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SHORT COMMUNICATION

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Preparation of the individual compact single-chain globular particulates of Poly (*N*-isopropylacrylamide)

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Abstract The compact single-chain (SC) particulates of Poly(*N*-isopropylacrylamide) (PNIPAM), which have been formed above its lower critical solution temperature in an aqueous solution containing the surfactant of sodium *n*-dodecyl sulfate (SDS), were recovered from the solution by freeze-drying. Under scanning electron microscopy, the compact particulate appears as a spherical or elliptical particulate individually dispersed in SDS, which acts as a solid solvent to prevent agglomeration. The conformation of the compact SC particulates of PNIPAM dispersed in SDS had been studied by the solid-state high-resolution ^{13}C NMR spectroscopy. The ^{13}C spin-lattice relaxation time T_1 of the SC sample was determined in comparison with that of the original one. It was found that the T_1 of the methyl carbon in the isopropyl group of the SC sample was about 45% higher than that in the original multi-chain sample, which revealed the differences in the motion of the methyl group in the different condensed states and illuminated the characteristic conformation of the compact SC globular particulates of PNIPAM.

Keywords Compact single-chain globular particulates · Poly (*N*-isopropylacrylamide) · Solid-state NMR · Spin-lattice relaxation time

Introduction

The study of the physical properties of macromolecular single-chain (SC) particulates in condensed state is an interesting research topic [1]. Compared with the conventional multichain samples, the interchain penetration is mostly avoided in SC samples, and only intrachain entanglement is possible. Therefore, the SC samples have to display some different behaviors. In the 1990s, Bu et al. [2–4] first observed the formation of SC single crystals of polyoxyethylene and isotactic polystyrene under transmission electron microscopy (TEM), and later Qian [5] and Wang [6, 7] reported some basic properties of the SC state of atactic polystyrene. Recently, Mi et al. [8] prepared a series of SC particulates of water-soluble polymers by spray-drying. However, in the obtained SC agglomerated sample, the surface of each SC particulate will be in contact with surrounding neighbors and will still undergo the van der Waals interaction. The preparation of a polymer SC sample in which every macromolecule is in an isolated state still remains a difficult task to be solved. One possible way is to disperse the polymer homogenously in some solid medium to avoid agglomeration. The present work attempts to use this principle to prepare SC particulates of

Poly(*N*-isopropylacrylamide) (PNIPAM) in sodium *n*-dodecyl sulfate (SDS).

PNIPAM [9–14] is a well-known thermo-sensitive polymer. Its aqueous solution has a lower critical solution temperature at around 32°C. Increasing the solution temperature from ambient up to 32°C, the PNIPAM molecules in random coil form will transit into compact globules within a few degrees. However, at the same time, aggregation of the globules will occur and lead to the phase separation of the solution. Recently, Wu et al. [15, 16] realized the really thermodynamically stable SC compact globule and studied the reversible process of globule-to-coil transition of PNIPAM by static and dynamic laser light scattering using a sample with an extremely high molar mass in an extremely dilute aqueous solution of 10^{-4} g/L to avoid aggregation. The use of extremely high molar mass sample is to ensure the necessary precision of light scattering detection in extremely dilute concentration regime. These experimental conditions seem rather rigorous for preparing solid SC compact globular particulates with sufficient amount.

Another experimental fact about the addition of a surfactant, sodium *n*-dodecyl sulfate, into PNIPAM aqueous solution is very attractive [17, 18]. The critical solution temperature of the PNIPAM solution increases with the SDS concentration (C_{SDS}) increase. When the C_{SDS} is higher than a threshold concentration as the critical aggregation concentration (CAC) at around 0.23 g/L, PNIPAM does not precipitate even above the critical solution temperature. In addition, the CAC is far lower than the critical micelle concentration value of SDS (about 2.3 g/L). Walter et al. [17] summarized the C_{SDS} dependence of the critical solution temperature of PNIPAM in water. Walter et al. [17] also investigated the conformation of the PNIPAM–SDS complex in water by the time-resolved florescence depolarization technique using different fluorescence probes and believed that the surfactant would form a surface layer around the polymer globule to prevent phase separation as the coil-to-globule transition took place. By this means, we have prepared and studied the SC PNIPAM coil-to-globule and globule-to-coil transition using a conventional sample at moderate concentration after removal of SDS by electrodialysis at higher temperature [19]. If the concentration of the surfactant is sufficiently high, the globular polymer chains formed at higher temperature will undergo intrachain dehydration and will form compact SC particulates as observed directly by TEM [20]. In this paper, a homogenous solid mixture of SC compact globular particulates of PNIPAM dispersed in SDS has been prepared and studied by solid-state nuclear magnetic resonance (NMR) technique to get information about the conformation and interactions between the components of the solid mixture.

