Synthesis, Characterization, and Properties of Amphiphilic Block Copolymer of Acrylamide-Styrene by Self-Emulsifying Microemulsion Method

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ABSTRACT: The copolymerization system of acrylamide (AM) and styrene (St) was acquired by using amphiphilic block copolymer PAM-*b*-PSt with lower molecular weight as polymeric surfactant, and then the microemulsion phase diagram was drawn. The appropriate copolymerization systems were chosen in the phase diagram, and higher molecular weight amphiphilic block copolymers PAM-*b*-PSt were prepared by self-emulsifying microemulsion method. The chemical composition and structure of the products were analyzed by FTIR, ^{1}H-NMR, ^{13}C-NMR, GPC, and UV; the block structure of products was characterized by DSC, and the hydrophobic association property of the products was studied by the fluorescence probe and rotating viscosity measurement. The results showed that O/W microemulsion was also acquired by using the polymeric surfactant; 3 g polymeric surfactant was only used to disperse 0.25 g St into aqueous solution, which showed higher emulsifying efficiency. At the same time, the use of self-emulsifying microemulsion copolymerizing system can avoid back treatment of small molecular surfactant and the purified block polymer was prepared in one step; the prepared copolymers have good hydrophobic association properties and their aqueous solution showed evident viscosity increment. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1457–1463, 2009

Key words: acrylamide; block copolymers; self-emulsifying microemulsion copolymerization; association; synthesis

INTRODUCTION

Amphiphilic block polymers (ABPs) have some unique physical and chemical properties, especially showing a strong assembling and order-forming ability[1–3] because of the hydrophilic/hydrophobic properties and microphase separation of their molecular chains. Water-soluble amphiphilic block copolymers can be formed by the introduction of a small amount of hydrophobic blocks into hydrophilic backbones. Because there were hydrophobic blocks in the molecules, these apolar moieties tend to exclude water in aqueous solution, so on the one hand, the surface absorption will occur, which leads to amphiphilic block copolymer has surface activity. On the other hand, more likely, the hydrophobic blocks tend to hold together and yield intramolecular or intermolecular association. These particular aqueous solution properties of amphiphilic block copolymers are of great technological importance, especially for enhanced oil recovery,[4] support of target drug,[5] polymeric compatilizer,[6,7] polymeric surfactant,[8] etc. However, the polarity difference between hydrophilic monomer and hydrophobic monomer is great, and they are mutually insoluble. Therefore, ABP is difficult to be synthesized by using general methods, and the micelle method is mostly used. In our previous study,[9–12] the block copolymerization of acrylamide (AM) and styrene (St) was realized in a microemulsion medium; a small amount of PSt blocks (<5 wt %) was introduced into polyacrylamide chains, and the amphiphilic block copolymer PAM-*b*-PSt with micro-block structure was prepared. At the same time, the rheological properties, the surface activity, and solubilization properties of PAM-*b*-PSt aqueous solution were studied in detail. The experimental results indicated that the molecular weight influenced the surface activity of PAM-*b*-PSt aqueous solution obviously and the lower the molecular weight was, the stronger the surface activity was.

In this article, the stable O/W microemulsion was acquired by using amphiphilic block copolymer PAM-*b*-PSt with lower molecular weight as polymeric surfactant, and the microemulsion system was made. Then a series of PAM-*b*-PSt with varied molecular composition and higher molecular weight was prepared by the self-emulsifying microemulsion method. As far as to we know, the preparation of PAM-*b*-PSt by this method was not reported. Compared with micelle method[13] and general microemulsion

method,[9] the method cannot only avoid the complicate purified back treatment of surfactant, but can also make the efficiency of block copolymerization higher.

MATERIALS AND METHODS

Materials

AM was purchased from China Medicine, Shanghai Chemical Reagent Corporation (Shanghai, China), and recrystallized twice from chloroform. St was purchased from Aldrich (Milwaukee, WI) and purified by vacuum distillation prior to use. Potassium persulfate ($K_2S_2O_8$), sodium dodecyl sulfate (SDS), 9-phenyl-3-fluorone (PFN), chloroform, azobisisobutyronitrile (AIBN), dioxane, toluene, and methanol were purchased from Beijing Chemical Factory (Beijing, China). Other materials mentioned above were used without further purification unless otherwise specified.

