Colloid Polym Sci (2006) 284: 710–717
DOI 10.1007/s00396-005-1409-z

ORIGINAL CONTRIBUTION

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Studies on the self-assembly behavior of the amphiphilic block copolymer of PSt-*b*-PAA in apolar solvents with polar fluorescent probe

Received: 15 March 2005
Accepted: 14 October 2005
Published online: 7 March 2006

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Abstract The block copolymer of polystyrene-*b*-poly(butyl acrylate) (PSt-*b*-PBA) with a well-defined structure was synthesized by atom transfer radical polymerization (ATRP); its structure was characterized, and the living polymerization was also validated by gel permeation chromatography, Fourier transform infrared, and ^{1}H NMR measurements. Then, the amphiphilic block copolymer of polystyrene-*b*-poly(acrylic acid) (PSt-*b*-PAA) has been prepared by hydrolysis of PSt-*b*-PBA, and copolymers of PSt-*b*-PAA with longer PSt blocks and shorter PAA blocks were obtained by controlling the conditions of ATRP polymerization. The reversed micelle solution of PSt-*b*-PAA in toluene was prepared by using the single-solvent dissolving method, and the reverse micellization behavior of PSt-*b*-PAA in toluene was mainly investigated in this paper. The fluorescent probe technique was used by using polar fluorescence compound *N*-(1-Naphthyl)ethylenediamine dihydrochloride (NEAH) as a polar fluorescent probe to study the reverse micellization behavior of PSt-*b*-PAA. It was found that the reverse micellization behaviors of PSt-*b*-PAA in toluene can be clearly revealed by using NEAH as a polar fluorescence probe, and the critical micelle concentrations (cmcs) can be well displayed. The experimental results showed that the self-assembling behavior of PSt-*b*-PAA in toluene depends apparently on the microstructure of the macromolecules and is also influenced by the temperature. For the copolymers of PSt-*b*-PAA with the same length of hydrophobic PSt blocks, the copolymer with a longer hydrophilic block PAA has lower cmc, and at higher temperature, the copolymer has lower cmc.

Keywords Amphiphilic block copolymer · Self-assembly · Reverse micelles · Polar fluorescent probe

Introduction

The amphiphilic block copolymers have a stronger assembling ability to form a molecular order system because of the hydrophilic/hydrophobic nature and microphase separation character of their molecular chains. In liquid media and under different conditions, amphiphilic block copolymers can self-assemble to form aggregates or micelles with a core/corona structure as well as nanosize and various morphologies, such as spheres, rod, vesicles, and others [1–6]. The aggregates have wide applications in many scientific and technical fields, such as biological simulation (vesicle), drug-delivery system, synthesis of functional nanoparticles, and so on, all of which are closely correlative to the self-assembly of amphiphilic block copolymers [7–9]. Hence, there was an increasing attention to the self-assembly behavior of amphiphilic block copolymers from the academe [10–12] in recent years. Many individ-

uals, including the likes of Astafieva et al. [13], Zhang and Eisenberg [14], Wang et al. [15], Tuzar [16], Kříž et al. [17], Vinogradov et al. [18], Bronich et al. [19], Discher et al. [20, 21], Wang et al. [22], and so on, are active in the field. A number of investigations show that when amphiphilic diblock copolymers are dissolved in a solvent that is selective for one of the blocks, they will self-assemble to form micelles with compact cores of insoluble blocks surrounded by a soluble corona composed of soluble blocks. These micelles are referred to as regular or reverse when obtained in polar or apolar solvents, respectively. Nanospace microreactors can be constructed for preparing inorganic nanoparticles by utilizing the reverse micellization behavior of the amphiphilic block copolymers in an apolar solvent [4], and the method to utilize the reverse micelles of amphiphilic block polymers as soft template for preparing functional inorganic nanoparticles has great potential [9, 23, 24]. Therefore, it is very significative to study the self-assembly behavior of amphiphilic block polymers in an apolar solvent. However, many investigations about the self-assembly behavior of the amphiphilic block copolymers focus on regular micelles in water [25–27], whereas investigations about reverse micellization are reported very rarely [28] owing to the difficulty of investigation, particularly due to the difficulty in determining critical micelle concentration (cmc) values and aggregation numbers (N_{agg}). It should be mentioned that Moffitt and Eisenberg [9] and Vinogradov et al. [18] have carried out more in-depth studies on this aspect. They synthesized amphiphilic diblock copolymers of polystyrene-*b*-poly(sodium acrylate) (PSt-*b*-PANa) and polystyrene-*b*-poly(acrylic acid) (PSt-*b*-PAA) by anionic polymerization, determined the aggregation numbers (N_{agg}) of reverse micelles of the two types of copolymers in organic solvent by combining size exclusion chromatography and static light scattering (SLS), and measured the cmc values of reverse micelles by combining SLS and Debye equation. In this paper, the amphiphilic diblock copolymers of PSt-*b*-PAA with a well-defined structure, which have longer PSt blocks and shorter PAA blocks, were synthesized by atom transfer radical polymerization (ATRP), and spherical reverse micelles in toluene were prepared by using the single-solvent dissolving method. The reverse micellization behavior of PSt-*b*-PAA in toluene was explored effectively by using the polar fluorescence compound *N*-(1-Naphthyl)ethylenediamine dihydrochloride (NEAH) as a polar fluorescence probe; the reverse micelle concentration values were determined, and the effects of microstructure of macromolecular chains and temperature on the reverse micellization behavior of PSt-*b*-PAA in toluene were investigated. It was found via the experimental results that the reverse micellization behavior of PSt-*b*-PAA in toluene could be revealed clearly by using NEAH as a polar fluorescence probe with the fluorescence spectroscopy method, and so far, an analogous study has not been reported.

