Colloid Polym Sci (2004) 282: 1008–1015
DOI 10.1007/s00396-003-1025-8

ORIGINAL CONTRIBUTION

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Studies on microstructure and aqueous solution properties of block copolymer of acrylamide-styrene

Received: 21 March 2003
Accepted: 30 October 2003

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Abstract Three series of block copolymers of acrylamide (AM) and styrene (St) as hydrophobic comonomer with varied microstructures were prepared in microemulsion medium by changing feed ratio of monomers, ratio of St to surfactant, and amount of initiator, respectively. The effects of microstructure factors of the amphiphilic block copolymers PAM-*b*-PSt on their aqueous solution properties were investigated by fluorescence probe technique and surface tension measurement in detail. The experimental results show that the aqueous solution properties of PAM-*b*-PSt are strongly dependent on their microstructure factors, such as the length and content of PSt hydrophobic blocks in the copolymers and their molecular weight. It was found that the main microstructure factors which effect the hydrophobic association behavior of the copolymer PAM-*b*-PSt are the length and content of PSt hydrophobic blocks in the copolymer, whereas the hydrophobic association behavior of the copolymer is not affected nearly so much by molecular weight in more dilute regions. At the same time, it was also found that the main microstructure factors which affect the surface activity of the copolymer are the content of PSt hydrophobic blocks in the copolymer and molecular weight, whereas the length of PSt blocks in copolymer does not affect surface activity of the copolymer nearly so much under fixed content of PSt hydrophobic blocks and molecular weight in the copolymer.

Keywords Amphiphilic block polymers · Microstructure · Fluorescence probe technique · Surface tension measurement

Introduction

The amphiphilic block polymers (ABP) possess many unique physical and chemical properties, in particular a stong assembling and order-forming ability [1], because of the hydrophilic/hydrophobic nature and microphase separation quality of their molecular chains. Water-soluble amphiphilic block copolymer is formed by the introduction of a small amount of hydrophobic blocks into hydrophilic backbones. Since there exist hydrophobic blocks in the molecules, these apolar moieties tend to exclude water in aqueous solution, so on one hand, surface absorption will occur, which leads to the amphiphilic block copolymer having a certain surface activity. On the other hand, more likely, the hydrophobic blocks tend to hold together, yielding intra- or intermolecular association. Above a certain concentration (i.e., the critical association concentration), the intermolecular associations prevail over the intramolecular ones, which leads to the formation of physical networks and hydrophobic domains [2], so that a special rheological property is exhibited. These particular aqueous solution properties of amphiphilic block copolymers are of great technological importance, especially for enhanced oil recovery [3], support of target drug [4], polymeric surfactant [5], etc. Since the polarity difference between hydrophilic monomer and hydrophobic monomer is great, and both are mutually insoluble, ABP is difficult to synthesize using general methods, and the micellar method is generally used. In our previous study [6, 7, 8, 9], the block copolymerization of acrylamide (AM) with styrene (St) was realized in a microemulsion medium, a small amount of PSt blocks (wt% < 5) were introduced into the main chains of polyacrylamide, and the amphiphilic block copolymer PAM-*b*-PSt with micro-blocky structure was prepared. At the same time, the blocky structure of the copolymer molecule was characterized more fully by differential methods, such as scanning calorimeter (DSC) method and the fluorescence probe technique. Afterwards, the rheological properties, surface activity and solubilization properties of PAM-b-PSt in aqueous solution were studied carefully. The experimental results indicated that the aqueous solution properties of copolymer PAM-*b*-PSt are strongly influenced by its microstructure. In this paper, the relationships between the hydrophobic association behavior of PAM-b-PSt in aqueous solution and their surface activities and various architecture parameters such as the length and content of PSt hydrophobic blocks in the copolymers and their molecular weight are investigated fully. After clarifying these relationships, it will become possible to control the aqueous solution properties of the amphiphilic copolymer PAM-*b*-PSt by changing their microstructure for some purposes.

Materials and methods

Materials AM (Merck) was recrystallized twice from chloroform. St (Aldrich) was purified by vacuum distilled prior to use. Potassium persulfate (Aldrich) was used as initiator without further purification. Sodium dodecyl sulfate (SDS) (Aldrich) was used as surfactant without further purification. Phenylfluorone (PFN) (Shanghai Reagent Factory) used as fluorescence probe was spectrally pure. The water used was deionized and then distilled.

Equipment A Shimadzu RF-540 fluorescence spectrophotometer, and the JZHY-180 interfacial tension meter of the Chengde instrument factory of China were used.

