

## Materials and Methods.

**1.1. Materials** Acrylamide (AM,J&K,99%), acrylonitrile(AN,J&K,99%), ammonium persulfate (APS,Sigma,99%), acetic anhydride (Adamas,98%), 1-tetradecene (Adamas,98%),pyrene (J&K,99%),  $\beta$ -cyclodextrin( $\beta$ -CD,Sigma,99%),benzophenone (J&K,99%), adamantanecarboxylic acid (ADA) and carboxyferrocene (Fc, Alfa Aesar,99%) were used as received . Water used in this study was deionized and then distilled. All the solvent were used as received.

**1.2. NMR Spectroscopy study.**  $^1\text{H}$  NMR measurements and 2D  $^1\text{H}$  NOESY NMR spectra were performed on AVANCE III HD-400 (400 MHz) spectrometer.

**1.3. FTIR Spectroscopy study.** The synthesized hydrophobically modified polymer was characterized by FT-IR spectroscopy. FT-IR spectra were recorded on a Nicolet 6700 spectrometer frequencies ranging from 400–4000  $\text{cm}^{-1}$ .

**1.4. Rheological measurements.** Rheological measurements were conducted to determine the sol-gel transition point on a HAAKE Paar Rotary Rheometer (HAAKE MARS III) rheometer using a cone-plate of 40 mm diameter with cone angle of  $1^\circ$ . Dynamic frequency spectra were obtained in the linear viscoelastic region of the samples, as determined by dynamic strain sweep experiments. A shear strain amplitude of 3% and an angular frequency of  $1 \text{ rad}\cdot\text{s}^{-1}$  were applied. To investigate the thermo-response property, samples were placed between the para-plate and the platform with special care to avoid evaporation of water.

**1.5. Fluorescence study.** Steady-state fluorescence spectra of pyrene were recorded on a SHIMADZU RF-5301PC luminescence spectrometer, equipped with a

circulating water bath. A stock ethanolic solution, containing  $1 \times 10^{-3} \text{M}$  pyrene, was used. The final concentration of the probe was  $6 \times 10^{-7} \text{M}$  and the excitation wavelength was 339nm. The intensity ratio ( $I_1/I_3$ ) of the first ( $I_1$ ) over the third ( $I_3$ ) vibronic band of the emission spectrum of pyrene, at 373 and 384 nm, respectively, was used to detect the formation of hydrophobic microdomains.

The micelle aggregation numbers of micelles,  $N_{agg}$ , for NaAMC14S was determined by the steady-state fluorescence quenching technique (SSFQ)<sup>[1]</sup>. This method is based on quenching of pyrene fluorescence by a hydrophobic quencher. Benzophenone was used as the quencher. Excitation of the probe was at 335 nm and the emission was monitored at 374 nm. By changing the quencher concentration,  $C_q$  (0–0.45 mmol/L<sup>-1</sup>), a linear relationship between  $\ln I_0/I$  and  $C_q$  was obtained, the corresponding equation is as follows:

$$\ln \frac{I_0}{I} = \frac{N_{agg}}{C - C_{cmc}} \times C_q \quad (1)$$

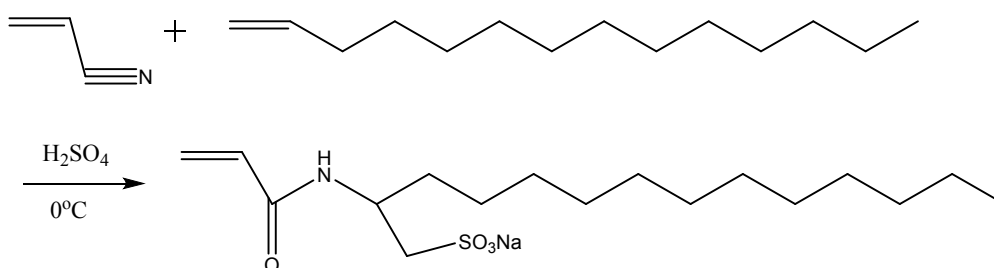
where  $I_0$  is the fluorescence intensity of the probe in the micellar solutions as in the absence of the quencher, and  $I$  is the fluorescence intensity of the probe in the presence of the quencher.  $C_{CMC}$  and  $C$  are the critical micellar concentration and the total concentration of the surfactant, respectively. According to the Eq. (1), the straight lines of logarithm of the intensity ratio versus the quencher concentration  $C_q$  were plotted, and the aggregation numbers ( $N_{agg}$ ) of NaAMC<sub>14</sub>S at a given concentration were obtained.