Experimental

Material

Styrene (Aldrich) was washed with 5% NaOH aqueous solution, washed to neutral with distilled water, dried for 24 h with anhydrous $CaCl_2$, and finally distilled under reduced pressure. Butyl acrylate of analytical purity was treated using a method similar to the one above. 1-Phenylethyl bromide (1-PEBr; ACROS) was directly used without prior treatment. 2,2′-Bipyridine (bpy) of analytical purity was directly used. Cuprous bromide (CuBr; ACROS) was washed repeatedly with glacial acetic acid and absolute ethanol, dried under vacuum, and stored under specific conditions (airproofing and light avoidance). Xylene, toluene, 1,4-dioxane, glacial acetic acid, ethanol, methanol, and tetrahydrofuran (THF) were all of analytical grade. NEAH (Shanghai Reagent Factory) was of analytical grade.

Equipment

Polymer molecular weights and molecular weight distributions were obtained via gel permeation chromatography (GPC) measurement that was carried out with a Waters 2410 instrument, by using THF as eluent, and calibration with polystyrene standards. ^{1}H NMR spectra were taken on a Bruker 400-MHz spectrometer at room temperature in $CDCl_3$. An 8400S Shimadzu Fourier transform infrared (FTIR) spectrometer was used for IR analyses. The fluorescence emission spectra of the probe NEAH in different media were determined on a PE LS-50B fluorescence spectrophotometer.

Synthesizing of samples of PSt-*b*-PAA with varying microstructures

The macromolecular initiator PSt-Br and the block copolymers of polystyrene-*b*-poly(butyl acrylate) (PSt-*b*-PBA) were synthesized in xylene by ATRP according to the composition, reaction conditions, and procedure reported in [29]; the macromolecular initiator and block copolymers of PSt-*b*-PBA were characterized, and the living polymerization was validated by GPC, FTIR, and ^{1}H NMR. After these, the block copolymers of PSt-*b*-PBA were thoroughly hydrolyzed under alkaline condition and were then acidized, and the amphiphilic block copolymers of PSt-*b*-PAA were prepared. PSt-*b*-PAA was also characterized by FTIR and ^{1}H NMR, and the ester groups were confirmed to be hydrolyzed completely. During the synthesization of PSt-*b*-PBA, three samples having the same length of PSt blocks but different lengths of PBA blocks, with longer PSt blocks and shorter PBA blocks,

were synthesized by controlling polymerization time, so that after hydrolyzing, three copolymer samples of PSt-*b*-PAA having longer PSt blocks and shorter PAA blocks, with different lengths of PAA blocks, were obtained.

Measuring polarity and fluorescence spectra of probe NEAH

Firstly, fluorescence excitation and emission spectra of probe NEAH in water were measured for the sake of determining its characteristic fluorescence emission peaks (Fig. 1). To determine the polarity of the compound, we measured its solubility and fluorescence emission in different solvents. The fluorescence emissions of NEAH in aqueous solution with different concentrations, saturated TFH solution, and saturated toluene solution were determined, respectively. To confirm the quenching effect of proton surrounding on the fluorescence probe, we dissolved acetic acid in methanol, which also contained certain amounts of NEAH, and the varying fluorescence emission of NEAH due to different acetic acid concentrations were determined. Similarly, acetic acid was dissolved in TFH, in which NEAH was saturated, and the varying fluorescence emission of NEAH due to different acetic acid concentrations was also determined.

