Preparation of Hydrophobic Association Polyacrylamide in a New Micellar Copolymerization System and Its Hydrophobically Associative Property

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ABSTRACT: This paper describes for the first time the combination of a polymerizable surfactant, sodium 2-acrylamido-dodecane sulfonate ($NaAMC_{12}S$), and a hydrophobic monomer to prepare water-soluble associating polymer via a new micellar process. In this method, the hydrophobic monomer, *N*-dodecylacrylamide ($C_{12}AM$) or *N*,*N*-didodecylacrylamide ($DiC_{12}AM$), was first solubilized within $NaAMC_{12}S$ micelles, whereas the hydrophilic monomer acrylamide (AM) was dissolved in the aqueous continuous medium. The micellar copolymerization, therefore, resulted in a ternary hydrophobic association polyacrylamide (HAPAM), namely, $C_{12}AM/NaAMC_{12}S/AM$ or $DiC_{12}AM/NaAMC_{12}S/AM$. The chemical structures of these ternary copolymers were characterized with Fourier transform infrared (FTIR) spectroscopy, and their hydrophobic associative behavior as well as the relationship between microstructure and hydrophobic associative property was studied by a combination of the fluorescence probe technique and viscosimetry. The experimental result shows, with the presented polymerizable surfactant or surface-active monomer $NaAMC_{12}S$, the micellar copolymerization of AM and hydrophobic monomer can be favorably realized. In addition, the surface-active monomer can be incorporated into the polymer backbone to result in the ternary copolymers, which show a much stronger hydrophobic associative property in comparison with the binary copolymer obtained in the conventional micellar copolymerization system with common surfactants. More importantly, this new micellar copolymerization system is simple because the complicated process to remove the surfactant is avoided. We found that the hydrophobic associative property of the obtained ternary HAPAM is strongly affected by the hydrophobe content and the length of hydrophobic microblocks in the polymer backbone.

1. Introduction

Polymerizable surfactants are a kind of functional surfactant. Their molecules not only have amphiphilic structure composed of a hydrophobic tail and hydrophilic headgroup but also contain polymerizable vinyl double bonds.[1,2] The special molecular architecture imparts them unique physicochemical properties: analogous to common surfactants, they have surface activity; similar to general vinyl monomers, they can be initiated by initiators and can be polymerized. Thus, they are called surface-active monomers by academia, or as a short form, "surfmers". The amphipathic property and polymerizability of surfmers lead to their wide applications in many science and technology fields. For example, surfmers can be used to prepare vesicles for performing biological simulation, to prepare functional polymer microspheres, to construct a soft template for synthesizing functional inorganic nanomaterials and inorganic/organic composite nanomaterials, to improve emulsion polymerization as polymerizable emulsifiers, and so on.[3–6] Especially, in the improvement of emulsion polymerization, surfmers play an active role.[7,8] The conventional emulsion polymerization system in which the common surfactants are used as emulsifiers has some drawbacks, such as poor stability of the latexes because the emulsifier attaches on the latex particle only in a physical manner, and some negative effects of the residual emulsifier for the property of the final film products.[9,10] To overcome these drawbacks, the conventional emulsion polymerization has been improved by using surfmers to substitute common surfactants. Surfmers not only play a role of emulsifier, but they also are copolymerized and then they are strongly attached onto the latex particles with covalent linkage, resulting in better stability of latexes and fine behavior of the final film products.[7,8]

Hydrophobically modified polyacrylamide (HMPAM) or hydrophobically associating polyacrylamide (HAPAM), with a small amount (generally less than 2 mol %) of hydrophobic monomer incorporated into the polymer backbone,[11,12] has received increasing attention on account of its unique rheological characteristics and applications, such as in enhanced oil recovery, drilling fluids, and coating.[13–15] One major difficulty in the synthesis of HMPAM originates from the insolubility of hydrophobic comonomers in water.[16,17] Up to now, most of researchers adapted the micellar copolymerization technique to prepare HMPAM. In this system, the hydrophobic comonomer is solubilized within the micelles and then copolymerized with the dissolved acrylamide (AM) in the aqueous solution, resulting in HMPAM with microblocky structure.[18,19] However, the conventional micellar copolymerization has some shortcomings.[20,21] For example, it needs to undergo the complicated post-treatment process to remove surfactants in order to obtain pure copolymer products. Besides, the common surfactants and their impurity will produce negative effects on the polymerization process.

Can the conventional micellar copolymerization be innovated by adopting surfmers instead of the conventional surfactants? Can HAPAM with better performance be prepared with a simpler procedure? This work just addresses these issues. Previously, we have synthesized some surfmers and studied their properties.[22,23] Here, we extend our works by applying a surfmer, sodium 2-acrylamido-dodecane sulfonate ($NaAMC_{12}S$), to copolymerize with AM and a strong hydrophobic comonomer, *N*-dodecylacrylamide ($C_{12}AM$) or *N*,*N*-didodecylacrylamide ($DiC_{12}AM$), in a new micellar copolymerization system. Two ternary copolymers, $C_{12}AM/NaAMC_{12}S/AM$ and $DiC_{12}AM/NaAMC_{12}S/AM$ are obtained because $NaAMC_{12}S$ can be incorporated into the copolymer backbone. The chemical structures of the two hydrophobic monomers, $C_{12}AM$ and