Synthesis of PAM-b-PSt samples with varying microstructures in series The amphiphilic block copolymers of PAM-*b*-PSt were synthesized in microemulsion medium according to the system, reaction conditions and procedure reported in [6], using SDS as surfactant, monomer AM itself as co-surfactant and potassium persulfate as the free radical initiator. A typical synthesis process was as follows. In a beaker, 13.00 g SDS was dissolved in 116.82 g AM aqueous solution in which the content of AM was 5% (wt%), then 0.18 g St was added and the system changed immediately by slight agitation. The microemulsion system was transferred into a four-necked 250 ml flask, equipped with a thermometer, mechanical stirrer, N_2 inlet and water condenser. After purging with N_2 for 30 min, the temperature was increased to 52 °C, initiator $K_2S_2O_8$(aqueous solution) was added, and the reaction system was maintained at 52 °C under a continuous flow of N_2. After 6 h, the polymerization was terminated, the polymers were precipitated by slowly pouring the reaction mixture into a constantly stirred six-times-excess of methanol. After filtration, the polymers were again dissolved in water, again precipitated by using methanol and were filtered. The operation was repeated three or four times to remove any trace of surfactant thoroughly. The polymers obtained were dipped into toluene for 24 h to extract the homopolymer polystyrene, then dried under reduced pressure at 50 °C for 7 h and conserved in a desiccator. Previous investigations [8, 9] showed that the copolymer PAM-*b*-PSt with continuously varying compositions and approximately uniform molecular weight could be obtained by changing the feed ratio of the two monomers at a fixed amount of initiator, and the copolymer PAM-*b*-PSt with successionally varying molecular weight and approximately uniform compositions could be obtained by changing the amount of initiator at a fixed feed ratio of two monomers. Furthermore, some investigations [10, 11] reported that the ratio of hydrophobe to surfactant controlled the length of hydrophobic blocks. So, in this study, the copolymer PAM-*b*-PSt with different contents of PSt block as series A are represented by using the copolymers prepared by varying the feed ratio of two monomers at a fixed amount of initiator and fixed ratio of St/SDS; the copolymer PAM-*b*-PSt with different lengths of hydrophobic blocks as series B are represented by using the copolymers prepared by varying the ratio of St/SDS at fixed amount of initiator and fixed feed ratio of the two monomers; and the copolymer PAM-*b*-PSt with different molecular weights as series C are represented by using the copolymers prepared by varying amount of initiator at a fixed feed ratio of the two monomers and a fixed ratio of St/SDS. The three series of the copolymers with different microstructures are listed in Table 1. For comparison, a homopolymer PAM was prepared under the same polymerization conditions and a random copolymer P (AM-co-PSt) was prepared by precipitation polymerization from dioxane with an AM, St, and asobisisobutyronitrile homogenous solution.

Determining molecular weight The molecular weight of the copolymers of series C were determined. The aqueous solutions of the copolymers were prepared by dissolving a given amount of the

Table 1 Copolymers with different microstructures

Copolymer	Feed ratio St/AM (w/w)	Amount of $K_2S_2O_8$[a] (wt%)	St/SDS (w/w)	M_η[b]
A-1	0.5:99.5	0.5	0.18:13	1.01×10^6
A-2	0.7:99.3	0.5	0.18:13	0.98×10^6
A-3	1.0:99.0	0.5	0.18:13	0.97×10^6
A-4	1.5:98.5	0.5	0.18:13	0.93×10^6
A-5	3.0:97.0	0.5	0.18:13	0.91×10^6
A-6	4.0:96.0	0.5	0.18:13	0.90×10^6
B-1	3.0:97.0	0.5	0.18:7	1.04×10^6
B-2	3.0:97.0	0.5	0.18:10	0.96×10^6
B-3	3.0:97.0	0.5	0.18:13	0.91×10^6
B-4	3.0:97.0	0.5	0.18:17	0.89×10^6
B-5	3.0:97.0	0.5	0.18:20	0.88×10^6
C-1	3.0:97.0	0.2	0.18:13	1.24×10^6
C-2	3.0:97.0	0.3	0.18:13	1.02×10^6
C-3	3.0:97.0	0.5	0.18:13	0.91×10^6
C-4	3.0:97.0	0.7	0.18:13	0.72×10^6
C-5	3.0:97.0	1.0	0.18:13	0.50×10^6

[a] Weight fraction of initiator in the total feed

[b] Relative molecular weight of viscoaverage

copolymer in water containing 1.0 mol l^{-1} NaCl. Viscosity measurements were carried out using an Ubbelohde viscometer at 25.0 ± 0.1 °C. The intrinsic viscosity $[\eta]$ of the copolymers was determined using the standard technique and the molecular weight was calculated according to the equation $[\eta] = k\overline{M}_{\eta}^{\alpha}$,, and here the values of k and $\alpha$of PAM were used approximately.