Preparing reverse micelle solution of PSt-*b*-PAA in toluene and investigating reverse micellization behavior

Reverse micellar solutions of PSt-*b*-PAA in toluene were prepared by using the single-solvent dissolving method. A certain amount of copolymer sample was dissolved in toluene, and the copolymer solution with a concentration of 0.1 g/l was prepared. The solution was placed statically for 48 h and was diluted step by step in the range of 5×10^{-2} to 5×10^{-6} g/l, so that toluene solutions of PSt-*b*-PAA with continuously varying concentrations were obtained. After placing statically for 24 h, 10 ml of these solutions was taken and added into a conical flask of 50 ml, respectively, and 6 μl of methanol solution of NEAH (concentration, 2 g/l) was added into these conical flask using a microinjector, so that every solution contained NEAH with a concentration of 4.6×10^{-6} mol/l. After these solutions were shaken ultrasonically for 60 min (40 kHz), the fluorescence emission of these solutions was measured, so that the self-assembly behaviors of PSt-*b*-PAA in toluene were explored and the cmcs were determined.

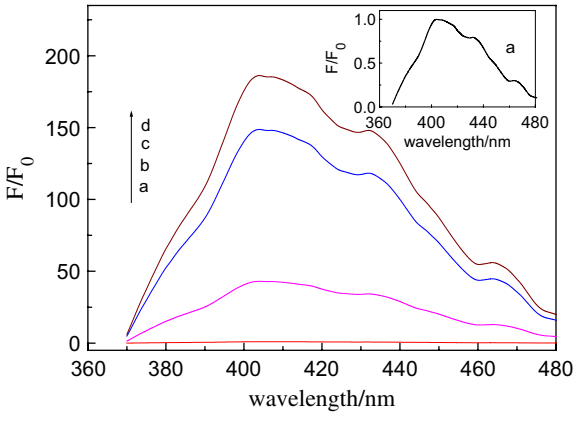


Fig. 1 Fluorescence emission spectra of NEAH in different media. **a** Saturated toluene solution of NEAH with a concentration of ~5×10^{6} mol/l. **b** Saturated THF solution of NEAH with a concentration of ~5×10^{5} mol/l. **c** Aqueous solution with a concentration of 5×10^{4} mol/l. **d** Aqueous solution with a concentration of 1×10^{3} mol/l. Excitation wavelength of ~330 nm

Examining influences of various factors on reverse micellization behavior of PSt-*b*-PAA in toluene

Toluene solutions of three copolymer samples with different length ratios of PSt/PAA, in which NEAH was contained, were all prepared according to the procedure described in "Preparing reverse micelle solution of PSt-*b*-PAA in toluene and investigating reverse micellization behavior." At a fixed temperature (15°C), fluorescence emission of these solutions was measured to investigate the influence of the microstructure of macromolecular chains of PSt-*b*-PAA on its reverse micellization behavior. For the given solutions of identical copolymer, fluorescence emissions of the solution at different temperatures were measured to examine the influence of temperature on the reverse micellization behavior of PSt-*b*-PAA.

Results and discussion

Synthesis of PSt-*b*-PAA with longer PSt blocks

As described in "Synthesizing of samples of PSt-*b*-PAA with varying microstructures," three copolymer samples of PSt-*b*-PAA having longer PSt blocks, with the same length of PSt blocks but with different lengths of PAA blocks, were synthesized using the ATRP method and by controlling polymerization conditions. The correlative data via GPC measurement are listed in Table 1.

Fluorescence spectrum character of NEAH

Polarity of fluorescence compound NEAH and its fluorescence emission spectra in different solvents

Toluene is a selective solvent for PSt. In addition, PSt blocks are much longer than PAA blocks in the macromolecular chains of the PSt-*b*-PAA synthesized in this in-

Table 1 Molecular characteristics of copolymers of PSt-*b*-PAA obtained by ATRP

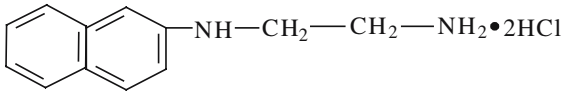
Copolymer	PS(*x*)-*b*-PAA(*y*)	M_n	PDI
C-1	150-*b*-27	17,500	1.49
C-2	150-*b*-20	17,000	1.56
C-3	150-*b*-15	16,700	1.62