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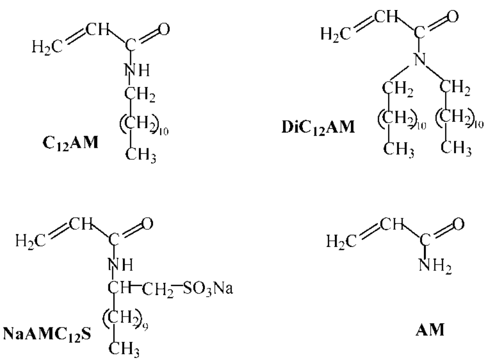
Scheme 1. Chemical Structures of Monomers and Surfmer



DiC$_{12}$AM, the surfmer NaAMC$_{12}$S, and AM are given in Scheme 1. It was found that, for the HAPAM obtained by copolymerization with twin-tail-type hydrophobic monomers, acrylamide DiC$_{12}$AM, the hydrophobic association behavior of the final terpolymer was greatly enhanced.[24,25] It is expected because there are two long hydrocarbon chains on the N atom in its molecule that the ternary copolymer DiC$_{12}$AM/NaAMC$_{12}$S/AM should produce a higher hydrophobic association property. To our knowledge, this is the first report on preparing water-soluble HAPAM with high performance in the new micellar copolymerization system.

On the other hand, the relationship between the chain structure and hydrophobically associativity for the ternary copolymers was also researched here. In conventional micellar copolymerization systems, in order to examine the effect of the chain structure on the hydrophobic associative property of HMPAM, the average hydrophobic microblock length is usually controlled by the number (N_H) of hydrophobic monomer molecules per micelle by varying the concentration ratio of hydrophobic monomer to surfactant.[17,19,26,27] Moreover, in this new micellar system, the hydrophobic microblock length in the copolymer chains was controlled by adding different amounts of NaCl electrolyte because it can change the micellar aggregation number of the surfactant NaAMC$_{12}$S.[22] In this way, we can change the solubilization amount of the hydrophobic monomer before copolymerization, which consequently changes the hydrophobic microblock length of HMPAM.

2. Experimental Section

2.1. Materials and Instruments. *N*-Dodecylacrylamide (C$_{12}$AM) and *N*,*N*-didodecylacrylamide (DiC$_{12}$AM) were self-synthesized as reported before.[28] Sodium 2-acrylamido-dodecane sulfonate (NaAMC$_{12}$S) was prepared according to the procedures described in ref 22. Acrylamide (Merck) was twice recrystallized from chloroform. Potassium persulfate (Aldrich) was used without further purification. Sodium dodecyl sulfate (SDS, Guanghua Science and Technology Co. Ltd., Shanghai). Pyrene (Aldrich) was recrystallized twice from ethonal before use. The water used here was deionized and then distilled. All other chemicals were of analytical grades.

A 721 spectrophotometer (The Third Analytical Instrument Factory of Shanghai) was used for determining the transmittance of the micellar solution in which hydrophobic monomer was solubilized. The infrared spectra of copolymers were determined using a Perkin-Elmer 1700 infrared spectrometer (Perkin-Elmer Company, U.S.). The apparent viscosities of copolymer solutions were measured using a NDJ-1 rotation viscosimeter (Shanghai Balance Plant), and the fluorescence emission spectra of the probe pyrene in aqueous solutions were determined with a HITACHI F-2500 fluorescence spectrophotometer (HITACHI Company, Japan). A THZ-82 constant temperature shaker equipped with a gas bath made in China was used.

2.2. Measuring the Solubilization Property of C$_{12}$AM and D$_i$C$_{12}$AM in Two Micellar Solutions with Nephelometry. Measuring the solubilization amount of C$_{12}$AM in SDS micellar solution: The aqueous solutions of SDS with different concentrations were prepared above the critical micellar concentration (cmc $= 87.1 \times 10^{-4}$ mol/L at 40 °C); 0.01 g of C$_{12}$AM was added serially into a conical flask containing SDS micellar solution with a certain concentration and with a certain volume, and the flask was shaken on a shaker to make C$_{12}$AM fully solubilized; after standing, the transmittance was determined at a fixed wavelength on a spectrophotometer, and the transmittance as a function of the added amount of C$_{12}$AM was plotted; the solubilization amount (mmol/100 mL) of C$_{12}$AM in SDS micellar solution with a certain concentration was determined by the curve break. With the same procedure, the solubilization amounts of C$_{12}$AM in SDS micellar solutions with different concentrations were determined, and the solubilization amount of C$_{12}$AM as a function of SDS concentration was figured; i.e., the solubilization curve was obtained.

According to the same procedures as described above, the solubilization curve of C$_{12}$AM in NaAMC$_{12}$S micellar solutions (cmc $= 10.2 \times 10^{-3}$ mol/L at 40 °C[22]) and the solubilization curves of DiC$_{12}$AM in SDS and NaAMC$_{12}$S micellar solutions were obtained, respectively.