Experimental

Materials The detailed preparation process of the PNIPAM sample has been mentioned in our previous work [20]. Its viscosity average molecular weight was 4.4×10^5 g/mol, calculated from intrinsic viscosity [21], and the ratio of weight average to number average molecular weight was about 1.85, as determined by size exclusion chromatog-

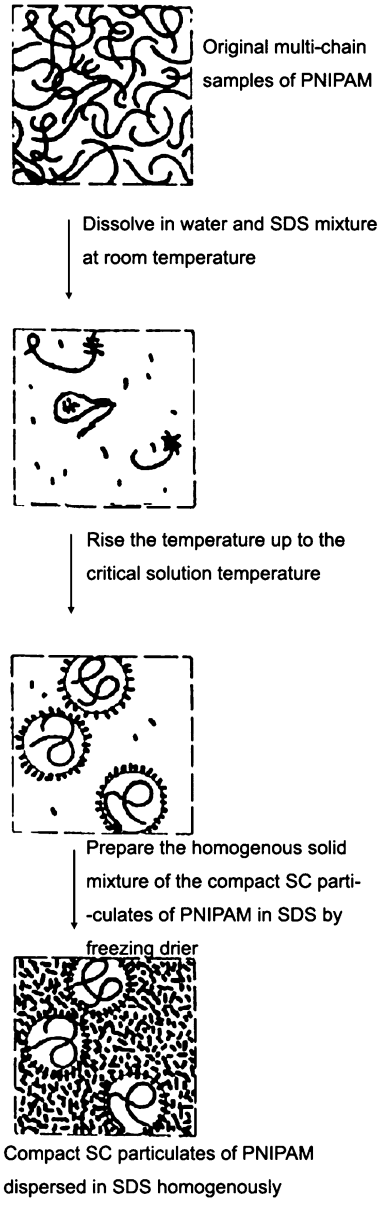

Fig. 1 Schematic of the preparation of the homogenous solid mixture of the compact SC particulates of PNIPAM dispersed in SDS