Polymerization condition: xylene as solvent, solvent/monomer=3:1 (v/v); M_n of PSt-Br=15,600; polydispersity index (PDI) of PSt-Br=1.31; [BA]/[PSt-Br]/[CuBr]/[bpy]=200:1:1:3 (mol ratio); polymerization temperature, 110°C; alkaline hydrolysis condition: 1,4-dioxane as solvent; temperature, 80°C

vestigation; hence, PSt-*b*-PAA will self-assemble to form star reverse micelles with hydrophilic PAA blocks as core and with hydrophobic PSt blocks as shell, and hydrophilic or polar microdomains exist inside the cores. Pyrene is an oil-soluble fluorescence compound; thus, it is often used as a fluorescence probe to investigate hydrophobic microdomains. With this in mind, NEAH was used in this investigation as a polar fluorescence probe to investigate hydrophilic microdomains and to examine the reverse micellization behavior of PSt-*b*-PAA in toluene. The chemical structure of NEAH is expressed in Scheme 1.

It can be seen from the chemical structural formula of NEAH that NEAH is a polar compound. Experimental results showed that NEAH is soluble in polar solvents such as water and methanol and is insoluble in apolar or weak polar solvents such as toluene and THF; in addition, NEAH exhibits a fluorescence characteristic. The emission spectra of NEAH in the aqueous solution, the saturated THF solution, and the saturated toluene solution are shown in Fig. 1.

In Fig. 1, the fluorescence emission spectra of NEAH in different media are expressed relatively (F/F_0) by using the emission intensity of NEAH in saturated toluene solution as the standard (F_0). NEAH is a polar compound and its saturated solubility in THF and toluene is very small; hence, its fluorescence emission spectra in the two saturated solutions are weak. In contrast, NEAH is easily soluble in water and other polar solvents, and its fluorescence emission increases with its concentration in a certain concentration range. Moreover, it can be seen in Fig. 1 that the shapes and positions of the emission peak of NEAH in different media basically remain unchanged, and its maximum emission peak locates at 402 nm.



Scheme 1 Chemical structure of NEAH

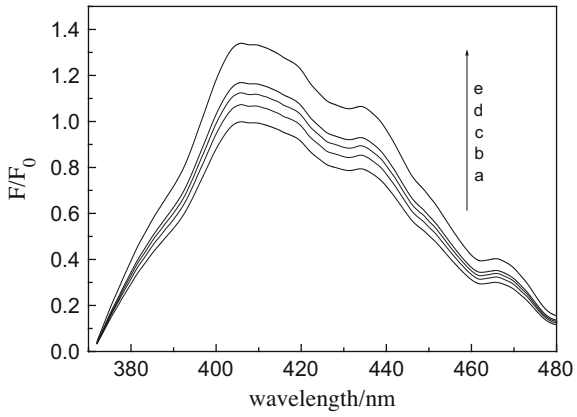


Fig. 2 Varying fluorescence emission of NEAH in methanol with HAC concentration (v/v): **a** 0.4 ml/20 ml, **b** 0.3 ml/20 ml, **c** 0.2 ml/20 ml, **d** 0.1 ml/20 ml, and **e** 0 ml/20 ml

Quenching effect of proton surrounding on fluorescence of NEAH

The varying fluorescence emission of NEAH in the methanol solution (NEAH concentration: 8×10^{-6} mol/L) due to different acetic acid concentrations is shown in Fig. 2, in which the spectrum curve with the weakest emission is used as the standard (F_0). It also shows that the fluorescence emissions of NEAH in methanol decrease with the concentration increase of acetic acid. Acetic acid in methanol will partially disassociate because methanol is a solvent with a proton character; thus, there are free protons in the methanol solution of acetic acid and there are also un-disassociated protons of carboxyl groups of acetic acid. The protons in the two states are all acceptors of electrons, and they all will affect the π-electron system of the NEAH molecule. Hence, they will play a role in quenching the fluorescence emission of NEAH. This action can be called "quenching effect of proton surrounding."

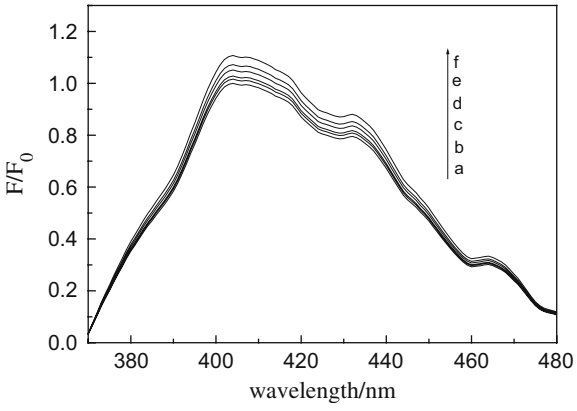


Fig. 3 Varying fluorescence emission of NEAH in THF with HAC concentration (v/v): **a** 0.5 mL/20 mL, **b** 0.4 mL/20 mL, **c** 0.3 mL/20 mL, **d** 0.2 mL/20 mL, **e** 0.1 mL/20 mL, and **f** 0 mL/20 mL