Measuring fluorescence spectra of the probe [6] The samples of three series block copolymers, homopolymer PAM and random copolymer were dissolved in saturated aqueous solutions of PFN ($[\mathrm{PFN}] \approx 1 \times 10^{-6}$ mol·l^{-1}) respectively, and polymer aqueous solutions with different concentrations were prepared. Fluorescence emission spectra of PFN in these aqueous solutions (excitation wavelength: 360 nm) were determined using a Shimadzu RF-540 fluorescence spectrophotometer.

Measuring surface activity [8] Block copolymer samples of 0.5–1.0 g were weighed accurately, and dissolved in a few milliliters of distilled water. No agitation was applied during the first day of dissolution (swelling of the polymer), then homogenization was ensured by gentle magnetic stirring for a further day. The solution was transferred into a 100 ml measuring flask, and distilled water was added to the scale to prepare a polymer solution of 100 ml. An appropriate quantity of the polymer solution was accurately transferred into another 100 ml measuring flask using a pipette to prepare a polymer solution with another concentration. Through repeatedly diluting like this, copolymer solutions of six concentrations (C) were prepared for each copolymer sample of every series. After leaving the polymer solutions for 24 h, the surface tension (σ) of every solution was measured by an interfacial tension meter (ring method). The curves of σagainst C were plotted, the critical micelle concentration (*CMC*) of every copolymer sample was determined, and the surface tension σ at *CMC* for every copolymer sample was measured. The curves of σ against C of an identical series copolymer were compared to examine the influence of various microstructure factors on the surface activity of the copolymer PAM-*b*–PSt.

Results and discussion

PAM-*b*–PSt with different microstructures

As described above, three series of copolymers were prepared in a ternary microemulsion system of AM aq./St/SDS. At a fixed amount of initiator and a fixed ratio of St/SDS, the copolymers with successionally varying content of PSt blocks and nearly similar molecular weight were prepared by varying the feed ratio of two monomers. At a fixed amount of initiator and a fixed feed ratio, the copolymers with successionally varying length of PSt block and nearly similar molecular weight were prepared by varying the ratio of St/SDS. At a fixed feed ratio and a fixed ratio of. St/SDS, the copolymers with successionally varying molecular weight were prepared by varying the amount of initiator added. The related data about copolymerization are summarized in Table 1.

Fluorescence emission spectra of probe in the aqueous solutions of copolymer PAM-b-PSt

Fluorescence emission spectra of probe in different polymer aqueous solutions Figure 1 shows the fluorescence emission spectra of PFN in different polymer aqueous solutions. The fluorescence probe PFN was sensitive to the polarity of the environment [6], and the weaker the polarity of the environment is, the stronger the fluorescence emission is. In Fig. 1 it is clearly shown that the fluorescence emissions of the probe in the aqueous solution of PAM-*b*-PSt are much more stronger than that in the aqueous solution of PAM and P(AM-co-PSt). The reason for that is as follows. When dissolved in aqueous solution, the hydrophobic blocks PSt in the molecular chains of the copolymer PAM-*b*-PSt are held together by hydrophobic interaction, forming micelles by intra or intermolecular association. Above critical association concentration (~0.2 wt%), the intermolecular aggregates prevail over intramolecular ones (see below), and clusters of hydrophobic microdomains are formed. PFN is a hydrophobic substance, and it will spontaneously enter into hydrophobic microdomains, thus giving rise to strong fluorescence emission. Conversely, there are no hydrophobically associating microdomains in PAM aqueous solution, and the very weak fluorescence emission is attributed to the water environment. There are few hydrophobic microdomains in P (AM-co-PSt) aqueous solution because in the molecular chains of P (AM-co-PSt), St units distribute randomly in the backbone of polyacrylamide and their hydrophobic intermolecular association in dilute solution is very weak, so fluorescence emission of the probe is also very weak.

Varying of fluorescence intensity of probe with the concentration of copolymer Figure 2 is the plot of the intensity of maximum fluorescence emission of probe at $\lambda = 420$ nm against the concentration of copolymers. It is seen that there is a critical value of concentration