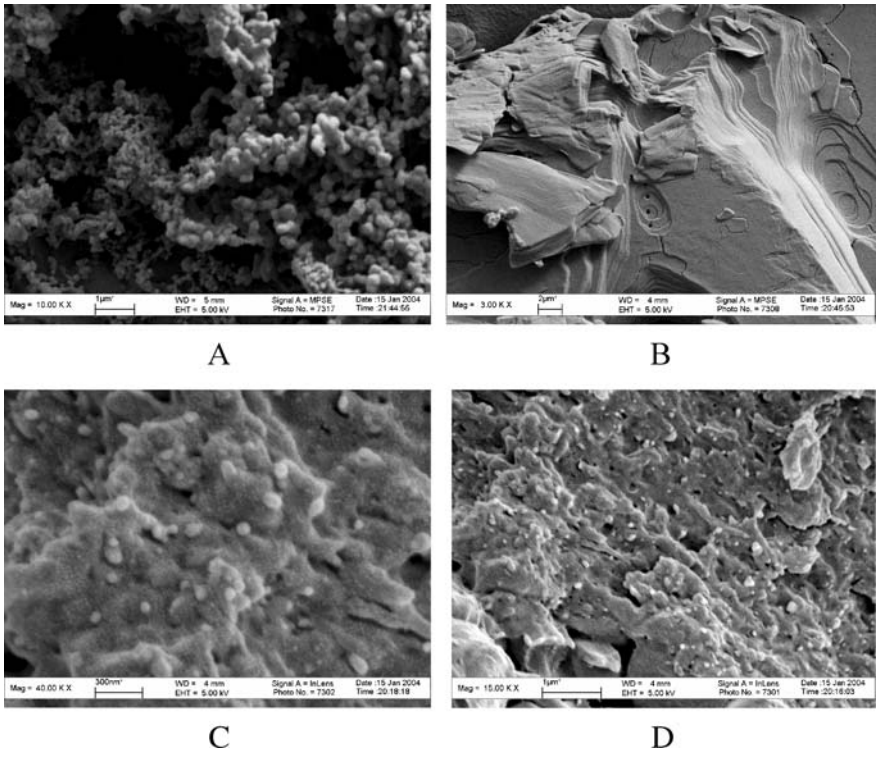

Fig. 2 The SEM images of the different PNIPAM samples and SDS. **a** original multichain sample of PNIPAM; **b** pure SDS sample; **c** and **d** the SC particulates of PNIPAM in SDS solid mixture

raphy. SDS was recrystallized three times from methanol solution before use.

Sample preparation All of the solutions were prepared by weighing and were kept in a vessel for at least 24 h at room temperature. Before taking any measurement, the solution was filtered using a Millipore filter with 0.45-μm pore diameter to remove dust. The deionized water was used in all experiments. The homogenous solid mixture of compact SC globular particulates of PNIPAM and SDS was prepared as described below. The mixing aqueous solution of PNIPAM and SDS was prepared as usual, and the concentrations of PNIPAM and SDS are 0.19 and 0.25 g/L, respectively. The temperature was kept at 40°C for 12 h, which is higher than its critical solution temperature. Then, the mixing solution was dripped drop by drop into the liquid nitrogen so as to be frozen instantaneously, and the solvent was subsequently removed by freeze-drying with LYPH·LOCK6 mode. Finally, the white fluffy solid samples were collected.

Scanning electron microscopy measurements The model of the scanning electron microscopy (SEM) is LEO 1530.

Nuclear magnetic resonance measurements The solid-state ^{13}C NMR spectra were obtained on a Bruker DSX-300 spectrometer with an ^{1}H resonance frequency of 300.13 MHz and a ^{13}C resonance frequency of 75.47 MHz. In the solid-state ^{13}C NMR experiments, the ^{13}C 90° pulse width is 4.5 μs; the spin rate of the 4-mm rotor is 5 kHz, and the number of scans is 1,024–2,048. Signal deconvolution was carried out by a Bruker-made software named "Winfit". All the NMR measurements are under room temperature.

Results and discussion

The homogenous solid mixture of the compact SC globular particulates of PNIPAM dispersed in SDS was recovered from the surfactant–polymer–water ternary system. The detailed procedure for preparing the special solid mixture was mentioned in the "Experimental" section, which was

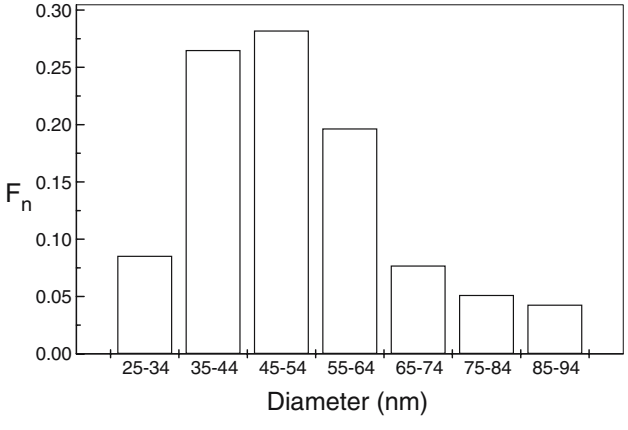

Fig. 3 The size distribution of the compact SC particulates of PNIPAM according to Fig. 2d