2.3. Preparing HAPAM in NaAMC$_{12}$S Micellar Solution. *2.3.1. Using C$_{12}$AM as a Hydrophobic Monomer.* A certain volume of NaAMC$_{12}$S micellar solution with a certain concentration (the correlative data will be listed in a below table) was poured into a four-necked flask equipped with a mechanical agitator, a reflux condenser, a thermometer, and a N$_2$ inlet. With a total monomer concentration of 6 wt %, AM and C$_{12}$AM in proper molar ratio were added into the micellar solution (the added amount of C$_{12}$AM must be in the solubilization range, and C$_{12}$AM is ensured to be solubilized within the micelles). After stirring, AM was dissolved and C$_{12}$AM was solubilized. Using $K_2S_2O_8$ as initiator and under N$_2$ atmosphere, the copolymerization was carried out at a constant temperature of 45 °C for 5 h. The resultant copolymers, C$_{12}$AM/NaAMC$_{12}$S/AM, were precipitated out with ethanol and washed with ethanol. They were dried under vacuum. With variation of the copolymerization conditions, the terpolymers C$_{12}$AM/NaAMC$_{12}$S/AM with serially changed microstructures were prepared.

In order to compare the new micellar copolymerization system with the conventional micellar copolymerization system, the micellar copolymerization of AM and C$_{12}$AM was performed in SDS micellar solution, and the bipolymer C$_{12}$AM/AM was gained.

2.3.2. Using DiC$_{12}$AM as a Hydrophobic Monomer. With the same procedures as that of preparing terpolymer containing C$_{12}$AM, the terpolymer DiC$_{12}$AM/NaAMC$_{12}$S/AM was obtained. With variation of the copolymerization conditions, the terpolymers DiC$_{12}$AM/NaAMC$_{12}$S/AM with serially changed microstructures were also prepared. Similarly, in the conventional SDS micellar solution, the bipolymer DiC$_{12}$AM/AM was also prepared for comparison.

2.4. Copolymer Characterization. The infrared spectra of various copolymers were determined with the KBr pellet method to characterize their chemical structures.

The molecular weights of copolymers were characterized relatively with intrinsic viscosities, and the intrinsic viscosities of copolymers were determined as follows. Using the aqueous solution of NaCl with a concentration of 1 mol/L as the solvent and at a constant temperature of 30.0 ± 0.1 °C, the viscosities of the aqueous solutions of copolymers were measured with a Ubbelohde viscometer, the intrinsic viscosities $[\eta]$ of copolymers were obtained with the dilution extrapolation method, and the molecular weights of copolymers were expressed with the intrinsic viscosities $[\eta]$ correspondingly. However, it should be pointed out that this treatment only is an approximate and coarse method due to the effect of intramolecular hydrophobic interaction on the determination of the viscosity-average molecular weight of HAPAM.

2.5. Measuring the Apparent Viscosity of Copolymer Aqueous Solutions. Copolymer sample was weighed accurately, swollen in distilled water for 3 days, and then placed on a constant temperature shaker and shaken for 10–12 days to make sure the copolymer was completely dissolved. Afterward, the solution was diluted and copolymer aqueous solutions with different concentra-

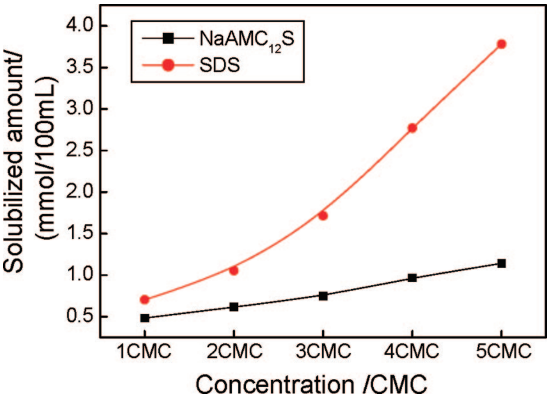


Figure 1. Plot of solubilized amount of $C_{12}AM$ vs concentration of SDS or $NaAMC_{12}S$. Temperature: 40.0 ± 0.5 °C.

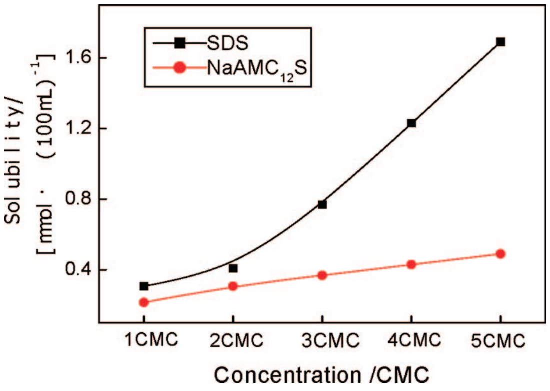


Figure 2. Plot of solubilized amount of $DiC_{12}AM$ vs concentration of SDS or $NaAMC_{12}S$. Temperature: 40.0 ± 0.5 °C.

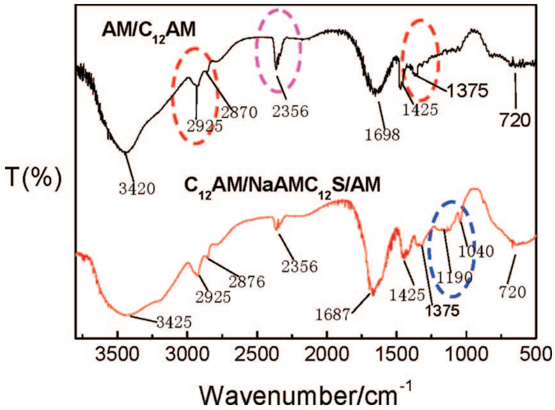


Figure 3. Fourier transform infrared (FTIR) spectra of copolymers $C_{12}AM/AM$ and $C_{12}AM$/ $NaAMC_{12}S/AM$.

tions were prepared. The apparent viscosities of various copolymer solutions were determined at a constant temperature of 30.0 ± 0.5 °C with a rotary viscosimeter at a low speed of 6 s^{-1}.

