# Influence of Sodium Dodecyl Sulfate on the Phase Transition of Thermoresponsive Hyperbranched Polymer in Water[*]

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**Abstract**   The influence of sodium dodecyl sulfate (SDS) on the cloud point temperature ($T_{cp}$) of the aqueous solution of thermoresponsive hyperbranched polyethylenimine derivative HPEI-IBAm was studied systematically. When pH was below 8.5, HPEI-IBAm was positively-charged. Initially, the $T_{cp}$ of HPEI-IBAm decreased significantly, followed by an obvious increase with the increase of SDS concentration. The lower the pH was, the higher the SDS concentration was required to achieve the minimum $T_{cp}$. When pH was above 8.5, HPEI-IBAm was neutral and raising the SDS concentration led to the gradual increase of $T_{cp}$. Compared to linear poly($N$-isopropyl acrylamide) (PNIPAm), the $T_{cp}$ of the current hyperbranched HPEI-IBAm was more sensitive to SDS. The thermoresponsive HPEI-IBAm/SDS complex was used as host to accommodate the non-polar pyrene in water. The lowest SDS concentration for effectively enhancing the solubility of pyrene in water was around 6.4 mmol·L$^{-1}$. When HPEI-IBAm was present, the SDS concentration threshhold was decreased to about 0.31 mmol·L$^{-1}$. Fluorescence technique with pyrene as the hydrophobic probe demonstrated that the SDS concentration of 7.2 mmol·L$^{-1}$ was required to form the hydrophobic domain to accommodate pyrene guests without HPEI-IBAm, while only 0.2 mmol·L$^{-1}$ of SDS was required in the presence of HPEI-IBAm.

**Keywords:** Hyperbranched; Polyethylenimine; Surfactant; Thermoresponsive.

**INTRODUCTION**

During the past decade polymers with stimuli-responsive properties, such as reversible and fast conformational or phase changes in response to variations in temperature, light or pH have attracted plenty of interest in many aspects[1–3]. One of the most appealing stimuli-responsive species is the thermoresponsive polymers with a lower critical solution temperature (LCST) in aqueous solutions, which show a large decrease in solubility in water above a specific temperature[4]. To date, the most studied thermoresponsive materials have been those with linear structure displaying LCST properties[4–6]. In other words, even though the thermoresponsive materials have some specific topology, such as cyclic[7], hydrogels[8], star or grafted polymeric structures[9–12] and polymeric micelles[13], their LCST properties are originated from their thermoresponsive linear polymer components.

Since 2004, thermoresponsive dendritic polymers as new member of the family of thermoresponsive polymers have occurred[14–26]. Compared to the traditional thermoresponsive linear polymers that usually adopt a loose coil conformation in solution, the dendritic polymer has a compact sphere-like structure. As a consequence of such a structure, the thermoresponsive dendritic polymer usually only has a minor conformation adjustment during the transition (*i.e.*, the globule-to-globule transition), different from the coil-to-globule transition

occurring during the transition of the traditional thermoresponsive linear polymer[27, 28]. Meanwhile, the thermoresponsive dendritic polymers exhibit obvious difference in properties compared to the traditional thermoresponsive linear polymers[29–33]. For instance, the phase transition temperature of thermoresponsive hyperbranched polymers is more sensitive to the addition of salts (including anions and cations) than that of the thermoresponsive linear ones[32–34].

Up to the present date, the effect of different additives, such as inorganic salts[35–43], surfactants[42–49] and organic compounds[50–54], on the LCST of thermoresponsive linear polymers has been well studied. As for the thermoresponsive dendritic polymers, the study of the additives' influence on their phase transition temperature is scarce[31–33, 55]. Our group has systematically studied the effect of anionic and cationic ions on the thermoresponsive hyperbranched polymers with a large amount of amide and amine groups[32, 33], where the phase transition temperature of the compact hyperbranched polymers exhibited higher sensitivity to ions than that of the traditional thermoresponsive linear polymers. Moreover, these thermoresponsive hyperbranched polymer systems were better than those thermoresponsive linear polymer systems[56] to mimic the interactions among ions and positively charged proteins[57–59].