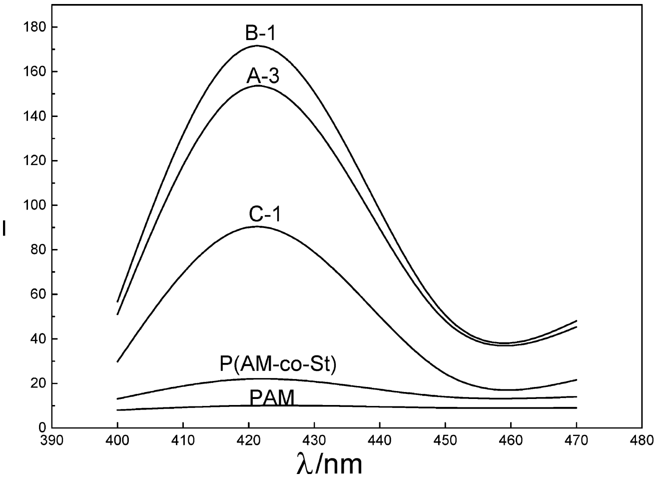

Fig. 1 Fluorescence emission spectra of phenylfluorone (PFN) in aqueous solutions of different polymers. The concentrations of polymers in the aqueous solutions are all 0.5 wt%. Excitation wavelength: 360 nm. *AM* Acrylamide, *St* styrene

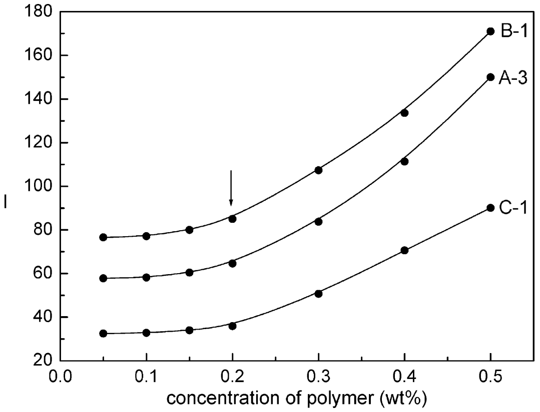

Fig. 2 Intensity of maximum fluorescence emission of PFN vs. the concentration of copolymers. *Arrow* Critical concentration value

(about 0.2 wt%) on the curve of *I* versus *C*. Below this concentration, the fluorescence emission is very weak and varies slowly with concentration, and above it, the fluorescence emission rapidly increases with the concentration. At low concentration, the hydrophobic blocks on separate copolymer chains have little interaction, and the intramolecular association effect is predominant, which leads to the contracting and coiling of chains, so hydrophobic microdomains are small in total and the fluorescence emission of the probe is weak. Above the critical concentration, intermolecular associations prevail over intramolecular associations, and the stronger intermolecular hydrophobic association contributes significantly to the formation of hydrophobic microdomains. After that, intermolecular hydrophobic association increases rapidly with concentration and hydrophobic microdomains enlarge swiftly, so fluorescence intensity increases rapidly with concentration. From this it is suggested that before and after this critical concentration of curve *I* versus *C* the chains of PAM-b-PSt hydrophobically associate with two different forms, basically, and this concentration can be called critical association concentration. In many applications of water-soluble amphiphilic copolymers, their intermolecular hydrophobic association properties are the most-used, so this paper mainly discusses the intermolecular hydrophobic association above the critical concentration for the hydrophobically associating behavior of PAM-b-PSt.

Effect of microstructure of the copolymer on its hydrophobic association behavior

Fluorescence emission spectra of PFN in the aqueous solutions of series A copolymers The fluorescence emission spectra of the probe in the aqueous solutions of series A copolymers are shown in Fig. 3. It shows that fluorescence emission of PFN in each solution of series A is markedly different, and the fluorescence emission in the solution of A-3 (feed ratio St/AM = 1.0:99.0) is the strongest, as its plot of *I* versus λ is at the top. This obviously indicates the effect of the content of PSt blocks in the copolymer on its hydrophobic association behavior at constant length of PSt blocks and molecular weight. Further, the plots of the strongest fluorescence emission intensities of every curve at $\lambda = 420$ nm in Fig. 3 against content of PSt blocks in copolymer are

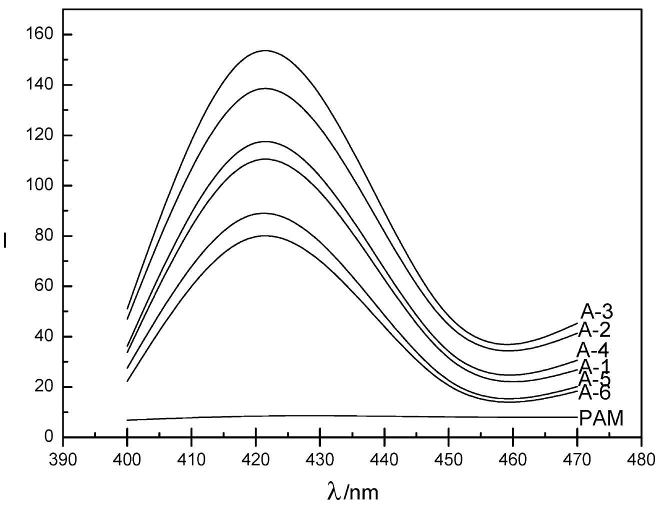

Fig. 3 Fluorescence emission spectra of PFN in copolymer aqueous solutions of series A. The concentrations of copolymers in the aqueous solutions are all 0.5 wt%. Excitation wavelength: 360 nm