2.6. Determining Fluorescence Spectra of the Probe Pyrene in Copolymer Solutions. The saturated aqueous solution of pyrene (the concentration of pyrene was about 7×10^{-7} $mol \cdot L^{-1}$) was prepared with redistilled water. Copolymer samples were dissolved in the saturated aqueous solution of pyrene. These copolymer solutions were further diluted with the saturated aqueous solution of pyrene, and the final copolymer solutions with different concentrations, which contain the probe pyrene, were prepared. The fluorescence spectra of the probe pyrene in various copolymer solutions were determined at 25 °C with excitation at 335 nm, with a slit width of 2.5 nm, and in a scanning range of 350−450 nm. The ratios (I_1/I_3) of the strength of the first peak to that of the third peak in pyrene emission spectra were calculated.

3. Results and Discussion

3.1. Solubilization Property of $C_{12}AM$ and $DiC_{12}AM$ in Micellar Solutions of Two Surfactants. The solubilization amounts of hydrophobic monomer $C_{12}AM$ in SDS and $NaAMC_{12}S$ micellar solutions with different concentrations (expressed as the multiple of cmc) were determined, respectively. The relationship curves between the solubilization amount and the concentration of the surfactant (SDS or $NaAMC_{12}S$) are shown in Figure 1 (i.e., the solubilization curve of $C_{12}AM$). Similarly, the solubilization amounts of the twin-tailed acrylamide $DiC_{12}AM$ in SDS and $NaAMC_{12}S$ micellar solutions with different concentrations were determined, and the solubilization curves of $DiC_{12}AM$ are given in Figure 2.

Figure 1 shows that the solubilization amount of $C_{12}AM$ increases with increasing concentration of the micellar solution. This is reasonable because the number of the micelle increases with the increase of the surfactant concentration and it results in the enhancement of the solubilization amount of $C_{12}AM$. Additionally, the solubilization amount of $C_{12}AM$ in $NaAMC_{12}S$ micellar solution is much smaller than that in SDS micellar solution, although the same hydrocarbon chain (dodecyl group) is contained in both molecules of $NaAMC_{12}S$ and SDS. The reason for this is that there are two hydrophilic groups in the $NaAMC_{12}S$ molecule (sulfonic group and acrylamino group), resulting in a smaller aggregation number (N_{agg}) of $NaAMC_{12}S$ micelle than that of SDS micelle (N_{agg} of the former is about 12,[22] and that of the latter is about 62), and the smaller aggregation number (N_{agg}) of $NaAMC_{12}S$ leads to the lower solubilization amount of $C_{12}AM$ in its micellar solution.

The above status also can be seen in Figure 2. Besides, by comparing Figure 2 with Figure 1, it can be found that in the micellar solutions with the same surfactant concentration, the solubilization amount of *N*,*N*-disubstituted acrylamide $DiC_{12}AM$ is smaller than that of *N*-monosubstituted acrylamide $C_{12}AM$. The reason for this is that there are two dodecyl hydrocarbon chains on the N atom of the acylamino group in the $DiC_{12}AM$ molecule, and the greater molecule size leads to the smaller solubilization amount.

On the basis of the above solubilization data, new micellar copolymerization systems were constituted by using the micellar solution of $NaAMC_{12}S$, and copolymerizations were conducted, resulting in the terpolymers $C_{12}AM/NaAMC_{12}S/AM$ and $DiC_{12}AM/NaAMC_{12}S/AM$. Simultaneously, in the conventional micellar solution of SDS, copolymerizations were also carried out and the bipolymers $C_{12}AM/AM$ and $DiC_{12}AM/AM$ were prepared for comparison.

3.2. Infrared Spectra of Copolymers. In Figure 3, the infrared spectra of the bipolymer and terpolymer containing $C_{12}AM$ are displayed, whereas, in Figure 4, the infrared spectra of the bipolymer and terpolymer containing $DiC_{12}AM$ are shown.

It can be seen from Figure 3 that there are the characteristic absorptions of acylamino groups on the two spectral curves, including the bands at about 3400, 1690, and 1423 cm^{-1}. On the curve of $C_{12}AM/AM$, the bands at 1425 and 720 cm^{-1} are attributed to the characteristic absorptions of methylene $-CH_2-$. The band at 2356 cm^{-1} is related to secondary acylamino probably, whereas the bands at 2870 and 2925 cm^{-1} are ascribed to symmetrical and asymmetrical stretching vibration absorptions of methyl $-CH_3$, respectively. The band at 1375 cm^{-1} is the symmetrical bending vibration absorption of methyl $-CH_3$. Just because $C_{12}AM$ is incorporated into the main chain of the copolymer, the above characteristic absorptions of secondary acylamino and methyl $-CH_3$ appear. The appearance of the above four bands indicates the formation of bipolymer $C_{12}AM$/