Synthesis of polymeric surfactant (lower molecular weight PAM-*b*-PSt)

The amphiphilic block copolymers of PAM-*b*-PSt with lower molecular weight were synthesized in microemulsion medium according to the reaction conditions and process reported by Gao et al.,[9] using SDS as surfactant, AM itself as co-surfactant, and potassium persulfate (4% of monomer total weight) as free radical initiator. A typical synthesis process was as follows. In a beaker, a certain amount of SDS and AM was dissolved in aqueous solution; then St was added and the reaction system changed immediately by slight agitation. The microemulsion system was transferred into a four-necked 250-mL flask, equipped with a thermometer, a mechanical stirrer, an N_2 inlet, and a water condenser. After purging with N_2 for 30 min, the temperature was increased to 52°C; then $K_2S_2O_8$ 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, and then the product was precipitated by slow pouring the reaction mixture into methanol with six times excess of reaction mixture under constant stirring. After filtration, the product was again dissolved in water, again precipitated in methanol, and filtered. The operation was thoroughly repeated for three or four times to remove any trace of surfactant. The obtained polymer was dipped into toluene for 24 h to extract polystyrene homopolymer and then dried under reduced pressure at 50°C for 7 h, and conserved in a desiccator.

Drawing of phase diagram of self-emulsifying microemulsion polymerization system

AM aqueous solution (15 wt %) and polymeric surfactant (lower molecular weight PAM-*b*-PSt) aqueous solution (5 wt %) according to a certain weight ratio

were added in a conical flask and kept at 25°C. Then St was dripped into the solution with shaking the conical flask. When the amount of dripping St reached a certain value, the system was changed from transparent to turbid suddenly, and at that time the conical flask was taken and weighted to acquire St weight. Subsequently, the weight fraction of the critical system was calculated and the corresponding dot in the phase diagram was attained. The weight ratio between AM aqueous solution and polymeric surfactant aqueous solution was changed and the abovementioned operation was repeated. Then the phase diagram of the self-emulsifying microemulsion copolymerization medium of ABP was plotted.

Copolymerization by self-emulsifying microemulsion

According to the scheduled feed ratio [m (St)/m (AM)], the point was selected in the microemulsion phase diagram, and the weight of each ingredient in the selected copolymerization system was calculated. Then all the reagent was added in a beaker, and the reaction medium was slightly agitated. The formed microemulsion system was transferred into a four-necked 250-mL flask, equipped with a thermometer and mechanical stirrer. After purging with N_2 for 30 min, a small amount of $K_2S_2O_8$ (0.5% of total monomer weight) was added, and the reaction temperature was kept at 52°C. After 6 h, the polymerization was terminated; the polymers were precipitated in methanol. The obtained polymers were dipped into toluene for 24 h to extract polystyrene homopolymer, then filtered, and dried under reduced pressure at 50°C for 7 h. The filtrate was analyzed by UV spectrophotometer, and the result showed the characteristic absorption of PSt was not observed at 263 nm.[10] For comparison, the PAM homopolymer was prepared under the same polymerization conditions and the random copolymer P(AM-*co*-PSt) was prepared by the precipitation polymerization from dioxane with an AM, St, and AIBN homogenous solution.

Graded precipitation of the product

The above obtained product was a mixture of lower molecular weight PAM-*b*-PSt (polymeric surfactant of microemulsion polymerization) and higher molecular weight PAM-*b*-PSt (object product of microemulsion polymerization). The mixture can be used straight in the industry fields (i.e., enhanced oil recovery) for lower requirement of molecule weight distribution, but the mixture must be separated by the solvent graded precipitation to study the composition and properties of the copolymer prepared by the self-emulsifying microemulsion method. The results of a
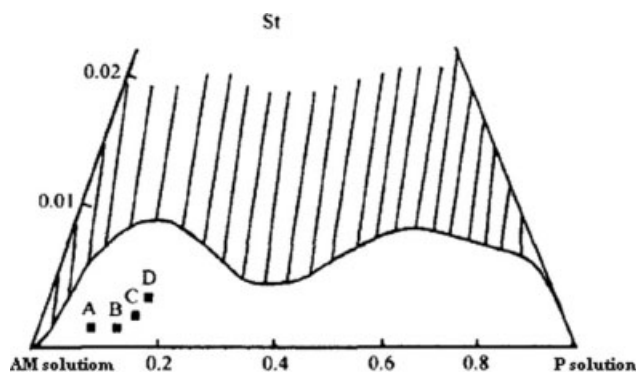
Figure 1 Phase diagram of three component microemulsion m (St) : m (AM): A 0.8 : 99.2; B 1.5 : 99.5; C 3 : 97.0; D 4 : 96.