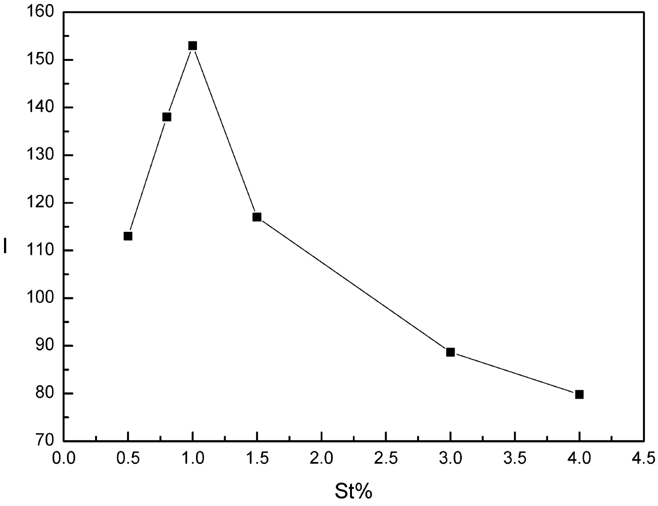

Fig. 4 Intensity of maximum fluorescence emission of PFN vs. the content of PSt in copolymers

drawn, and the result is shown in Fig. 4. The influence of content of PSt blocks in the copolymer on hydrophobic association behavior is revealed more clearly in Fig. 4. When the content of hydrophobic blocks of PSt is too small (A-1, A-2), intermolecular associations are weaker, and hydrophobic microdomains are smaller, so the fluorescence emission intensity of PFN is smaller; when the content of hydrophobic blocks of PSt is excess (A-4.0, A-5 A-6), the tendency of associations of hydrophobic blocks in a molecular chain increases: it is favorable for intramolecular hydrophobic associations, and weakens the intermolecular associations, so the size of hydrophobic microdomains decreases as a whole, and the fluorescence emission intensity of PFN also becomes smaller; when the content of hydrophobic blocks of PSt is right (A-3), intermolecular associations are the most advantaged, so there are the largest hydrophobic microdomains, and the fluorescence emission of the probe is the strongest.

Fluorescence emission spectra of PFN in the aqueous solutions of series B copolymer The fluorescence emission spectra of the probe in the aqueous solutions of series B copolymers are shown in Fig. 5. As previously related, the ratio of St/SDS controls the length of hydrophobic blocks [10, 11] (the greater the ratio of St/SDS is, the longer the length of hydrophobic blocks), so the value of the ratio can be used to represent the length of hydrophobic blocks. In Fig. 5 it is demonstrated that the fluorescence emission of PFN in each solution of series B is markedly different, and that it becomes stronger with increasing length of hydrophobic block PSt. Obviously the fluorescence emission depends on the length of hydrophobic block PSt. This indicates the effect of the length of PSt blocks in the copolymer on its intermolecular hydrophobic association behavior at constant content of PSt blocks and molecular weight. Further, the plots of the strongest fluorescence emission intensities of every curve at $\lambda = 420$ nm in Fig. 5 against content of PSt blocks in copolymer is drawn, and the result is shown in Fig. 6. The influence of the length of PSt blocks in copolymer on its intermolecular hydrophobic association behavior can be displayed more clearly in Fig. 6. There is a more strongly hydrophobic interaction between longer blocks of PSt, so the hydrophobic association effect between macromolecular chains becomes stronger, the size of hydrophobic domains becomes larger with increasing the length of PSt blocks, which results in the fluorescence emission becoming stronger with increasing length of hydrophobic block PSt in the copolymer.

Fluorescence emission spectra of PFN in the aqueous solutions of series C copolymer The fluorescence emission spectra of the probe in the aqueous solutions of series c copolymers are shown in Fig. 7. It is shown that fluorescence emission of PFN in each solution of series B is nearly the same, so that the five curves of *I*versus λ are almost superimposed. This indicates that the fluorescence emission intensity is not really affected by molecular weight (i.e. by the variation of the initiator concentration); that is to say, the hydrophobic association behavior of the copolymer PAM-*b*-PSt, in semi-dilute regime, is not really affected by molecular weight at constant length and content of PSt blocks. Further, the plot of the strongest fluorescence emission intensities of every curve at $\lambda = 420$ nm in Fig. 7 against molecular