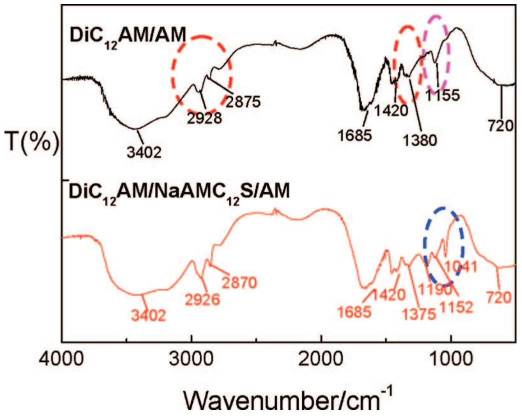


Figure 4. FTIR spectra of copolymers DiC$_{12}$AM/AM and DiC$_{12}$AM/NaAMC$_{12}$S/AM.

AM which is prepared in the micellar solution of SDS. On the curve of C$_{12}$AM/NaAMC$_{12}$S/AM which is prepared in the micellar solution of NaAMC$_{12}$S, the bands at 1190 and 1040 cm^{-1} are attributed to the characteristic absorption of sulfonic acid group, and their appearance implies that NaAMC$_{12}$S has been incorporated into the main chain of the copolymer and terpolymer C$_{12}$AM/NaAMC$_{12}$S/AM has been formed.

Analogous to curves in Figure 3, on the curve of DiC$_{12}$AM/AM which is prepared in the micellar solution of SDS, the characteristic absorptions of acylamino groups appear at 3402, 1685, and 1420 cm^{-1}. The characteristic absorptions of methylene $-CH_2-$ are at 1420 and 720 cm^{-1}, and the characteristic absorptions of methyl $-CH_3$ are at 2875, 2928, and 1380 cm^{-1}. A special band appears at 1155 cm^{-1}, and it is ascribed to the stretching vibration absorption of the C$-$N bond of the tertiary acylamino group. The above characteristic absorptions of the methyl $-CH_3$ and C$-$N bond of the tertiary acylamino group suggest that DiC$_{12}$AM has been incorporated into the main chain of the copolymer and the bipolymer DiC$_{12}$AM/AM has been formed. Similarly, on the curve of C$_{12}$AM/NaAMC$_{12}$S/AM which is prepared in the micellar solution of NaAMC$_{12}$S, the characteristic absorptions of a sulfonic acid group appear at 1190 and 1041 cm^{-1}, and this fact proves that terpolymer DiC$_{12}$AM/NaAMC$_{12}$S/AM has been formed.

3.3. Copolymerization Mechanism in the New Micellar Copolymerization System and Property of HAPAM.

3.3.1. Copolymerization Mechanism. The HAPAM prepared by micellar copolymerization has microblocky structure; namely, the hydrophobic monomer is distributed along the copolymer backbone in a microblocky manner.[17,18] In the micellar copolymerization system, the hydrophobic monomer is solubilized within surfactant micelles, whereas AM is dissolved in the aqueous continuous medium. AM first is initiated and polymerized by the water-soluble initiator. When a growing radical moves and encounters a micelle, the hydrophobic monomers within the micelle are immediately polymerized and they are incorporated in the main chain of polymer in batches due to their high local concentration, resulting in the hydrophobic microblocky structure of the copolymer. Hance, in SDS micellar solution, the product of the copolymerization of AM and C$_{12}$AM (or DiC$_{12}$AM) is bipolymer C$_{12}$AM/AM (or DiC$_{12}$AM/AM), in whose backbone C$_{12}$AM (or DiC$_{12}$AM) is distributed in a microblocky manner. The copolymerization mechanism is illustrated in Figure 5.[17,18]

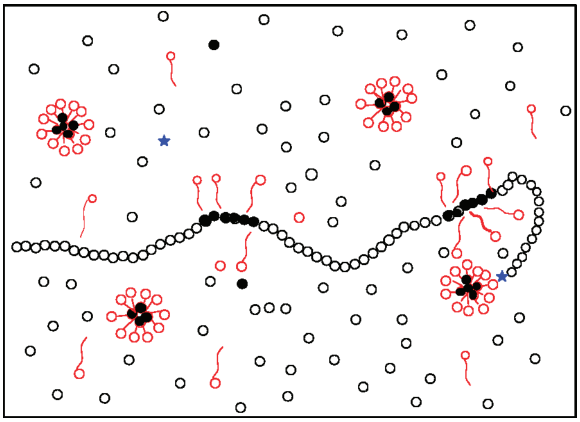


Figure 5. Schematic representation of the micellar copolymerization mechanism in the conventional micellar system: ○, water-soluble monomer; ●, hydrophobic monomer; red circles with attached line, surfactant.

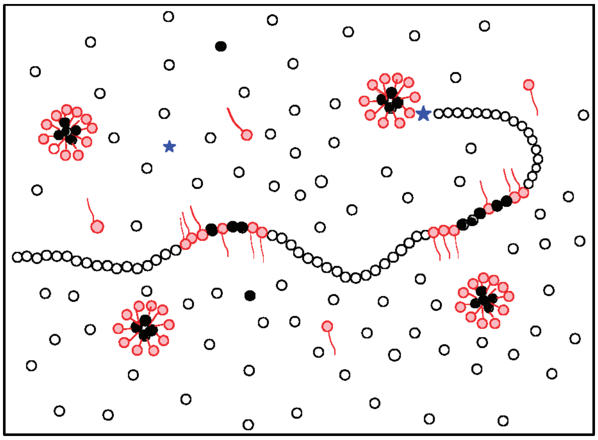


Figure 6. Schematic representation of the micellar copolymerization mechanism in the new micellar system: ○, water-soluble monomer; ●, hydrophobic monomer; red circles with attached line, surfmer.