The anionic surfactant sodium $n$-dodecyl sulfate (SDS) as additive has received particular attention in the system of thermoresponsive linear polymers because it can raise the LCST of thermoresponsive linear polymers through their peculiar interactions[48, 49]. To our best knowledge, how SDS influences the phase transition temperature of thermoresponsive hyperbranched polymers has never been reported. In this contribution, we systematically studied the effect of SDS on the thermoresponsive property of hyperbranched polymers containing a large amount of amide and amine groups. Furthermore, the potential of the obtained complexes as nanocarriers to accommodate the hydrophobic guest was explored.

## EXPERIMENTAL

### Materials

Hyperbranched polyethylenimine (HPEI, Aldrich) samples with a number-average molecular weight ($M_n$) of $1.0 \times 10^4$ g·mol$^{-1}$ and a polydispersity ($M_w/M_n$) of 2.5, was dried under vacuum prior to use. Triethyl amine (A.R., TEA) was dried over CaH$_2$ and distilled before use. Isobutyric anhydride (98%) and pyrene (98%) were purchased from Alfa Aesar and used without further purification. Sodium dodecyl sulfate (SDS, $M_w$ = 288.38 g·mol$^{-1}$) and azobis(isobutyronitrile) (AIBN) were purchased from Tianjin University Jiangtian Chemical Company. Deionized water was double-distilled before use. Benzoylated cellulose tubing (MWCO 1000) was purchased from Sigma and used as received. Triethyl amine (A.R., TEA) was dried over CaH$_2$ and distilled before use. Linear poly($N$-isopropyl acrylamide) (PNIPAm, $M_n$ = $8.2 \times 10^3$ g·mol$^{-1}$, $M_w/M_n$ = 1.8) was synthesized through the radical polymerization with AIBN as the initiator and methanol as the solvent.

### General Procedure for the Synthesis of HPEI Terminated with Large Amount of Isobutyramide Groups (HPEI-IBAm)

Under nitrogen atmosphere, isobutyric anhydride (27.45 g, 0.1735 mol) was added dropwise to the mixture of HPEI (12.77 g, 0.2169 mol of terminal groups) and triethyl amine (19.31 g, 0.1910 mol) in 50 mL of chloroform at room temperature with vigorous stirring. Subsequently, the reaction mixture was kept at room temperature for 24 h. Finally, the reaction temperature was raised to 72 °C for 2 h to finalize the reaction. The chloroform was removed under vacuum and the residue was dissolved in 50 mL of methanol. Five grams of potassium carbonate was added to the solution and the mixture was stirred at room temperature for 4 h. After centrifugation, the solution was concentrated to ~10 mL and then purified by dialysis against methanol using a benzoylated cellulose membrane (MWCO 1000 g·mol$^{-1}$) for 2 days. Finally, the methanol solvent was removed under vacuum, and the product was dried in vacuum for 24 h. $^1$H-NMR (CDCl$_3$): $\delta$ = 1.08 ((CH$_3$)$_2$CHCON—); 2.20−3.90 ((CH$_3$)$_2$CHCON—, ethylene protons of HPEI polymeric backbone). The degree of substitution of IBAm groups in the primary and secondary amines of HPEI is 80%. The average $M_n$ value of this HPEI-IBAm polymer is $1.93 \times 10^4$, $M_w/M_n$ = 2.6.

### Characterization

^{1}H-NMR spectra were recorded on a Varian INOVA 500MHz spectrometer. UV-Vis spectra were obtained from a Purkinje General (China) T6 UV/Vis Spectrophotometer. Gel permeation chromatography (GPC) of the samples was carried out using a Viscotek GPC270 system. Freshly-distilled DMF was filtered through membrane with an average pore size of 0.22 μm and used as an eluent at 55 °C. The flow rate was set to be 0.6 mL·min$^{-1}$. The solutions of the samples in DMF (5–6 mg·mL$^{-1}$) were kept at room temperature for 24 h, and then were filtered through membrane filters with an average pore size of 0.22 μm. Fluorescence-emission spectra were recorded by using a Cary Eclipse EL06063917 luminescence spectrometer at a detection wavelength of 390 nm with a scan rate of 600 nm·min$^{-1}$.