**1.6. Sample preparation.** Amounts of polymer was dissolved in DI water by

heating for 2-3h at 65 °C and then stirred at room temperature for 12h.  $\beta$ -CD was then mixed with polymer solution, and further stirred for 24h at 20°C. All the samples were sealed without stirring to reach equilibrium at room temperature for at least 48 h prior to test. The glass tubes (volume 10 mL) containing the samples were immersed in an thermostatic bath with temperature increase at rate of 1°C in order to check whether the sample flowed or not.

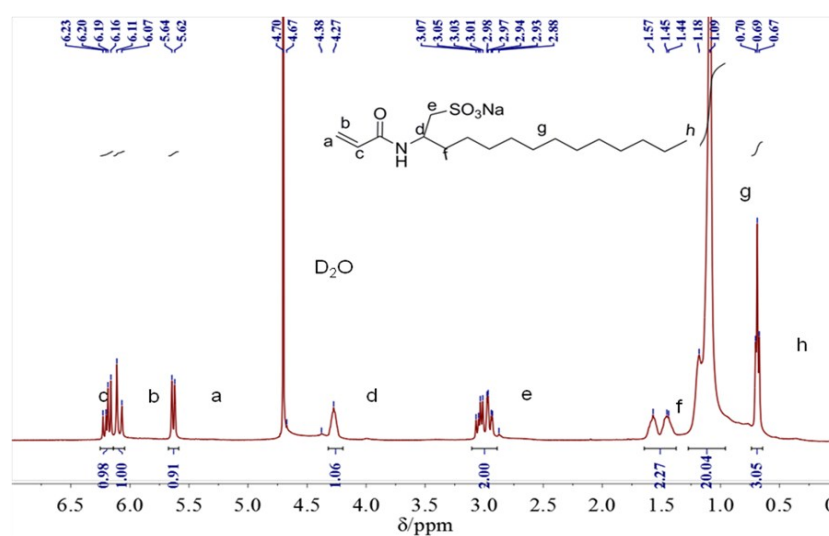
## 2. Synthesis, Characterization and Preparation.

### 2.1 Synthesis and characterization of sodium 2-acrylamido-tetradecane sulfonate (NaAMC<sub>14</sub>S)



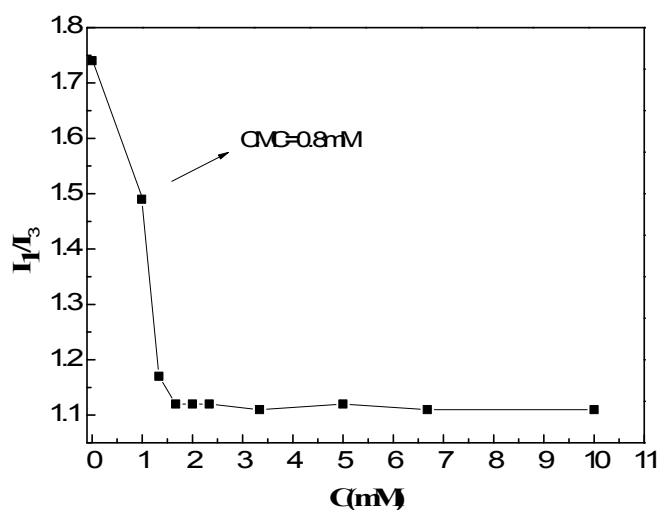
Sodium 2-acrylamido-tetradecane sulfonate (NaAMC<sub>14</sub>S) was synthesized by using tetradecene, acrylonitrile, acetic anhydride and oleum as raw materials. Tetradecene (25mL), acrylonitrile (8mL), acetic anhydride (25mL) and dichloroethane (20mL) were added to a three-neck bottle equipped with a agitator, a dropping funnel and a thermometer, and the content was cooled below 0°C. Oleum (9mL) in the dropping funnel was added dropwise with stirring, and the temperature was kept below 0°C during dropping. After finishing the addition of oleum, the temperature of the content was left to stir at room temperature for another 12 h. The product was then cooled to 4°C and filtrated to obtain white powder. The crude product was then washed with acetone and further dissolved in distilled water, and then neutralized with NaOH