However, in NaAMC$_{12}$S micellar solution, the copolymerization mechanism is different from that in SDS micellar solution. When a growing radical of PAM moves and encounters a micelle, both of the hydrophobic monomers within the micelle, C$_{12}$AM and NaAMC$_{12}$S or DiC$_{12}$AM and NaAMC$_{12}$S, are immediately polymerized and they are all together incorporated in the main chain of polymer in batches, resulting in the hydrophobic microblocky structure. It is obvious that the microblock consists of two kinds of monomer, hydrophobic monomer C$_{12}$AM or DiC$_{12}$AM and surface-active monomer NaAMC$_{12}$S, and the copolymerization product is the terpolymer, C$_{12}$AM/NaAMC$_{12}$S/AM or DiC$_{12}$AM/NaAMC$_{12}$S/AM. The copolymerization mechanism in the new micellar copolymerization system can be illustrated in Figure 6.

3.3.2. Hydrophobic Association Property of HAPAM Prepared in the New System. Under basically identical conditions, bipolymers and terpolymers were prepared in two kinds of micellar solutions, the conventional micellar solution of SDS and the new micellar solution of NaAMC$_{12}$S, respectively. The correlative data are listed in Table 1.

The bipolymer BiCP-1 and terpolymer TerCP-1 were prepared with *N*-monosubstituted acrylamide C$_{12}$AM as hydrophobic monomer under basically identical conditions in two copolymerization systems, as shown in Table 1. The variation of the apparent viscosity of their aqueous solutions with copolymer concentration is given in Figure 7. Similarly, the bipolymer BiCP-2 and terpolymer TerCP-2 were prepared with *N*,*N*-disubstituted acrylamide DiC$_{12}$AM as hydrophobic monomer under basically identical conditions in two copolymerization systems, and the variation of the apparent viscosity of their aqueous solutions with copolymer concentration is shown in Figure 8.

Table 1. Correlative Data for Contrast Groups of Copolymers

	copolymer	feed ratio AM (mol %)	feed ratio SDS or NaAMC$_{12}$S (mol %)	feed ratio hydrophobe (mol %)	amount of $K_2S_2O_8$ (wt %)	[η]
BiCP-1	C$_{12}$AM/AM	96.3	3.5	0.2	0.5	763.5
BiCP-2	DiC$_{12}$AM/AM	96.3	3.5	0.2	0.5	620.6
TerCP-1	C$_{12}$AM/NaAMC$_{12}$S/AM	96.3	3.5	0.2	0.5	652.2
TerCP-2	DiC$_{12}$AM/NaAMC$_{12}$S/AM	96.3	3.5	0.2	0.5	520.5

It is seen clearly from Figures 7 and 8 that the apparent viscosities of TerCP solutions are higher than those of BiCP solutions. The reason is due to the fact that, for the terpolymer, surfmer is copolymerized and incorporated into the polymer backbone, and the total hydrophobe content is increased from 0.2 mol % (bipolymer) to 3.7 mol % (terpolymer), resulting in a stronger hydrophobic association property. Obviously, to constitute the new micellar copolymerization system using surfmer instead of common surfactant is advantageous to the enhancement of the association property of HAPAM.

By comparing Figure 8 with Figure 7, it still can be found that the HAPAM containing the twin tail-type acrylamide DiC$_{12}$AM has a much stronger associative property than that of the HAPAM containing the mono tail-type acrylamide C$_{12}$AM. The terpolymer DiC$_{12}$AM/NaAMC$_{12}$S/AM in Figure 8 and the terpolymer C$_{12}$AM/NaAMC$_{12}$S/AM in Figure 7 have nearly identical compositions, as indicated in Table 1: 0.2 mol % of hydrophobic monomer, 3.5 mol % of surfmer, and 96.3 mol % of acrylamide. However, the apparent viscosities of their aqueous solutions have great differences. For instance, with a copolymer concentration of 0.25%, the apparent viscosity of the aqueous solution of DiC$_{12}$AM/NaAMC$_{12}$S/AM is 6 times as great as that of C$_{12}$AM/NaAMC$_{12}$S/AM, and they are 277 and 46.2 mPa s^{-1}, respectively. Only 0.2 mol % of DiC$_{12}$AM is contained in C$_{12}$AM/NaAMC$_{12}$S/AM, but an unusual thickening property is exhibited. Apparently, because there are two hydrocarbon chains in the molecule of twin-tailed acrylamide, the hydrophobic microblocks of the tercopolymer have denser hydrophobic side chains, leading to a high association property of HAPAM.