also represented schematically in Fig. 1. Based on the knowledge regarding the C_{SDS} dependence of the critical solution temperature of PNIPAM in water [17], the critical solution temperature of this mixing solution is near 32°C as the C_{SDS} is about 0.25 g/L. To ensure that the macromolecules in coil form have fully transited into the compact globules, the temperature of this mixing solution was increased to 40°C. After the compact globules of PNIPAM have been formed, the mixing solution has been frozen instantaneously by dropping the solution into liquid nitrogen drop by drop, and the solvent of water was removed efficiently by freeze-drying. The solid mixture thus obtained is not a simple blend of polymer with surfactant, but the compact globule covered with a layer of SDS on its surface is retained in its original conformation in the solution. Hence, the SC particulates enwrapped by SDS looks just like a solvated solute in solution, which could be dispersed homogenously in excess surfactant. Direct observation of the solid mixture was carried out by SEM as shown in Fig. 2. Figure 2c and d are the SEM images of the compact SC globular particulates of PNIPAM dispersed in SDS with different magnifications. It could be seen that there is a quantity of spherical or elliptical particulates with diameter ranging from 25 to 100 nm in the substrate. The size distribution of the compact SC PNIPAM particulates was measured and shown in Fig. 3. Compared with the SEM images of the original multichain PNIPAM and of the pure SDS shown in Fig. 2a and b, respectively, it is evident that the PNIPAM particulates have been dispersed individually and homogenously.

Various PNIPAM samples and SDS were studied by solid-state ^{13}C NMR to investigate the conformation of the SC particulates. Figure 4a and b show the solid-state ^{13}C CP/MAS/DD spectra of the original multichain PNIPAM sample and pure SDS, respectively. The original PNIPAM sample was collected directly from the precipitation in *n*-hexane during the synthesis process. The assignment of the peaks in the ^{13}C NMR spectra was made according to the previous work [22]. The signal of the methyl carbon in the isopropyl group was at ~22 ppm, and that of the methylene carbon in the isopropyl group and the methylene carbon in the main chain superposed together at ~41 ppm as shown