The varying fluorescence emission of NEAH in the saturated THF solution as a result of different acetic acid concentrations is shown in Fig. 3, in which the spectrum curve with the weakest emission is used as the standard (F_0). It also shows that the fluorescence emissions of NEAH in the saturated THF solution decrease with the concentration increase of acetic acid, although the varying extent is smaller than that in Fig. 2. THF is a weak polar solvent wherein acetic acid molecules exist as a molecular state; hence, there are a number of un-disassociated protons of carboxyl groups in the THF solution of acetic acid. It is obvious that these un-disassociated protons also exhibit the quenching effect of proton surrounding on the fluorescence emission of NEAH, so that the fluorescence emissions of NEAH in saturated THF solution decrease with the concentration increase of acetic acid.

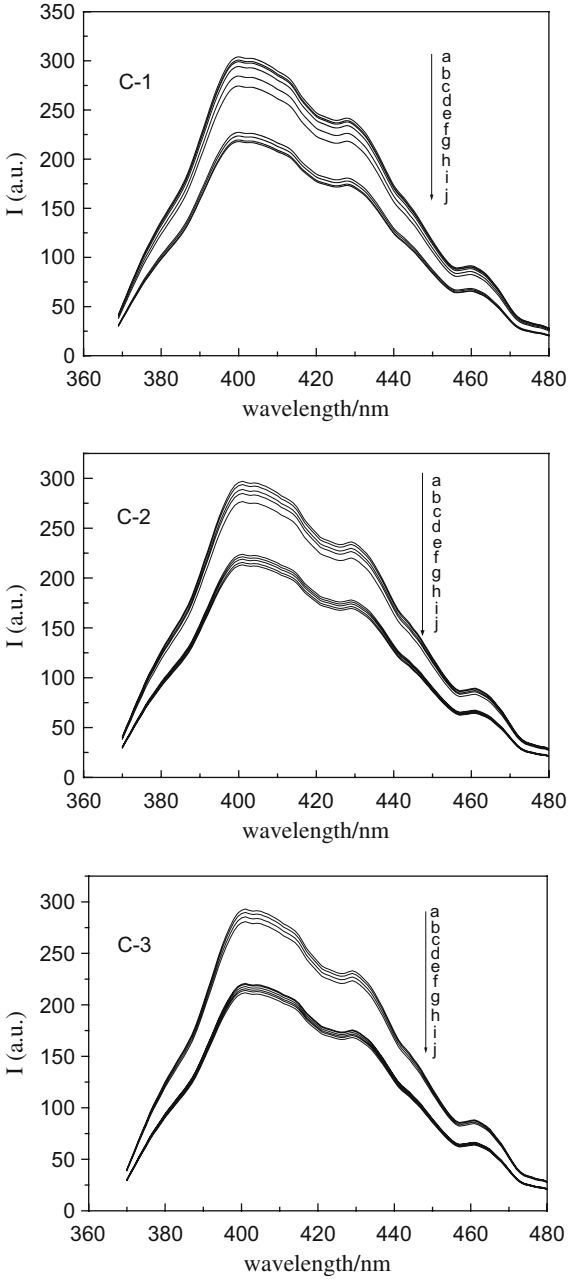


Fig. 4 Varying fluorescence emission of NEAH in copolymer toluene solution with copolymer concentration (g/L) for different copolymers: **a** 5×10^{6}, **b** 1×10^{5}, **c** 5×10^{5}, **d** 1×10^{4}, **e** 5×10^{4}, **f** 1×10^{3}, **g** 5×10^{3}, **h** 1×10^{2}, **i** 5×10^{2}, **j** 1×10^{1}

Reverse micellization behavior of PSt-*b*-PAA in toluene

As described in "Examining influences of various factors on reverse micellization behavior of PSt-*b*-PAA in toluene," toluene solutions of the three copolymer samples with different length ratios of PSt/PAA were prepared, the concentrations of the copolymers were continuously changed, and these solutions contained NEAH with the same concentration of 4.6×10^{-6} mol/l. Figure 4 shows the varying fluorescence emission of NEAH due to the different copolymer concentrations for the toluene solutions of the three copolymer samples.