3.4. Effects of Two Kinds of Monomers on the Rheological Behavior of Terpolymer. As described above, the incorporation of surfmer enhances the association property of the terpolymers. However, which is the main contributor for the strong thickening property of the terpolymer between the two kinds of monomers, hydrophobic monomer or surfmer? For comparison, in the new micellar copolymerization system consisting of NaAMC$_{12}$S, C$_{12}$AM, and AM, with a fixed total monomer feed amount (mole) of C$_{12}$AM and NaAMC$_{12}$S, via changing the proportions of NaAMC$_{12}$S and C$_{12}$AM in series, terpolymers C$_{12}$AM/NaAMC$_{12}$S/AM with different compositions were prepared and they are designated as series A. The relevant data are listed in Table 2. The relationship curves between the apparent viscosity of the terpolymer solutions and concentration for the copolymers of series A are given in Figure 9.

It can be found from Figure 9 that the viscosity increases with the increase of C$_{12}$AM feed. In other words, the viscosity increases with the decrease of NaAMC$_{12}$S feed under the condition of a fixed total feed amount of C$_{12}$AM and NaAMC$_{12}$S. Obviously, the strong hydrophobic monomer C$_{12}$AM is the main contributor for the rheological behavior of the terpolymer C$_{12}$AM/NaAMC$_{12}$S/AM. Although the molecule of NaAMC$_{12}$S contains the same hydrocarbon chain (dodecyl) as the molecule of C$_{12}$AM, two hydrophilic groups in its molecule,[22] acylamino group and sulfonic acid group, lead to the poorer hydrophobic associativity of its molecule. As a result, the contribution of NaAMC$_{12}$S for the rheological behavior of the terpolymer is smaller and secondary with respect to that of C$_{12}$AM.

3.5. Effects of Microstructures on the Hydrophobic Associative Property of Terpolymer. *3.5.1. Terpolymer DiC$_{12}$AM/NaAMC$_{12}$S/AM with Different Microstructures.* The content of the hydrophobe and the length of the hydrophobic mictoblock are two main factors affecting the hydrophobic association property of HAPAM.[17] In the new micellar copolymerization system consisting of NaAMC$_{12}$S, DiC$_{12}$AM, and AM, by varying the copolymerization conditions, two series of terpolymer DiC$_{12}$AM/NaAMC$_{12}$S/AM with serially changed microstructures were prepared, and they are designated as series B and series C, respectively. The correlative data are listed in Table 3.

For the terpolymers of series B, the feed amount of DiC$_{12}$AM is gradually increased in turn, so the content of the hydrophobe is progressively increased according to priority.

By changing the added amount of NaCl, the terpolymers of series C were prepared. NaAMC$_{12}$S is an ionic surfactant, so the addition of electrolyte can increase the aggregation number (N_{agg}) of its micelle[29–31] and can increase the solubilization amount of DiC$_{12}$AM before copolymerization. Therefore, the length of the hydrophobic microblocks of the terpolymer can

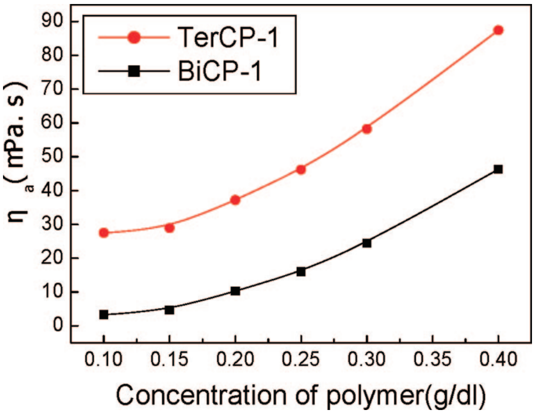


Figure 7. Apparent viscosity of aqueous solution as a function of copolymer concentration for BiCP-1 andTerCP-1. Temperature: 30.0 ± 0.5 °C. Shear rate: 6 s^{-1}.

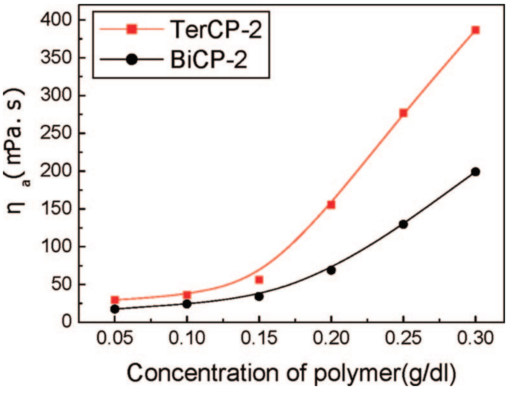


Figure 8. Apparent viscosity of aqueous solution as a function of copolymer concentration for BiCP-2 andTerCP-2. Temperature: 30.0 ± 0.5 °C. Shear rate: 6 s^{-1}.

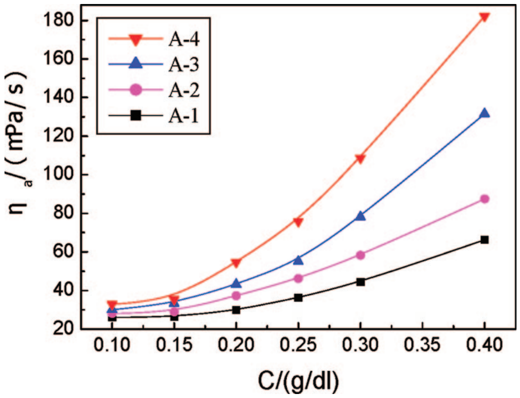


Figure 9. Apparent viscosity of copolymer aqueous solution vs polymer concentration for series A. Temperature: 30.0 ± 0.5 °C. Shear rate: 6 s^{-1}.