### Turbidity Measurement

HCl (4 mol·L$^{-1}$) or NaOH (2 mol·L$^{-1}$) was used to adjust the pH of the aqueous solution of polymer with hydrophilic dyes. Light transmittance of the solution was measured on a temperature-controlled Purkinje General (China) T6 UV/Vis spectrophotometer using a 660 nm light source, and the heating rate was 0.2 K/2min. The cloud-point temperature ($T_{cp}$) was taken from the intersection of the maximal slope tangent and the initial horizontal tangent in the heating curve. The temperature error is ± 0.1 K.

### Accommodating Non-polar Guest

Ten milligram of pyrene was added to 5 mL of the aqueous solution of the mixture of HPEI-IBAm and SDS. The flask containing this mixture was under ultrasonic for 3 h, and then was placed in refrigerator at 5 °C overnight. The supernatant was filtered by the membrane with an average pore size of 0.22 μm and then measured by a UV-Vis spectrometer. The amount of pyrene in water phase could be calculated according to the Lambert-Beer law, and the mole extinction coefficient of pyrene ($4.56 \times 10^4$ L·mol$^{-1}$ cm at 334 nm) in acetone was used.

## RESULTS AND DISCUSSION

### Influence of SDS on the Phase Transition of Thermoresponsive Polymer

The thermoresponsive HPEI-IBAm used here has a HPEI core of $M_n = 1.0 \times 10^4$ and the degree of substitution of IBAm groups in the primary and secondary amines of HPEI is 80%, which can be calculated from ^{1}H-NMR[26]. This HPEI-IBAm bears secondary amine, tertiary amine and IBAm functional groups (Chart 1) and their average numbers are 36, 63 and 134, respectively.
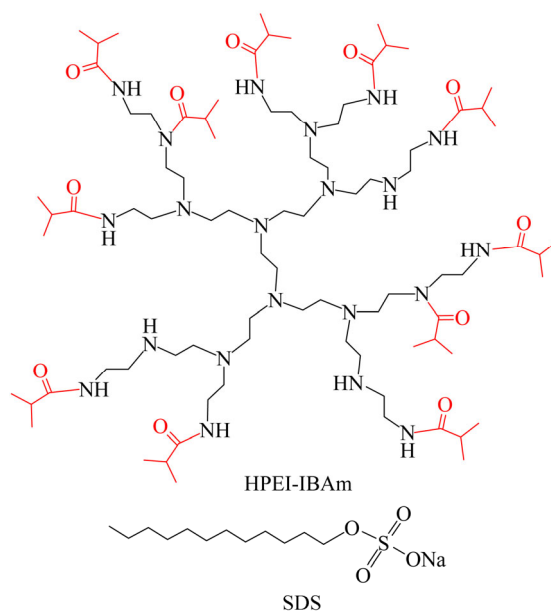