large number of experiments showed that the mixture of methanol and water [V (methanol) : V (water) = 1 : 1.2] can totally dissolve lower molecular weight PAM-b-PSt ($M_n = 1 \times 10^4$ to 1×10^5 g/mol) and cannot dissolve higher molecular weight PAM-b-PSt ($M_n > 1 \times 10^5$ g/mol). The above obtained product was dealt with the mixture solution, and the process was repeated three times. Then higher molecular weight PAM-b-PSt was acquired.

Measurements

Infrared analysis was carried out on a Bruker Equinox 55 FTIR spectrometer and the spectra were recorded in the range of 4000 to 350 cm^{-1}. The gel permeation chromatography (GPC) experiments were carried out by passing N,N-dimethylformamide (DMF) solution of the polymers through a Waters Associates model 510 high-pressure chromatograph. A GPC calibration curve was obtained by using polystyrene standards. UV measurement was processed on a Shanghai Unic 2602 UV spectrophotometer. The St amount of the copolymer molecular chain was acquired by the UV spectrophotometer measurement.[10] Fluorescence spectra were attained from Shimadzu RF-540 fluorescence spectrophotometer. The thermal behavior was analyzed by a DSC calorimeter (DuPont DSC 910). The DSC scanning was performed at a heating rate of 20°C/min under inert atmosphere. The apparent viscosities of various polymer aqueous solutions were measured by using a Brookfield DV-II viscometer.

RESULTS AND DISCUSSION

Phase diagram of self-emulsifying microemulsion

The phase diagram of self-emulsifying microemulsion of AM aqueous solution (15 wt %), polymeric surfactant (lower molecular weight PAM-b-PSt) aqueous solution (5 wt %), and St is shown in Figure 1. The left coordinate is the weight percentage of

St and the region under critical curve is a microemulsion region in Figure 1. It is obvious that O/W microemulsion can be made by using polymeric surfactant.

Product of self-emulsifying microemulsion

The copolymerization was carried out and four self-emulsifying microemulsion systems were selected from Figure 1 (corresponding to A, B, C, and D points). The feed ratios of monomer, the amounts, and molecular weights of product were listed in Table I. In these systems, only 3 g polymeric surfactant was used, but at least 10 g SDS was used to disperse 0.25 g St (system D) into aqueous solution in the micelle or general microemulsion copolymerization using small molecule as surfactant.[11,14] The hydrophobic chains of amphiphilic block copolymer can cross-associate and a larger hydrophobic region was developed by using amphiphilic block copolymer as surfactant, which will make St disperse more easily. At the same time, PSt chain can be anchored on the microemulsion of St surface easily,[15] which is advantageous to develop stable microemulsion. As a result, the required amount of polymeric surfactant is less than the small molecular surfactant in the copolymerization of AM and St. It is obvious that the self-emulsifying microemulsion copolymerization has higher efficiency.

IR analysis

Figure 2 showed FTIR spectra of self-emulsifying microemulsion copolymer PAM-b-PSt (Spectrum a) and PAM homopolymer (Spectrum b). As illustrated in Figure 2, four new absorption peaks (at 1491, 1454, 768, and 699 cm^{-1}) were observed in the spectrum of PAM-b-PSt (Spectrum a) as compared with that of PAM homopolymer (Spectrum b). They are all characteristic absorbances of the phenyl group. Additionally, the peaks at 3361 and 1653 cm^{-1} corresponding to acrylamide group were also seen in Spectrum a. Therefore, it can be testified that the product is the copolymer of AM and St.