solution. The mixture was kept static below 4°C for 12 h until the white crystal, NaAMC<sub>14</sub>S, was produced. In order to pure NaAMC<sub>14</sub>S, the white crystal was recrystallized twice from the mixed solvent of saturated Na<sub>2</sub>CO<sub>3</sub> water and acetone. The <sup>1</sup>H NMR spectrum of sodium 2-acrylamido-tetradecane sulfonate (NaAMC<sub>14</sub>S) in D<sub>2</sub>O (Figure S1) demonstrated the successful synthesis.

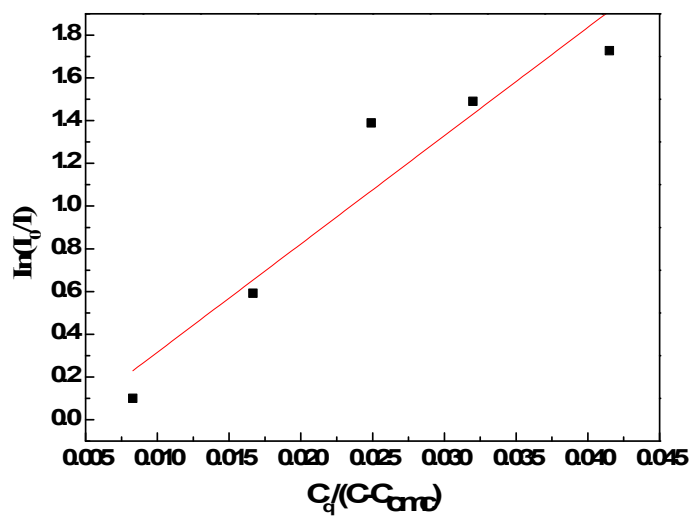


**Figure S1** <sup>1</sup>H NMR spectrum of NaAMC<sub>14</sub>S in D<sub>2</sub>O

The critical micellar concentration(CMC) has been determined as 0.8mM at 50°C using steady-state fluorescence probe(Figure S2), and the micelle aggregation numbers of micelles, N<sub>agg</sub>, for NaAMC<sub>14</sub>S of 16CMC was determined as 50 at 50°C by the steady-state fluorescence quenching technique(Figure S3) .



**Figure S2** Varying of the  $I_1/I_3$  ratio of pyrene in NaAMC<sub>14</sub>S solutions in pure water with NaAMC<sub>14</sub>S concentration. Temperature=50 °C

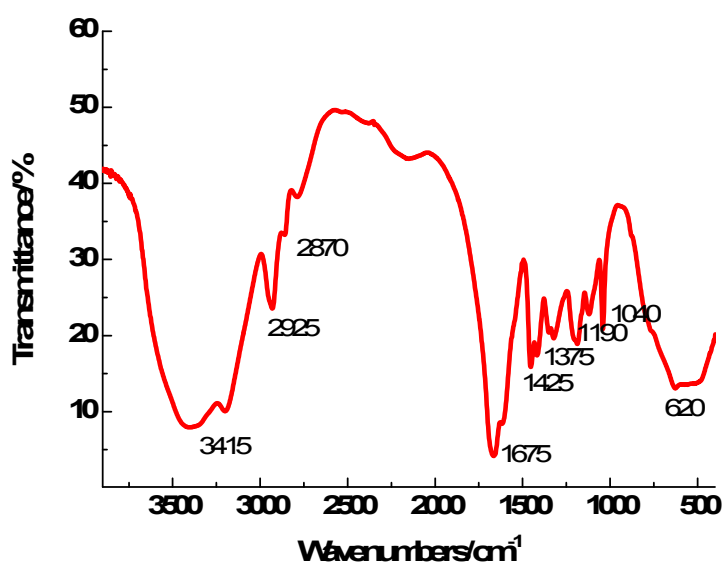


**Figure S3** Plot of  $\ln(I_0/I)$  vs.  $C_q/(C - C_{CMC})$ . Concentration of NaAMC<sub>14</sub>S: 16CMC.

## 2.2. Synthesis and characterization of hydrophobically modified polyacrylamide (PC<sub>14</sub>AM) of blocky structure