**Chart 1** Chemical structures of HPEI-IBAm and SDS

Figure 1(a) shows the typical temperature-dependent light-transmittance curve of the HPEI-IBAm aqueous solution, and the obvious phase transition can be observed in both heating and cooling processes, indicating that HPEI-IBAm employed here is thermoresponsive. The heating and cooling cycles do not overlap and the obvious hysteresis can be attributed to the strong hydrogen-bonds among HPEI-IBAm moieties[60]. The phase transition temperature named as the cloud point temperature ($T_{cp}$), can be taken from the intersection of the maximal slope tangent and the initial horizontal tangent in the heating curve. The thermoresponsive property of HPEI-IBAm is pH-sensitive (Fig. 1b). The pH of the aqueous solution of HPEI-IBAm (0.83 mmol·L$^{-1}$) is close to 8. The enhanced acidity significantly increases the $T_{cp}$. Conversely, adjusting the pH to about 8.5 obviously lowers the $T_{cp}$. The $T_{cp}$ variation becomes insignificant in the pH range of 8.5–10.5. The pH response of HPEI-IBAm demonstrates that all the amine groups of HPEI-IBAm are in neutral state above pH 8.5, whereas decreasing the pH below 8.5 leads to the transformation of partial amine groups into the ammonium groups. The lower the pH is, the more the ammonium groups are generated. It is well-known that increasing the hydrophobicity of thermoresponsive polymers decreases the phase transition temperature, however, raising the polarity of thermoresponsive polymers increases the phase transition temperature[38]. Since ammonium is more polar than amine, HPEI-IBAm with more ammonium groups has a higher $T_{cp}$.
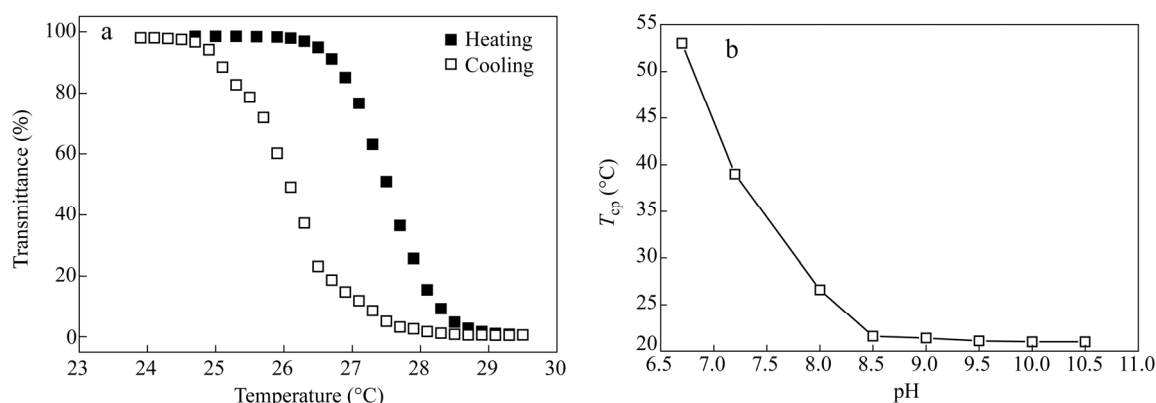


**Fig. 1**  (a) Typical temperature-dependent light transmittance of the HPEI-IBAm aqueous solution at pH 8 and (b) $T_{cp}$ of HPEI-IBAm influenced by different pH ([HPEI-IBAm] = 0.83 mmol·L$^{-1}$ = 16 mg·mL$^{-1}$).

A typical anionic surfactant SDS (Chart 1), whose critical micelle concentration (cmc) is 2.3 mg·mL$^{-1}$ (8.0 mmol·L$^{-1}$)[61], was mixed with the aqueous solution of HPEI-IBAm without pH adjustment (pH is around 8) and the influences of SDS concentration on the $T_{cp}$ of HPEI-IBAm were plotted at Fig. 2(a). Initially, the $T_{cp}$ of HPEI-IBAm decreased remarkbly, followed by an obvious increase with the increase of SDS concentration. It is known that anionic surfactants can always increase the LCST of thermoresponsive linear PNIPAm[44–47], and the mechanism is thought as follows: The direct hydrophobic interaction between the long hydrocarbon chain of surfactants and the hydrophobic moieties of PNIPAm leads to the complex formation of PNIPAm and surfactants.  The anionic group of surfactant has a higher contribution than the aliphatic chain of surfactant to the overall polarity of the polymer and surfactant complex, which renders the complex higher polarity than the thermoresponsive polymer itself, leading to the increase of LCST at higher surfactant concentrations. The different influence of SDS on the $T_{cp}$ of HPEI-IBAm in Fig. 2(a) may be correlated with the abundance of amino groups of HPEI-IBAm. When HPEI-IBAm is dissolved into the neutral deionized water, its amino groups will be partially quaternized due to the weak acid-base interaction. The ion-pairing between ammonium and anionic groups of SDS molecules shall screen the electrostatic repulsion inside and among the polymers, thereby promoting the salting-out behavior. Moreover, the introduction of hydrophobic chains of SDS molecules into HPEI-IBAm also reduces the polarity of the complex of HPEI-IBAm and SDS, leading to the salting-out behavior. Therefore the electrostatic interaction between ammonium of HPEI-IBAm and anionic groups of SDS