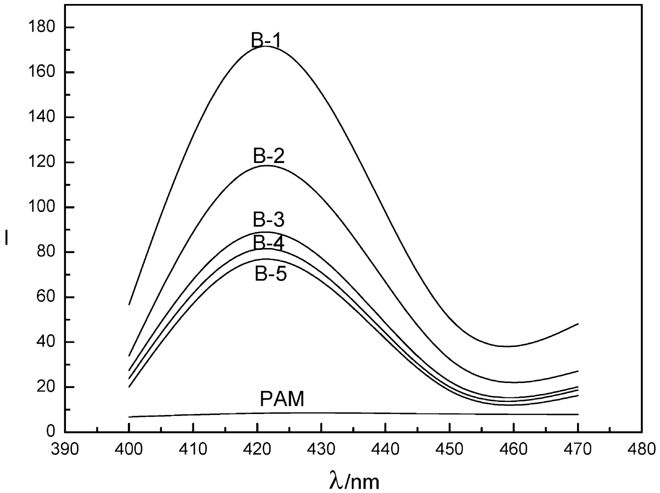

Fig. 5 Fluorescence emission spectra of PFN in copolymer aqueous solutions of series B. The concentrations of copolymers in the aqueous solutions are all 0.5 wt%. Excitation wavelength: 360 nm

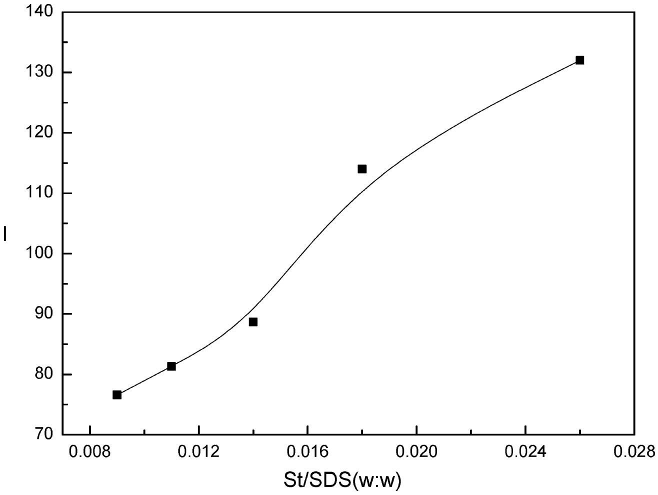

Fig. 6 Intensity of maximum fluorescence emission of PFN vs. the length of PSt in copolymers. *SDS* Sodium dodecyl sulfate

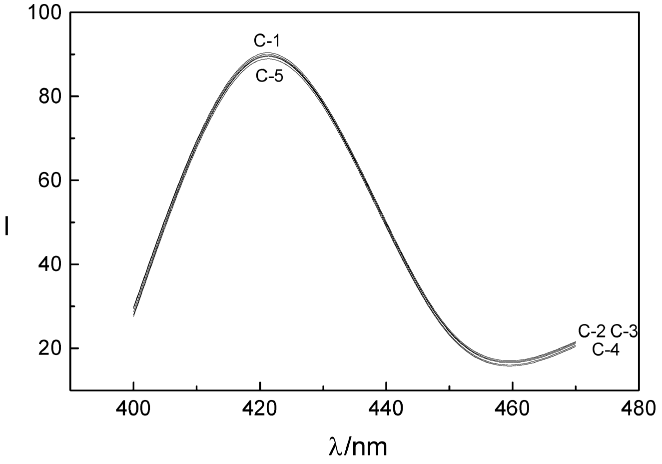

Fig. 7 Fluorescence emission spectra of PFN in copolymer aqueous solutions of series C. The concentration of copolymer in the aqueous solutions are all 0.5 wt%. Excitation wavelength: 360 nm

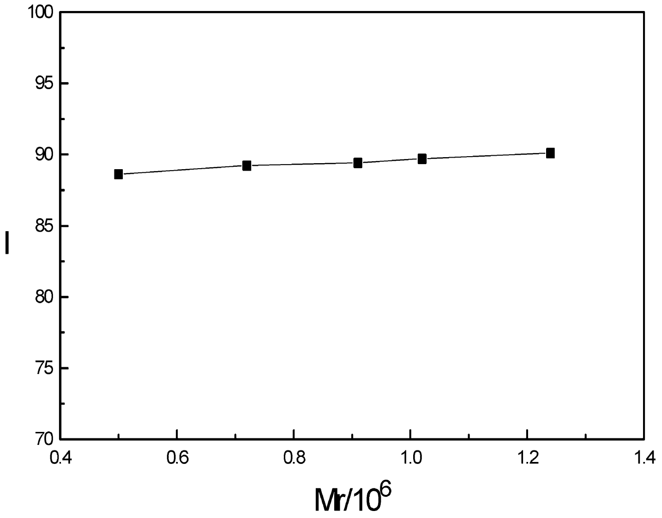

Fig. 8 Intensity of maximum fluorescence emission of PFN vs. the molecular weight of copolymers

weight of the copolymers is drawn, and the result is shown in Fig. 8. The plot is almost a straight line, showing more clearly that the molecular weight of the copolymer PAM-*b*-PSt has little influence on its molecular hydrophobic association behavior in the semi-dilute concentration range. By combining Fig. 4 and Fig. 6, the experimental results show distinctly that the main microstructure factors effecting on the hydrophobic association behavior of the copolymer are the length and content of PSt hydrophobic blocks, and the influence of the length of PSt hydrophobic blocks is particularly remarkable.