PC<sub>14</sub>AM of blocky structure was synthesized by the free-radical micellar copolymerization of AM and NaAMC<sub>14</sub>S in an aqueous medium. To illustrate the

synthetic procedure, we give details for the preparation of PC<sub>14</sub>AM by micellar copolymerization: NaAMC<sub>14</sub>S (0.48g, 1 mol%) was dissolved in 98.0 mL deionized water at 60 °C to obtain a transparent solution. After adding and dissolving acrylamide (9.5g,99 mol%), nitrogen was bubbled through for another 1 hour. Finally, 2mL of an APS stock solution (6.5 mM) was added to initiate the reaction. The reaction was carried out at 50 °C for 12 h. After polymerization, the product was dialyzed against pure water for 1 week. Finally, the polymer was recovered by freeze drying and white powder was obtained. The chemical structure of the PC<sub>14</sub>AM was characterized by FTIR as showed in Figure S4.



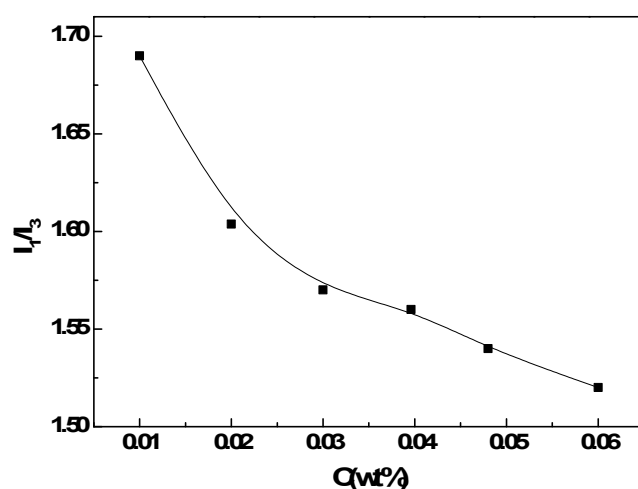
**Figure S4** FTIR spectrum of PC<sub>14</sub>AM of blocky structure

The molecular weight of polymer sample was determined in formamide solution by classical light scattering using a multiangle spectrometer (AMTEC Model MM1). Biggs et al.<sup>[2]</sup> showed that the presence of a small amount of a hydrophobic comonomer (5 mol %) does not significantly affect the refractive index increment,

$d_n/d_c$ , of polyacrylamide in formamide solution ( $d_n/d_c$ ) is 0.111. The molecular weight of polymer sample (Mw) has been determined as  $5 \times 10^5$ .

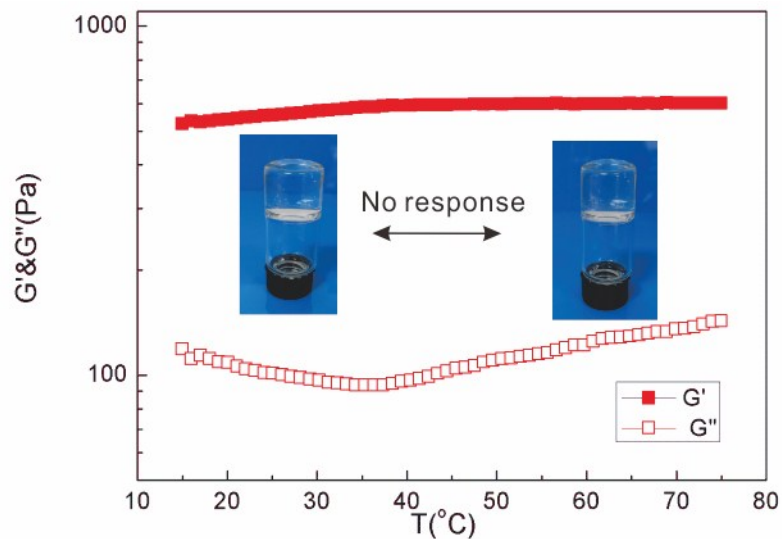
In general, the hydrophobe content in hydrophobically associating polyacrylamides is very limited to maintain the solubility in water. Consequently, it is often impossible to determine the degree of hydrophobe incorporation, especially for comonomers consisting of long alkyl chains. Thus most studies have regarded the hydrophobe content as same to the initial feed composition<sup>[3-5]</sup>. In this study, the hydrophobe content has been seen as 1 mol%.