Figure 4 shows that there are similar principles among the three curves. When the concentrations of copolymers are lower, the fluorescence emissions of NEAH slightly decrease with the concentrations of copolymers or they can be regarded unchanged, whereas as the concentrations of copolymers increase to a certain value, the fluorescence emission of NEAH decreases sharply; after this, the emissions again remain constant. The abrupt changes of the fluorescence emissions of NEAH reveal the formations of reverse micelles. When the concentrations of the copolymers are much lower, the macromolecules disperse in the solvent as single chains and do not aggregate, and the ambience around the NEAH molecule is basically that of an apolar surrounding, consisting of toluene molecules; thus, the fluorescence emissions of NEAH do not vary

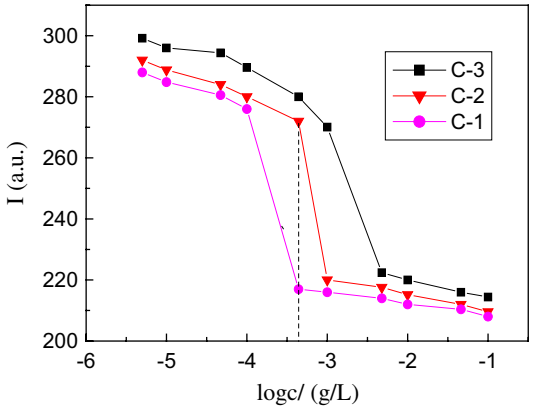


Fig. 5 Dependence of fluorescence intensity of NEAH in copolymer solution of toluene at 402 nm on copolymer concentrations

much. As the concentrations of copolymers increase to a certain value, reverse micelles begin to form, and the polar molecules of NEAH transfer toward the polar microdomain of the inner micelle. Meantime, the carboxyl groups of PAA blocks inside the micelle cores constitute a strong proton surrounding for the NEAH molecule, and the strong proton surrounding exhibit a strong quenching effect, which results to an abrupt decrease in the fluorescence emissions of NEAH. After this, only the number of reverse micelles increases with the enhancing of copolymer concentrations, and the proton surrounding of NEAH no longer varies, resulting in unchanged fluorescence emissions. The experimental results in Fig. 4 indicate that NEAH can be used as a polar fluorescence probe, and it can be used to explore macroscopically the reverse micellation behavior of the amphiphilic block copolymer of PSt-*b*-PAA in toluene. For the toluene solution of PSt-*b*-PAA, reverse micelles, which have cores consisting of hydrophilic PAA blocks and shells consisting of hydrophobic PSt blocks, will form by self-assembling at a certain concentration.