molecules results in the depression of $T_{cp}$. It is well-known that electrostatic interaction is much stronger than other noncovalent interactions and the ion-pairing between ammoniums of HPEI-IBAm and anionic groups of SDS molecules can be saturated. On the basis of these two points, it can be deduced that at the beginning a majority of the anionic groups of SDS molecules shall prefer to interact with the positive groups of HPEI-IBAm. After being close to the ion-pairing saturation, the noncovalent hydrophobic interaction between aliphatic chains of SDS molecules and hydrophobic units of HPEI-IBAm becomes dominant, and the accompanied free sulfate groups of SDS molecules increase the polarity of the complexes, resulting in the $T_{cp}$ increase with further increase of SDS concentration.
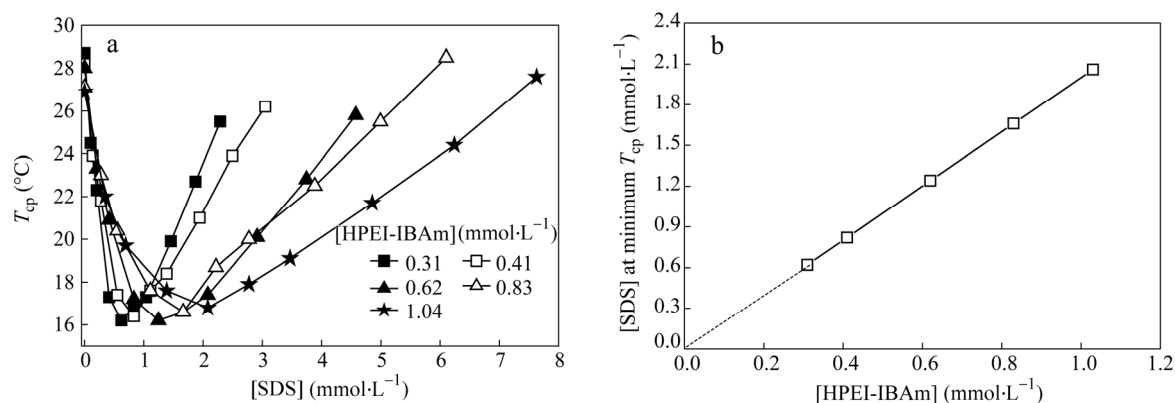


**Fig. 2**  (a) Influence of SDS concentration on the $T_{cp}$ of different concentrations of HPEI-IBAm at pH = 8, and (b) the relationship between the concentration of HPEI-IBAm and the SDS concentration at the minimum $T_{cp}$

From the above discussion, it is known that the required SDS concentration to achieve the minimum $T_{cp}$ represents the maximal number of SDS molecules that interact with one HPEI-IBAm molecule through electrostatic interaction. From Fig. 2(b) it can be seen that the required SDS concentration to achieve the minimum $T_{cp}$ increases linearly with the increase of the HPEI-IBAm concentration. With the assumption that each anionic SDS molecule can efficiently form ion-pair with one ammonium group of HPEI-IBAm, the number of positive charges in each HPEI-IBAm can be deduced from the slope of Fig. 2(b). It is clear that each HPEI-IBAm carries about two positive charges when it is dissolved into deionized water without pH adjustment (pH is around 8).

The influence of SDS on the $T_{cp}$ of HPEI-IBAm at different pH was further studied. From Fig. 3 it can be seen that the $T_{cp}$ variation behavior of HPEI-IBAm infuenced by different concentrations of SDS at pH 7.2 is similar to that at pH 8.0. The difference lies that at pH 7.2 more SDS molecules are required to achieve the minimum $T_{cp}$, which is because HPEI-IBAm at pH 7.2 carries more positive charges than that at pH 8.0. Moreover, the minimum $T_{cp}$ value at pH 7.2 is also lower than that at pH 8.0. At the minimum $T_{cp}$, the positive charges of HPEI-IBAm are neutralized by the polar groups of SDS molecules. Furthermore, the hydrophobic chains of SDS molecules are also introduced into HPEI-IBAm. The neutral complex of HPEI-IBAm/SDS containing more hydrophobic chains should be less polar resulting in a lower $T_{cp}$. Further decrease of pH to 6.5 leads to that the $T_{cp}$ of HPEI-IBAm depresses gradually with the increase of SDS concentration and the minimum $T_{cp}$ can not be detected. When the pH is adjusted to 9.0 or higher, SDS has no ability to reduce the $T_{cp}$ of HPEI-IBAm and the $T_{cp}$ of HPEI-IBAm increases gradually with the increase of SDS concentration just like in the system of PNIPAm/SDS. This is because HPEI-IBAm at pH 9.0 or higher is in the neutral state. The main interaction between SDS and HPEI-IBAm is the hydrophobic interaction between aliphatic chains of SDS molecules and hydrophobic units of HPEI-IBAm. The accompanied free sulfate groups of SDS molecules increase the polarity of the complexes, resulting in the increase of $T_{cp}$. Higher SDS concentration leads to more