TABLE I
Copolymers from Self-Emulsifying Microemulsion

Sample	m (St) : m (Am)	Weight of polymer (g)	w (PSt) (%)	M_n[a]
A-0	0 : 100	5.89	0	1.37×10^5
A-0.8	0.8 : 99.2	5.71	0.67	1.23×10^5
A-1.5	1.5 : 98.5	5.84	1.38	1.48×10^5
A-3.0	3.0 : 97.0	5.93	2.81	1.34×10^5
A-4.0	4.0 : 96.0	5.90	3.64	1.62×10^5

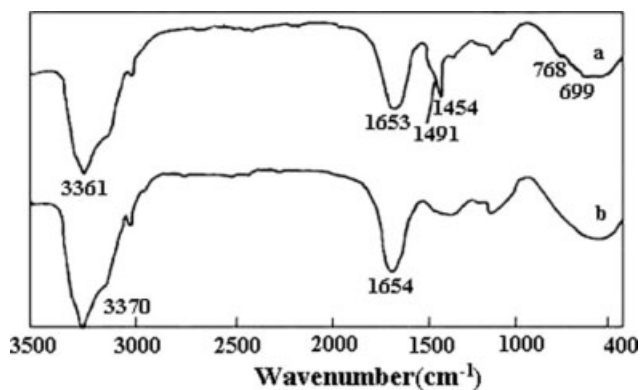Other conditions: polymeric surfactant, 3 g; Am, 6 g; initiator, 0.5 wt %.
[a] By GPC.

Figure 2 FTIR spectra of (a) self-emulsifying microemulsion copolymer PAM-*b*-PSt and (b) PAM homopolymer.

^{1}H-NMR and ^{13}C-NMR characterization

The ^{1}H-NMR spectrum of self-emulsifying microemulsion copolymer PAM-*b*-PSt is shown in Figure 3. It is evident that the peaks appear between 7.028 and 7.787 ppm, which is assigned to the protons of phenyl. Some peaks between 1.500 and 1.783 ppm are relative to the methylene protons of acrylamide and styrene chains; the peaks assigned to the methenyl protons of acrylamide and styrene appear between 2.105 and 2.446 ppm. Besides, the peaks at 4.716 ppm corresponding to the —CONH$_2$ protons of acrylamide are also observed in the ^{1}H-NMR spectrum.
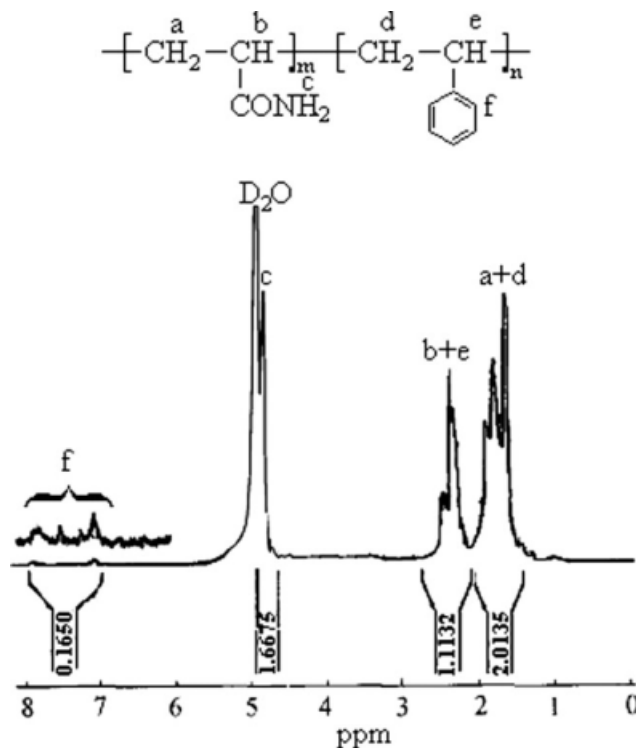

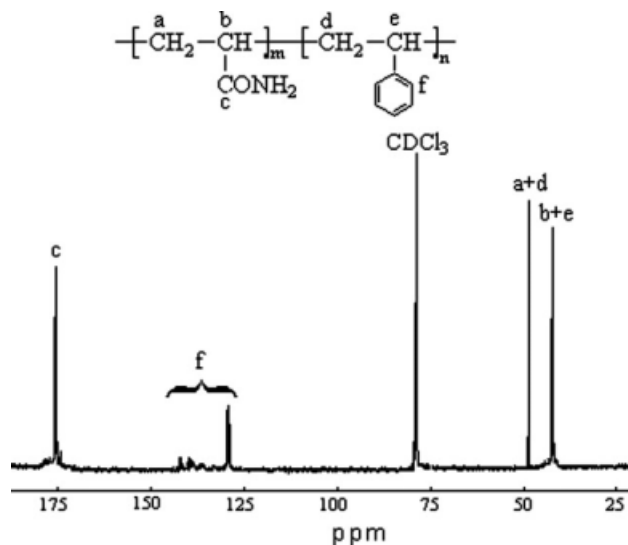**Figure 3** ^{1}H-NMR spectrum of self-emulsifying microemulsion copolymer PAM-*b*-PSt.