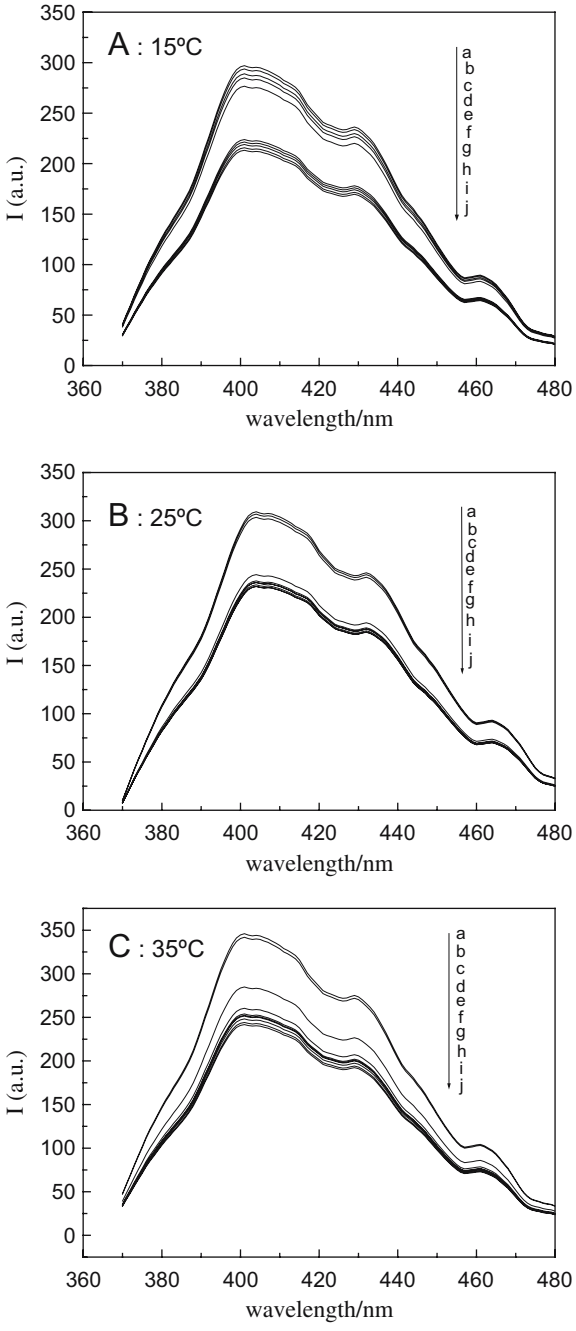


Fig. 6 Varying fluorescence emission of NEAH in copolymer toluene solution with copolymer concentration (g/L) under different temperatures: **a** 5×10^{6}, **b** 1×10^{5}, **c** 5×10^{5}, **d** 1×10^{4}, **e** 5×10^{4}, **f** 1×10^{3}, **g** 5×10^{3}, **h** 1×10^{2}, **i** 5×10^{2}, **j** 1×10^{1}

Influence of the microstructure of macromolecular chains on reverse micellization behavior of PSt-*b*-PAA

To display clearly the cmcs, we plotted the curves of emission intensity at λ=402 nm against the copolymer concentration, as shown in Fig. 5.

There are three curves corresponding to three copolymer samples in Fig. 5, and the concentrations corresponding to the turning points on these curves are the cmcs of the three copolymer samples, respectively. The cmcs of the three copolymer samples are 1×10^{-3} g/L for C-1, 5×10^{-4} g/L for C-2, and 1×10^{-4} g/L for C-3. By comparing these data, it can be found that for the three copolymer samples with the same length of PSt block but different lengths of PAA block, the longer the PAA block is, the lower the cmc is. The result is completely identical with the conclusion of Khougaz et al., and the above data regarding cmcs are also consistent with those of Khougaz et al. [28]. The cmc of the amphiphilic block copolymer in the selective solvent for one of the blocks depends greatly on the length of the insoluble blocks, and the copolymer with longer insoluble blocks has a lower cmc. The reason for this is that, in toluene, PAA blocks are insoluble blocks and the solubility of single chains of copolymer with longer PAA blocks will

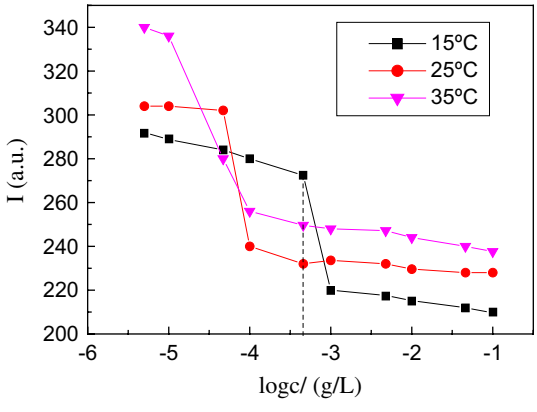


Fig. 7 Dependence of fluorescence intensity of NEAH in copolymer solution of toluene at 404 nm on temperature

be much poorer; hence, the reverse micelles will form easily at a lower concentration.

Influence of temperature on reverse micellization behavior of PSt-*b*-PAA

As described in "Examining influences of various factors on reverse micellization behavior of PSt-*b*-PAA in toluene," the fluorescence emissions of NEAH in the toluene solutions of the identical copolymer (C-2) at different temperatures were measured, and Fig. 6 shows the varying fluorescence emission of NEAH due to the different copolymer concentrations at different temperatures.

There are three curves corresponding to three temperatures in Fig. 6; the abrupt changes of the fluorescence emissions of NEAH reveal the formations of reverse micelles, and the concentrations corresponding to the abrupt changes are the cmcs of copolymer C-2 at three different temperatures.

To display more clearly the dependence of cmcs on temperature, we plotted the curves of emission intensity at λ=402 nm against the copolymer concentration at different temperatures, as shown in Fig. 7. The cmcs of C-2 are 5×10^{-4} g/l at 15°C, 5×10^{-5} g/l at 25°C, and 1×10^{-5} g/l at 35°C.

By comparing these data, it can be found that the higher the temperature is, the lower cmc is. This is probably due to the following: the heat motion of macromolecules is intensified because of temperature increase, the force of sticky retarding between macromolecules decreases, and the formation of reverse micelles of the macromolecules becomes easier. A thermodynamic reason may also explain this. It is known that the formation of micelles is a process driven by entropy. Perhaps the entropy change ΔS of micelle formation increases as the temperature increases; thus, the critical micellar concentration decreases. The thermodynamic reason for the dependence of cmcs on temperature needs to be explored further.