Effect of microstructure of the copolymer on its surface activity

Surface activity of series A copolymer As described, the surface tensions of the aqueous solutions of series A copolymer were measured, and the results are displayed in Fig. 9. From the curves of σversus C, two processes can be seen:

(1). At low concentration, early surface tensions of the aqueous solutions decrease with concentration increase, then decrease rapidly and finally tend towards being stable at a certain concentration. When the concentration of PAM-*b*-PSt is lower, the macromolecules of PAM-*b*-PSt are mainly absorbed onto the solution surface. The hydrophilic backbones are joined into water, whereas hydrophobic blocks arrange outside water, so the surface tensions of the solution decrease rapidly with increasing concentration. When the concentration rises to a certain value i.e., to the *CMC*, the surface absorption becomes saturated, whereas inside the solution intramolecular and intermolecular associations of the macromolecular chains of PAM-*b*-PSt may occur due to the hydrophobic interaction of the block sections of PSt. At that time, the surface tensions of the copolymer aqueous solutions no longer decrease.

(2). The copolymer with greater content of PSt blocks has smaller surface tensions at *CMC*, i.e., has higher surface activity. Obviously, the surface activity of the copolymer PAM-*b*-PSt increases with increasing content of PSt blocks at constant length of PSt blocks and molecular weight. The reason is that the greater the content of PSt blocks in chains, the more easily the macromolecule escapes from the

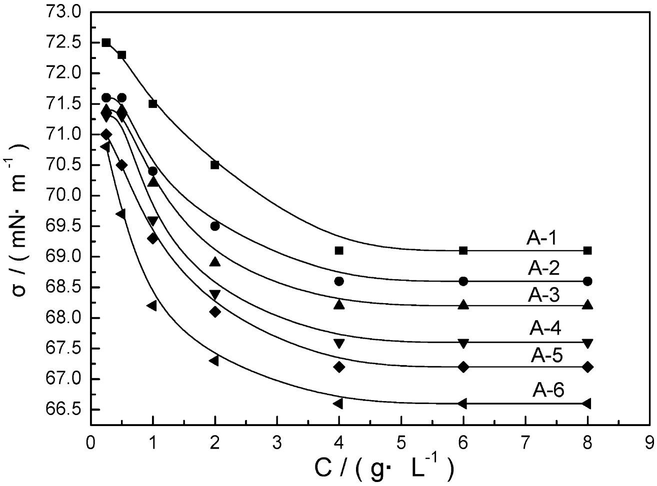

Fig. 9 The surface tension of aqueous solution of PAM-*b*-PSt with different content of PSt vs. concentration of copolymer

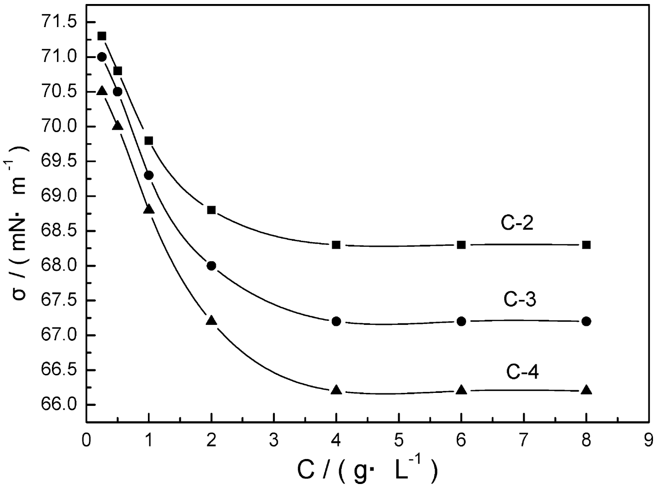

Fig. 10 The surface tension of aqueous solution of PAM-*b*-PSt with different molecular weight vs. concentration of copolymer