Figure 4 ^{13}C-NMR spectrum of self-emulsifying microemulsion copolymer PAM-*b*-PSt.

It can be seen further from the ^{13}C-NMR spectrum of self-emulsifying microemulsion copolymer PAM-*b*-PSt (Fig. 4) that several peaks from 127 to 140 ppm corresponding to aromatic carbons are observed. The peaks at 175 ppm are attributed to the carbons of C=O in the AM chains. The peaks centered at 40 ppm are assigned to the carbons of —CH—. The peaks at 48 ppm are attributed to the carbons of —CH$_2$—. It can be testified that the copolymer of AM and St had been prepared by the ^{1}H-NMR, ^{13}C-NMR, and IR analyses.

Hydrophobic association and block property of copolymer molecular chain

DSC analysis

The DSC measurement result was shown in Figure 5. It can be seen that the T_gs of PAM and PSt homopolymer are observed at 165 and 90°C, respectively.
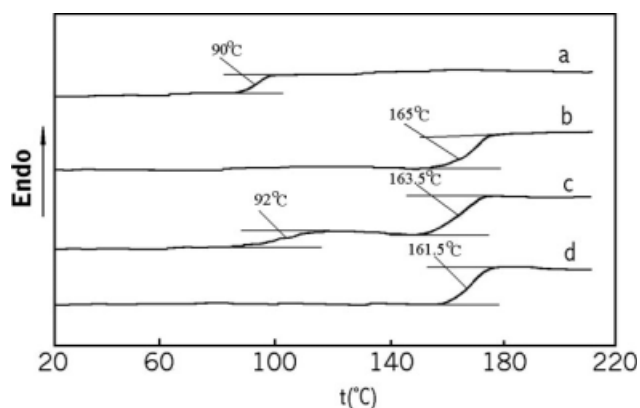

Figure 5 DSC curves of (a) PSt, (b) PAM, (c) self-emulsifying microemulsion copolymer PAM-b-PSt, (d) PAM-co-PSt.
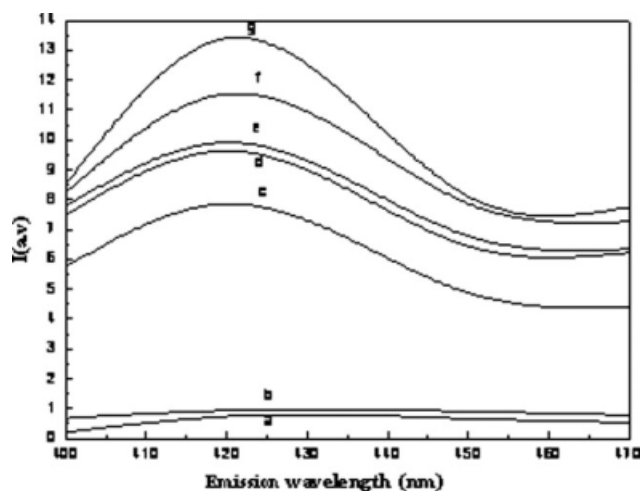
Figure 6 Emission spectra of PFN in various media: (a) in water; (b) in solution of PAM; (c) in micelle solution of SDS; (d) in solution of A-4.0; (e) in solution of A-3.0; (f) in solution of A-0.8; (g) in solution of A-1.5. Excitation wavelength: 360 nm. All of the contents of polymer in the polymer solutions are 0.5%, and the concentration of SDS is 10 times of CMC.