Conclusions

The amphiphilic block copolymers of PSt-*b*-PAA having a well-defined structure, with longer hydrophobic PSt blocks and shorter hydrophilic PAA blocks, can be synthesized by ATRP. The reverse micelle solution of the PSt-*b*-PAA in toluene can be prepared with the single-solvent method, and the reverse micelles consist of PAA blocks as core and PSt blocks as shell. NEAH is a polar fluorescence compound, and proton surrounding exhibits a quenching action upon fluorescence emission. When NEAH is dissolved in the toluene solution of copolymer PSt-*b*-PAA, NEAH will be transferred inside the polar cores of the reverse micelles once the reverse micelles form. In the polar cores, the proton surrounding, consisting of carboxyl groups of PAA, quenches strongly the fluorescence emission of NEAH. Thus, the reverse micelle formation of PSt-*b*-PAA in toluene can be explored macroscopically and clearly, and the cmc can be determined. Hence, it is implied that NEAH can be used as a fluorescence probe to explore clearly the reverse micelle formation of PSt-*b*-PAA in apolar solvents, and the conclusion can still be extended to other amphiphilic block copolymers of which the hydrophilic blocks are acetic. A study analogous to this has yet to be reported. The results show that the main factor influencing the reverse micellization behavior of PSt-*b*-PAA is its microstructure, and the longer the hydrophilic PAA block is, the lower its cmc for the copolymer PSt-*b*-PAA with the same length of PSt blocks; that is, under the condition of longer PAA blocks, reverse micelles form much more easily. Besides, temperature can also influence the reverse micellization behavior of PSt-*b*-PAA, and the higher the temperature is, the easier reverse micelle formation is.

Acknowledgement The authors are grateful to the Science Foundation of Shanxi Province of China for its financial support for this work.

References

1. Cameron NS, Corbierrre MK, Eisenberg A (1999) Can J Chem 77:1311
2. Yu Y, Zhang L, Eisenberg A (1998) Macromolecules 31:1144
3. Shen H, Eisenberg A (2000) Macromolecules 33:2561
4. Zhang L, Eisenberg A (1996) J Am Chem Soc 118:316
5. Zhang L, Eisenberg A (1998) Polym Adv Technol 9:677
6. Desbaumes L, Eisenberg A (1999) Langmuir 15:36
7. Riess G (1999) Colloids Surf A 153:99
8. Kwon GS, Kataoka K (1995) Adv Drug Deliv Rev 16:295
9. Moffitt M, Eisenberg A (1997) Macromolecules 30:4363
10. Forster S, Antonietti M (1998) Adv Mater 10:195
11. Zhang L, Shen H, Eisenberg A (1997) Macromolecules 30:1001
12. Zhang L, Eisenberg A (1995) J Sci 268:1728
13. Astafieva I, Zhong X, Eisenberg A (1993) Macromolecules 26(26):7339
14. Zhang L, Eisenberg A (1995) Science 268:721
15. Wang XS, Winnik MA, Manners I (2002) Macromol Rapid Commun 23 (3):210
16. Kříž J, Mazař B, Pleštil J, Tuzar Z, Pospišil H, Doskočilová D (1998) Macromolecules 31:41
17. Prochazka K, Martin TJ, Webber SE, Munk P (1996) Macromolecules 29:6526
18. Vinogradov SV, Bronich TK, Kabanov AV (2001) Adv Drug Deliv Rev 54 (1):135
19. Bronich TK, Vinogradov SV, Kabanov AV (2001) Nano Lett 1(10):535
20. Discher BM, Bermudez H, Hammer DA, Discher DE, Won YY, Bates FS (2002) J Phys Chem B 106(11):2848

21. Discher BM, Hammer DA, Bates FS, Discher DE (2000) Curr Opin Colloid Interface Sci 5(1–2):125
22. Wang XS, Winnik MA, Manners I (2002) Macromol Rapid Commun 23 (3):210
23. Moffitt M, Eisenberg A et al (1995) Chem Mater 7:1185
24. Ruokolainen J, Mäkinen R, Torkkeli M et al. (1998) J Sci 280:557
25. Ding J, Liu GJ (1997) Polymer 38:5497
26. Jenekhe SA, Cheng XL (1998) J Sci 279:1903–1907
27. Jenekhe SA, Cheng XL (1999) J Sci 283:372–375
28. Khougaz K, Zhong XF, Eisenberg A (1996) Macromolecules 29:3937
29. Tang ZZ, Gao BJ, He SX (2005) J North Univ China 26:37