polar sulfate groups in the HPEI-IBAm/SDS complex, hence the $T_{cp}$ increases gradually with the increase of SDS concentration.
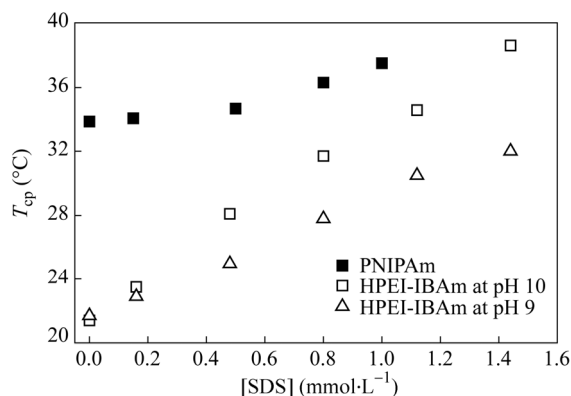


**Fig. 3** Influence of SDS concentration on the $T_{cp}$ of HPEI-IBAm at different pH ([HPEI-IBAm] = 0.83 mmol·L$^{-1}$).

The efficiency of SDS in altering the $T_{cp}$ of the aqueous solution of thermoresponsive hyperbranched HPEI-IBAm was compared with that of the traditional thermoresponsive linear PNIPAm polymer (Fig. 4). In the system of PNIPAm/SDS, the increase of SDS concentration results in gradual increase of the $T_{cp}$ of PNIPAm. From the above results, it is known that SDS shows the same effect on the $T_{cp}$ of HPEI-IBAm only when pH is above 8.5. Thus, the influences of SDS on the $T_{cp}$ of HPEI-IBAm at pH 9 and 10 are compared with the PNIPAm/SDS system. From Fig. 4 it is obvious that the $T_{cp}$ of the hyperbranched HPEI-IBAm is more sensitive to the added SDS than that of linear PNIPAm. The similar phenomenon has been also found in the previous study on the influence of inorganic salts on the $T_{cp}$ of the thermoresponsive hyperbranched and linear polymers, where the compact morphology of the thermoresponsive hyperbranched polymer is thought to be more crucial for the higher sensitivity toward the added salts than the loose-coil morphology of the normal thermoresponsive linear polymer[32].
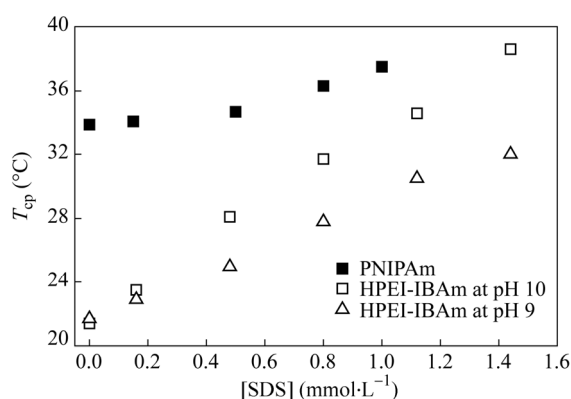


**Fig. 4** Comparison of the influence of SDS concentration on the $T_{cp}$ of thermoresponsive linear PNIPAm and thermoresponsive hyperbranched HPEI-IBAm at pH 9 and 10 ([polymer] = 16 mg·mL$^{-1}$).