The critical aggregate concentration (CAC) of the PC14AM was measured by steady-state fluorescence probe method, and the CAC has been determined as 0.02wt%.



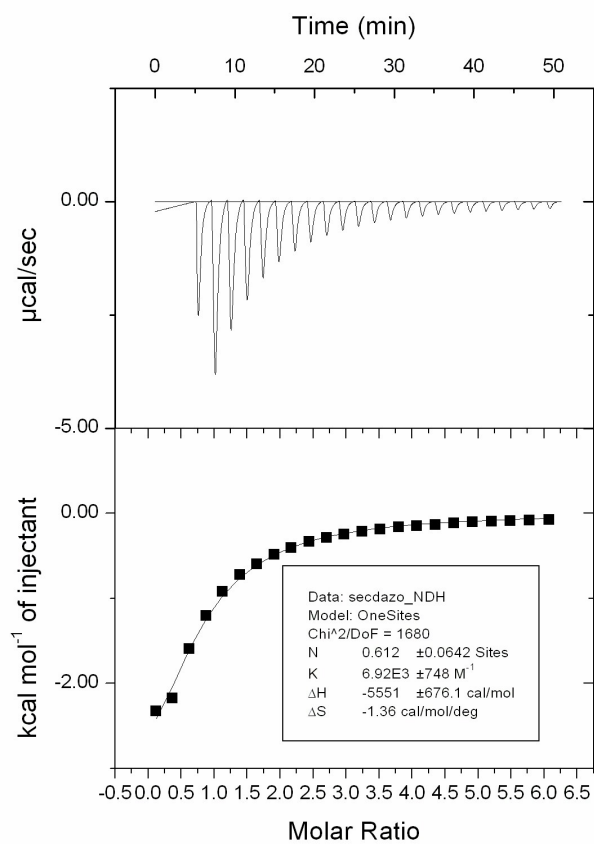
**Figure S5** Varying of the  $I_1/I_3$  ratio of pyrene in polymer solutions in pure water with polymer concentration. Temperature=20 °C

### 2.3 The rheological study of temperature behavior of 3wt% PC<sub>14</sub>AM of blocky structure in the absence of $\beta$ -CD



**Figure S6** Storage modulus  $G'$  (filled symbols) and loss modulus  $G''$  (open symbols) as a function of temperature for 3 wt% PC14AM.

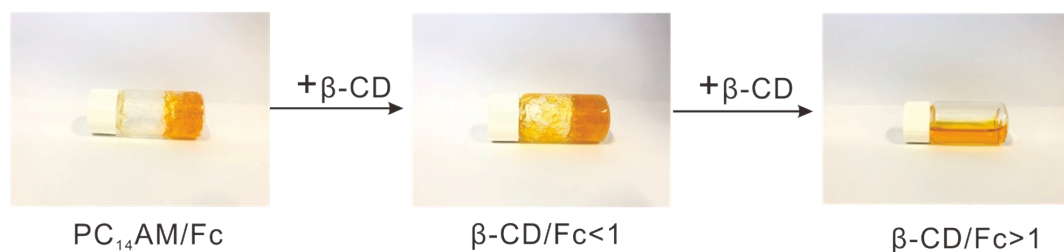
#### 2.4. The isothermal titration calorimetry (ITC) result of $\beta$ -CD /Fc





**Figure S7.** The isothermal titration calorimetry result of  $\beta$ -CD /Fc determined at 20°C.

### 2.5 The competitive effect between $\beta$ -CD, PC<sub>14</sub>AM and Fc



**Figure S8.** The competitive effect between  $\beta$ -CD/PC<sub>14</sub>AM and  $\beta$ -CD/Fc.

### Reference

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