The copolymers having two segments can be random or block polymers. There is a T_g for random copolymers, and there are two T_gs for block copolymers. Generally said, the T_g of random copolymer is between the T_gs of the homopolymer. In Figure 5, a similar phenomenon can be found, and the T_g of random copolymer PAM-co-PSt can be observed at 161.5°C (between the T_g of PAM and PSt) in Figure 5. In addition, two transition temperatures (163.5 and 92°C) for the copolymer prepared by the self-emulsifying microemulsion copolymerization can be observed in Figure 5. The reason that the two T_gs is different from the T_g of PAM and PSt homopolymers is caused by the intramolecular interaction from PAM chains and PSt chains. Therefore, the copolymer prepared by the self-emulsifying prepared by the self-emulsifying microemulsion is block copolymer.

Fluorescence emission spectra of probe

Fluorescence emission spectra of PFN in the various media (excitation wavelength: 360 nm) were obtained by using a Shimadzu RF-540 fluorescence spectrophotometer. Figure 6 showed the fluorescence emission spectra of PFN in the various media. The fluorescence probe PFN was sensitive to the polarity of the environment,[9] and the weaker the polarity of the environment is, the stronger the fluorescence emission is. In Figure 6, it is clearly shown that the fluorescence emissions of the probe in water are weaker, but that in micelle solution of SDS is stronger. The reason is as follows. PFN is a hydrophobic substance and will spontaneously enter apolar

micelle kernel made of dodecyl chain, then will emit stronger fluorescence. The environment around PFN is nearly polar resulting from water in homopolymer PAM aqueous solution; as a result, the fluorescence emission of the probe in PAM aqueous solution is weaker. However, when dissolved in PAM-b-PSt 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 intramolecular or intermolecular association. PFN will enter hydrophobic microdomains, thus giving rise to strong fluorescence emission. It can be also seen from Figure 6 that the fluorescence intensity varied with different St weight percentage. This shows that hydrophobic association of PAM-b-PSt is correlated with its composition.

Figure 7 is the plot of the intensity of maximum fluorescence emission of probe at emission wavelength (λ = 420 nm) against the content of PSt block in copolymer. The influence of the content of PSt blocks in the copolymer on hydrophobic association behavior is revealed more clearly in Figure 7. When the content of hydrophobic blocks of PSt was smaller (A-0.8), intermolecular associations were weaker and hydrophobic microdomains were smaller, so the fluorescence emission intensity of PFN was smaller. When the content of hydrophobic blocks of PSt was in excess (A-3.0 and A-4.0), the tendency of associations of hydrophobic blocks in the molecular chain increased (12), which is favorable for intramolecular hydrophobic associations and weakens the intermolecular associations, so the size of hydrophobic microdomains decreased as a whole, and the fluorescence emission intensity of PFN also became smaller. When the content of hydrophobic blocks of PSt was right (A-1.5), intermolecular associations were the most advantageous so they were the largest
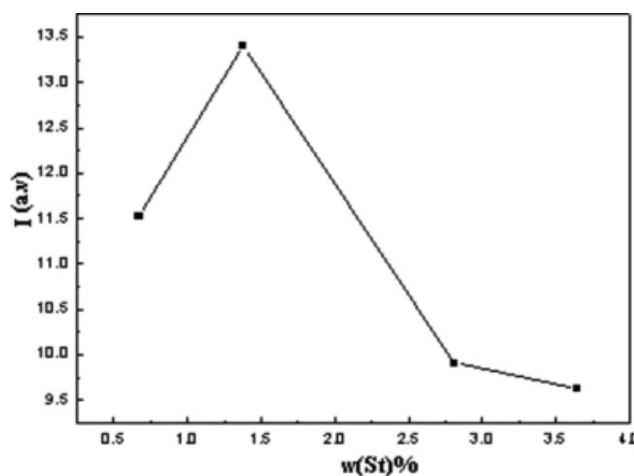

Figure 7 Plot of maximum emission intensity of PFN (λ = 420 nm) vs. the weight percentage of PSt in copolymers.

hydrophobic microdomains, and the fluorescence emission of the probe was the strongest.

