant: sodium dodecyl sulfate, SDS. (b) Cationic surfactant: dodecyl pyridinium bromide, DPB.

swelling of the PNIPAM microgels cannot be simply attributed to the association of the hydrophobic tail with the PNIPAM chains or microgel networks since SDS and DPB have an identical hydrophobic tail. Previously, we have attributed this difference to the polymer network assisted SDS micelle formation inside the PNIPAM microgel network on the basis of the interaction between a polyelectrolyte gel and oppositely charged surfactant molecules [3,10,11].

Under the driving forces of both the osmotic pressure and the relatively more hydrophobic environment inside the PNIPAM microgel, surfactant molecules diffuse into the microgel network. Local surfactant concentration inside the PNIPAM microgel could be higher than its CMC even though the overall surfactant concentration in the solution is lower. Therefore, surfactant can form micelles inside the microgel network. Since both the carboxylic and amide groups on the PNIPAM chain are electron rich, it is expected that the approach of anionic SDS molecules inside the PNIPAM microgel networks towards the PNIPAM chains would be less favorable. In other words, SDS would be locally concentrated in the water

encapsulated inside the PNIPAM microgel network resulting in the formation of the SDS micelles. The repulsion between such SDS micelles and the PNIPAM network leads to further swelling of the microgel particle.

On the other hand, it should be more favorable for cationic DPB molecules inside the microgel networks to approach the PNIPAM chains so that DPB has less chance to form DPB micelles inside the microgel network. The approach of DPB to the PNIPAM chain tends to reduce its hydrophilicity. This is exactly why the microgel particle is shrinking, instead of swelling, in the presence of DPB. However, there is no direct evidence to support this kind of micelle formation inside the PNIPAM microgel. In this communication, we report for the first time NMR evidence of the micelle formation inside the PNIPAM microgel network.

In the NMR experiment, all PNIPAM microgel solution contained ~15 wt% of the particles, ~72 wt% of D_2O and ~13 wt% of water (water should be present as HOD because of the fast exchange of hydrogen with deuteron), and the concen- [illegible] [illegible] PNIPAM unit). All SDS and DPB solutions were prepared in D_2O. All solutions, with or without adding the PNIPAM microgel, were degassed three times by successive freeze–thaws. The spin-lattice relaxations of the protons on both SDS and DPB were measured using a Bruker ARX500 pulse Fourier-transform NMR spectrometer operating at 500.13 MHz for proton. The inversion-recovery pulse sequence was used with a relaxation delay set at > 5 times the longest H_{T1} in each case. The $\pi/2$- and π-pulse widths were 10 and 20 μsec, respectively. A total of 16 scans were accumulated for each measurement in order to obtain a reasonable signal-to-noise ratio. H_{T1} was calculated using a three-parameter nonlinear least square fitting software package supplied by Bruker.

Table 1 summarizes the H_{T1} values of two protons (H^a and H^b defined in a foot note to Table 1) on both SDS and DPB at two different surfactant concentra-

TABLE 1

Summary of the Concentration Dependence of the Spin-Lattice Relaxation Times (H_{T1}) of the Protons (H^a and H^b) on Surfactants SDS and DPB With and Without Adding Poly(*N*-isopropylacrylamide) Microgel Particles at 25°C

Surfactant	$C_{surfactant}$	PNIPAM microgels	H_{T1}[a] (sec) H^a	H^b
SDS (CMC ~ 8 mM)	4.0 mM	No	2.4±0.1[b]	1.4±0.1
		Yes	1.9±0.1	1.1±0.1
	12.0 mM	No	1.9±0.1	1.1±0.1
DPB (CMC ~ 12 mM)	8.0 mM	No	2.6±0.1	1.2±0.1
		Yes	2.6±0.1	1.2±0.1
	15.0 mM	No	2.0±0.1	0.9±0.1

[a]Definition of H^a and H^b:
Anionic SDS: sodium dodecyl sulfate $CH_3^aCH_2(CH_2)_8CH_2CH_2^b(SO_3)^-Na^+$
Cationic DPB: dodecyl pyridinium bromide $CH_3^aCH_2(CH_2)_8CH_2CH_2^b(NC_5H_5)^+Br^-$
[b]The uncertainty associated with each H_{T1} measurement is actually small and this maximum uncertainty in H_{T1} is the result of four repeated measurements.

tions: one concentration is lower and the other is higher than its corresponding CMC. As expected, for pure surfactant solutions without the presence of the PNIPAM microgel particles, individual SDS or DPB surfactant molecules (i.e., when $C_{surfactant}$ < CMC) have a longer H_{T1} than those surfactant molecules associated in the form of micelles (i.e., when $C_{surfactant}$ > CMC) because individual surfactant molecules are more mobile.

On the other hand, when the PNIPAM microgel particles are added in the SDS solution (C_{SDS} = 4.0 mM), shorter H_{T1} values were obtained because of faster spin-lattice relaxation rates. In principle, the formation of the SDS micelles is not expected under this condition since C_{SDS} < ~8.0 mM. However, after adding the PNIPAM microgels, H_{T1} became identical as in the case of C_{SDS} = 12.0 mM where SDS has formed the SDS micelles. This is a direct evidence of the formation of SDS micelles inside the PNIPAM microgel networks. As for the case of DPB, when C_{DPB} < ~12.0 mM, there is no change in H_{T1} whether PNIPAM microgel particles are added or not. This implies that DPB exists as individual DPB molecules inside the PNIPAM microgel network, and that there is no aggregation of the hydrophobic tails (namely, no micelle formation), otherwise we would see a decrease of H_{T1} towards the values of H_{T1} in the case of C_{DPB} = 15.0 mM.

In summary, a combination of LLS and NMR results clearly shows that surfactant molecules can move into the PNIPAM microgels. Anionic surfactant SDS is able to form SDS micelles inside the PNIPAM microgel network even in the case when the overall concentration of SDS is lower than its critical micelle concentration. Therefore, the additional swelling of the PNIPAM microgel observed in dynamic LLS can be attributed to the repulsions between the SDS micelle and the PNIPAM chain. In contrast, cationic surfactant DPB cannot form the DPB micelles inside the PNIPAM microgel network, but rather exists as individual molecules inside. Considering that the carboxylic and amide groups on the PNIPAM chain are electron rich, we can explain these two different types of interactions on the basis of a repulsive or attractive interaction between the PNIPAM chain and surfactant molecules. This result is similar to that predicted for the interaction between a polyelectrolyte gel and oppositely charged surfactant molecules [10,11]. The shrinking observed in dynamic LLS indicates that the approaching of cationic surfactant DPB molecules towards the PNIPAM chain reduces the hydrophilicity of the PNIPAM microgel particles.

ACKNOWLEDGMENT

The financial support of the RGC (the Research Grants Council of the Hong Kong Government) Earmarked Grant 1994/95 (CUHK 454/95P, 221600460) is gratefully acknowledged.

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Received June 23, 1996
Revised September 15, 1996
Accepted September 17, 1996