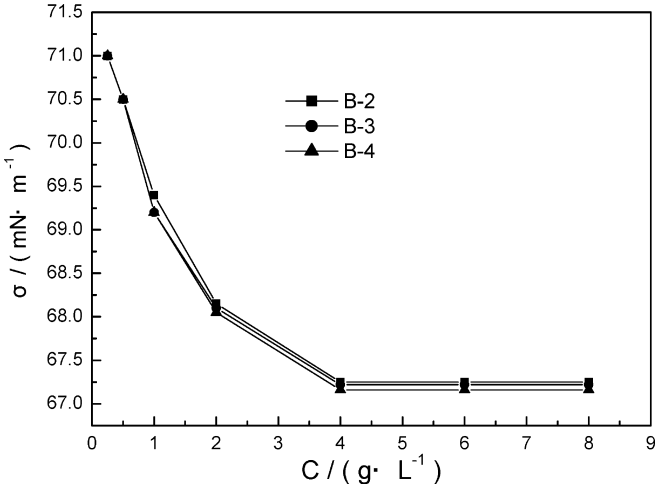

Fig. 11 The surface tension of aqueous solution of PAM-*b*-PSt with different length of PSt block vs. concentration of copolymer

water phase and is absorbed on the surface, so the higher the surface activity is.

Surface activity of series C copolymer The surface tensions of the aqueous solutions of series C copolymer were measured, and the results are displayed in Fig. 10. From the curves of σversus C, again, two processes can be seen: The first is the same as that for Fig. 9. The second is as follows. The copolymer with smaller molecular weight has smaller surface tensions at CMC, i.e., has higher surface activity. Obviously, the surface activity of the copolymer PAM-*b*-PSt increases with decreasing molecular weight at constant content and length of PSt blocks. The reason is that there is less tangling effect between chains for the copolymer with smaller molecular weight, so that the macromolecules move more easily to the surface and arrange, so that such a copolymer has a stronger ability to decrease surface tension, i.e., has higher surface activity. Simultaneously, From Fig. 9 and Fig. 10, as well as Fig. 11, it is seen that the surface activity of PAM-*b*-PSt synthesized in this investigation is not high, although its *CMC* is smaller, and the surface tensions of aqueous solution can only be decreased to about 66 mN/m. The main reason is that the PAM-*b*-PSt synthesized have higher molecular weight, and the macromolecular chains of PAM-*b*-PSt mutually tangle easily, so that the moving towards the surface and arranging at the surface for the molecules are affected [12].

Surface activity of series B copolymer The surface tensions of the aqueous solutions of series B copolymer were measured, and the results are displayed in Fig. 11. It is demonstrated that the ability to decrease surface tension for each copolymers of series B is almost the same, so that the three curves are nearly superimposed. This indicates that the surface activity of the copolymer PAM-*b*-PSt is little affected by the length of PSt blocks at constant content of PSt blocks and molecular weight. By combining Fig. 9 and Fig. 10, the experimental results show clearly that the main microstructure parameters affecting the surface activity of the copolymer PAM-*b*-PSt are the content of PSt hydrophobic blocks in the copolymer and the molecular weight of the copolymer.

In conclusion, the amphiphilic block copolymers of PAM-b- PSt synthesized in microemulsion medium possess particular aqueous solution properties. These properties are strongly dependent on their microstructure parameters such as the content and length of PSt blocks and molecular weight, which are decided by the ratio of monomer feed, the ratio of St to surfactant and the amount of initiator added respectively. The main microstructure factors bearing on the hydrophobic association behavior of PAM-*b*-PSt are the length and content of PSt in the copolymer. The intermolecular hydrophobic association behavior of PAM-*b*-PSt increases with increasing length of the PSt hydrophobic blocks (i.e., with increasing ratio of St to surfactant) at constant content of PSt blocks. It varies with the content of PSt hydrophobic blocks (i.e. with the feed ratio of St) at constant length of PSt blocks, and at an appropriate content of PSt (i.e. at a appropriate feed ratio of St) the copolymer PAM-*b*-PSt exhibits the strongest intermolecular hydrophobic association behavior. The hydrophobic association behavior of the copolymer is little affected by molecular weight in the more dilute concentration region (i.e., the semi-dilute regime) at constant length and content of PSt in the copolymer. The main microstructure factors affecting the surface activity of PAM-*b*-PSt are the content of PSt blocks and molecular weight. The surface activity of PAM-*b*-PSt increases with increasing content of PSt hydrophobic blocks (i.e. with increasing feed ratio of St) at constant molecular weight, and it increases also with decreasing molecular weight (i.e., with increasing initiator amount added) at constant content of PSt blocks, whereas the surface activity of PAM-*b*-PSt is little affected by the length of PSt blocks in the copolymer at fixed content of PSt blocks in the copolymer and molecular weight of the copolymer.

Acknowledgements The authors are grateful to the Science Foundation of Province Shanxi of China for financial support of this work (contact No: 94012).

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