### Accommodating Non-polar Guest by the HPEI-IBAm/SDS Complex

The accommodation ability of the thermoresponsive HPEI-IBAm/SDS complex toward non-polar guest in water was further investigated. Pyrene was selected as the typical non-polar guest. The concentration of pyrene in water can be calculated from the UV-Vis absorbance intensity and its mole extinction coefficient according to the Lambert-Beer Law. Figure 5 shows the influence of SDS concentration on the solubility of pyrene in water in the presence of different concentrations of HPEI-IBAm. It should be noted that HPEI-IBAm alone has negligible

influence on the solubility of pyrene in water. SDS alone can effectively enhance the solubility of pyrene in water only when its concentration in water is above a certain threshhold (around 6.4 mmol·L$^{-1}$). When both HPEI-IBAm and SDS are present in water, the lowest SDS concentration required for effectively enhancing the pyrene solubility in water was decreased pronouncedly and the threshhold value is about 0.31 mmol·L$^{-1}$. The over-soluble pyrene molecules above the SDS threshhold should be accommodated by the hydrophobic domain formed by the hydrophobic chains of SDS molecules due to their similar polarity.
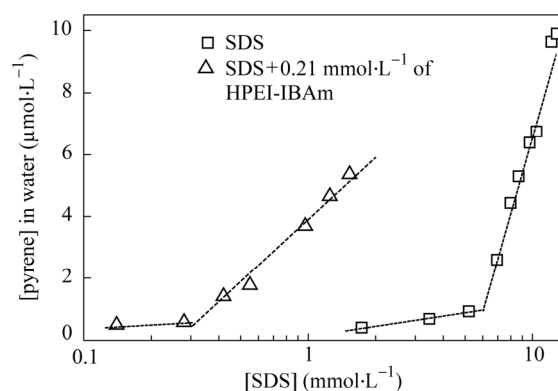


**Fig. 5** Influence of SDS concentrations on the water solubility of pyrene in the presence or absence of HPEI-IBAm

SDS alone and SDS/HPEI-IBAm mixture show so pronounced difference in enhancing the water solubility of pyrene. The basic reason is that their efficiencies in forming hydrophobic domains are different. The well-known fluorescence technique with pyrene as the hydrophobic probe was used to detect their efficiencies in forming the hydrophobic domain. The intensity ratio of the peaks at 373 ($I_1$) and 384 ($I_3$) nm in the emission spectra of pyrene reflects the microenvironment around pyrene molecules. The smaller $I_1/I_3$ implies that the microenvironment around pyrene molecules is less polar. From Fig. 6 it is clear that in the absence of HPEI-IBAm, about 7.2 mmol·L$^{-1}$ of SDS is required to form the hydrophobic domain to accommodate the pyrene guests. Whereas, in the presence of HPEI-IBAm, only around 0.2 mmol·L$^{-1}$ of SDS is required to form the hydrophobic domain to accommodate the pyrene guests.



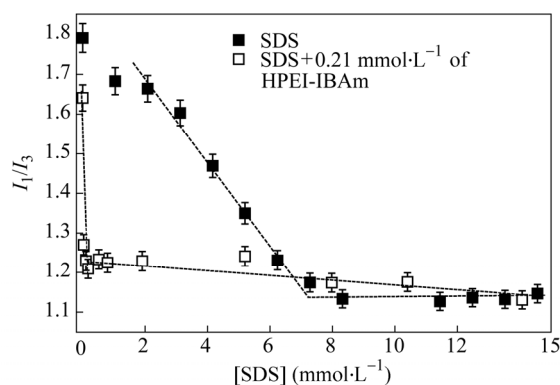**Fig. 6** Influence of SDS concentration on the $I_1/I_3$ intensity ratio of the pyrene emission in the presence or absence of HPEI-IBAm (0.21 mmol·L$^{-1}$)

## CONCLUSIONS

The influence of SDS on the $T_{cp}$ of HPEI-IBAm in cationic and neutral states was different. In cationic state, the initial increase of SDS concentration led to the $T_{cp}$ decrease of HPEI-IBAm. After the SDS concentration reached a certain limit, further increase of SDS concentration led to an obvious $T_{cp}$ increase. When HPEI-IBAm

carried more positive charges, more SDS molecules were required to achieve the minimum $T_{cp}$. When HPEI-IBAm was in neutral state, the increase of SDS concentration led to the gradual increase of the $T_{cp}$ of HPEI-IBAm. The $T_{cp}$ of the hyperbranched HPEI-IBAm was more sensitive to the added SDS than that of thermoresponsive linear PNIPAm. The formed thermoresponsive HPEI-IBAm/SDS complex was more efficient as the host to accommodate non-polar guest than SDS.

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