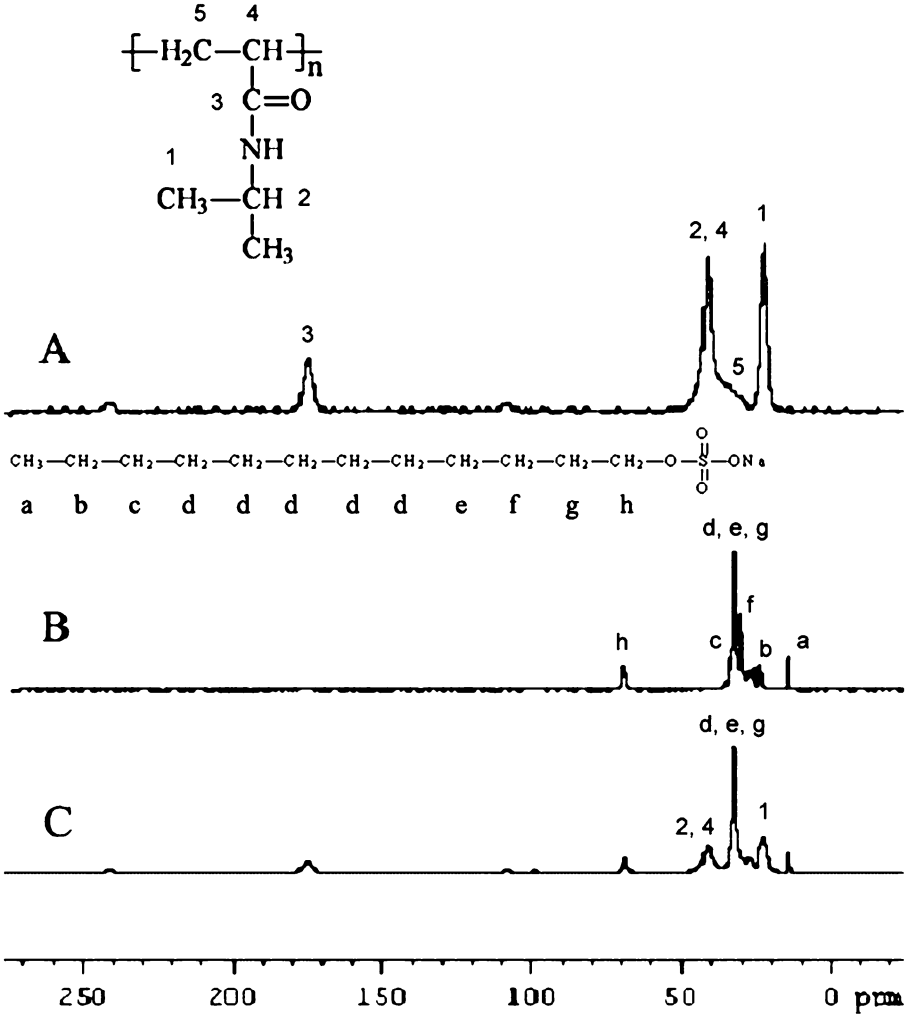

Fig. 4 ^{13}C CP/MAS/DD spectra of the different PNIPAM samples and SDS. **a** original multichain sample of PNIPAM. **b** pure SDS sample. **c** the SC particulates of PNIPAM in SDS solid mixture

in Fig. 4a. The peak of SDS at ~29 ppm in Fig. 4b, which corresponds to the methylene carbons of SDS, is the characteristic signal of SDS. The solid mixture of the compact SC globular particulates of PNIPAM in SDS was also measured by the ^{13}C CP/MAS/DD experiment, the spectrum of which are shown in Fig. 4c. It was found, obviously, that the intensity of the characteristic peak of SDS at 29 ppm is much higher than that of the polymer signal.

The spin-lattice relaxation time T_1 of the various PNIPAM samples was also determined. The obtained results are listed in Table 1. It was found that the T_1 of the methyl carbon in the isopropyl group both in the SC sample and in the original one were far lower than that of the methylene carbon in the main chain, which is ascribed to the different mobility between the main chain and the side group in the condensed state. However, it is interesting that the T_1 of the methylene carbon in the main chain of the SC sample has little difference with that of original sample, whereas the T_1 of the methyl carbon in the isopropyl group of the SC sample was about 45% higher than that of the original sample. Because T_1 is closely related to the molecular motion at the megahertz region, the differences in the T_1 values of these two samples suggest that the mobility of the methyl group in SC sample is much different from that of the methyl group in the original sample, which is ascribed to the characteristic conformation of the different PNIPAM samples in the different condensed states. It has been mentioned above that during the preparation process of the SC particulates of PNIPAM from the surfactant–polymer–water ternary system, the hydrophilic interaction would change to hydrophobic interaction as the polymer coil has transited into the globule in the solution above its critical solution temperature. The hydrophobic isopropyl group would extend outside of the globule [23–25] efficiently, and SDS coated on the polymer globule surface as a protection layer to avoid phase separation [17]. Hence, the isopropyl group is very near the SDS molecules and available to form the van der Waals interaction with the alkane chain of SDS, and thus leads the isopropyl group and SDS possessing coupled. The conformation of the formed PNIPAM–SDS complex in the solution has been retained in the condensed state after removal of the water. The interaction between the PNIPAM and SDS would influence the mobility of the isopropyl group and lead to the increase of its T_1 value, whereas the isopropyl group of the original sample is distributed randomly.

Table 1 ^{13}C solid-state NMR spin-lattice relaxation time T_1 of the different PNIPAM samples

	Original sample (s)	SC particulates dispersed in SDS solid mixture (s)
Methyl carbon in isopropyl group (–CH_3)	0.514	0.734
Methylene carbon in main chain (–CH)	41.1	44.5

Conclusion

In this paper, an efficient method has been provided to prepare full-isolated SC particulates in a special solid mixture to avoid agglomeration, which affords facilities for investigation of the conformation of the SC sample in condensed state. Based on this knowledge, the conformation of the compact SC globular particulates of PNIPAM dispersed in the surfactant of SDS had been learned by the solid-state ^{13}C NMR technology. The NMR results illustrated the dominant conformation of the hydrophobic isopropyl group on the surface of the compact SC globule in condensed state.

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