Apparent viscosity of copolymer aqueous solution

The apparent viscosities of PAM-*b*-PSt prepared by self-emulsifying microemulsion and PAM homopolymer aqueous solution are shown in Figure 8. The three following laws can be seen from Figure 8:

1. The apparent viscosities of PAM-*b*-PSt aqueous solution were larger than PAM aqueous solution. The reason is that the hydrophobic blocks of PSt in the molecular chains of the copolymer PAM-*b*-PSt form hydrophobic association, and larger intermolecular physical cross network is developed and hydromechanical volume of macromolecule chain is increased, which lead to appear higher apparent viscosity.
2. The apparent viscosity increased with the increment of copolymer concentration when copolymer concentration is higher than critical value (about 0.2%). Before critical concentration, the hydrophobic association in PAM-*b*-PSt chain is favorable for intramolecular associations. Above critical concentration, intermolecular associations are the most advantageous, with the increment of copolymer concentration and intermolecular hydrophobic associations becoming stronger.[4,12] It shows that the apparent viscosity increases fast. However, the change of the apparent viscosity of PAM aqueous solution was not evident with the increasing concentration. The reason is that PAM chains cannot develop intermolecular associations.
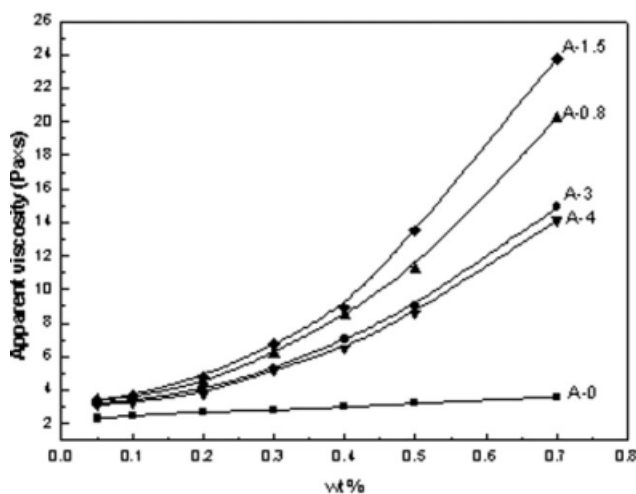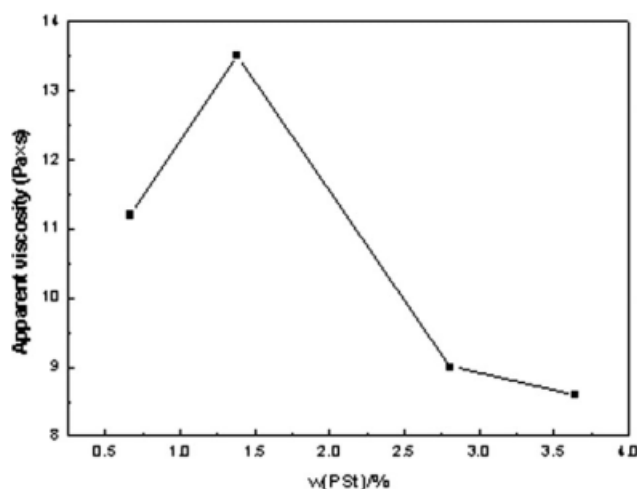
Figure 9 Plot of apparent viscosity of copolymer aqueous solution vs. PSt content in copolymers.

3. The apparent viscosity was correlated with copolymer composition. The apparent viscosity of PAM-*b*-PSt (A-1.5) with 1.38% St (weight percentage) was the largest.

Further, the plots of the apparent viscosity of copolymer aqueous solution with 0.5% (weight percentage) in Figure 8 against content of PSt blocks in copolymer were drawn, and the result is shown in Figure 9. It can be clearly seen that the apparent viscosity of copolymer aqueous solution increases earlier and decreases afterward with the increment of PSt weight percentage of the chain. The reason is that when the content of PSt hydrophobic chain in the copolymer is less, intermolecular associations are weaker, so the apparent viscosity is smaller; when the content of hydrophobic blocks of PSt increases, intermolecular associations become stronger, so the apparent viscosity become larger. When the content of hydrophobic blocks of PSt is excessive, intermolecular associations are weakened by larger PSt self association, so the apparent viscosity also falls.

CONCLUSIONS

The amphiphilic block copolymers of PAM-*b*-PSt were synthesized by the self-emulsifying microemulsion method. The structure of the prepared copolymers was characterized by FTIR, ^{1}H-NMR, UV, and DSC. The self-emulsion microemulsion method cannot only avoid complicated back operation of small surfactant but also has higher copolymerization efficiency. The prepared copolymers have good hydrophobic association property.

Figure 8 Effects of polymer concentration on the apparent viscosity of its aqueous solution. Temperature (25°C ± 0.1°C), shear rate 6 s^{-1}.

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