Table 2. Correlative Data about Series A of Copolymer $C_{12}AM/NaAMC_{12}S/AM$

copolymer	feed ratio AM (mol %)	feed ratio $NaAMC_{12}S$ (mol %)	feed ratio $C_{12}AM$ (mol %)	amount of $K_2S_2O_8$ (wt %)	$[\eta]$
A-1	96.0	4.0	0.0	0.5	655.7
A-2	96.0	3.8	0.2	0.5	652.2
A-3	96.0	3.6	0.4	0.5	649.3
A-4	96.0	3.4	0.6	0.5	650.5

be increased by adding electrolyte NaCl. For the terpolymers of series C, the NaCl concentration of the copolymerization system increases in turn, so the length of the hydrophobic microblocks of the terpolymer is increased gradually according to priority, as shown in Table 3. For the HAPAM prepared in the conventional micellar copolymerization system, the length of the hydrophobic microblock is calculated according to eq 1,[19] whereas, for the HAPAM prepared in the new micellar copolymerization system, it should be calculated according to eq 2

$$N_H = \frac{[M_H]}{([S] - \text{cmc})/N_{agg}} \tag{1}$$

$$N_H = \frac{[M_H]}{([S] - \text{cmc})/N_{agg}} + N_{agg} \tag{2}$$

where $[M_H]$ is the concentration of the hydrophobic monomer and [S] is the concentration of the surfactant (the concentration of the surfmer for the new system).

3.5.2. Effect of Hydrophobe Content. The terpolymers of series B have varying hydrophobe contents but have the same length of hydrophobic microblock and basically identical molecular weight (as indicated by the intrinsic viscosities in Table 3). In Figure 10, the relationship curves of the apparent viscosity of terpolymer solutions and concentration for series B are displayed. The following features can be found in Figure 10: (1) An abrupt change occurs at about 0.15% on all four curves, and this is the critical association concentration (C^*) at which the intramolecular association begins to transfer into intermolecular association. Obviously, C^* of the terpolymers of series B is smaller (generally C^* is about 0.2 wt %), and it suggests that the terpolymers of series B have a very strong hydrophobic associative property. (2) Over C^*, the apparent viscosities enhance remarkably with the increase of copolymer concentrations, and unusual apparent viscosities are displayed for the four terpolumers. Beyond C^*, the extent of intermolecular association is strengthened with the shortening of the distance between macromolecules, resulting in the augmentation of the association network volume and the increase of the association network number, causing the rapid increase of the apparent viscosity. The unusual apparent viscosities for the terpolymers of series B imply that great dynamic physical cross-linking networks are formed between macromolecules, and it is mainly attributed to the twin tail-type acrylamide $DiC_{12}AM$, which is a quite strong hydrophobic monomer. (3) At the same concentration, the greater the hydrophobe content of the copolymer, the higher the apparent viscosity of the copolymer solution. The reason for this is that the copolymer with a higher hydrophobic microblock content in the macromolecular chains will possess stronger intermolecular hydrophobic association ability, and larger and denser cross-linking networks in the aqueous solution will be formed, resulting in a higher apparent viscosity of the solution.

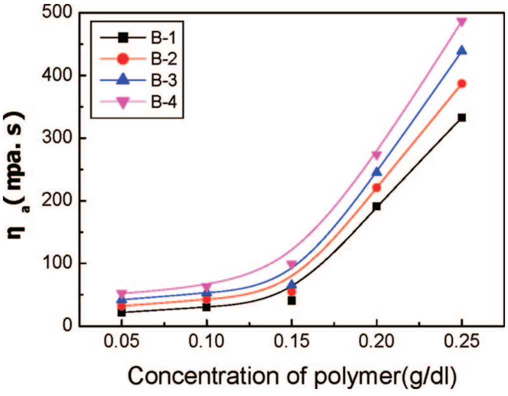


Figure 10. Apparent viscosity of aqueous solution as a function of copolymer concentration for series B. Temperature: 30.0 ± 0.5 °C. Shear rate: 6 s^{-1}.

The change of the apparent viscosity of HAPAM solutions is a macroscopic behavior of their hydrophobic associative property, whereas the fluorescence probe can reveal their hydrophobic associative property at the molecule level. The ratio of the first band intensity to the third band intensity of pyrene emission, I_1/I_3, is usually called the "polarity scale", and the weaker the polarity of the microenvironment around the pyrene molecule, the smaller the value of I_1/I_3. The values of I_1/I_3 as a function of copolymer concentrations for series B are plotted and shown in Figure 11. The following features can be observed: (1) On the curves of I_1/I_3 for the four copolymers, all of the values of I_1/I_3 diminish abruptly at a concentration of about 0.15%, and this is an indication of the transformation of association type from intramolecular association into intermo-

Table 3. Correlative Data about Series B and C of Copolymer $DiC_{12}AM/NaAMC_{12}S/AM$

copolymer	feed ratio AM (mol %)	feed ratio $NaAMC_{12}S$ (mol %)	feed ratio $DiC_{12}AM$ (mol %)	amount of $K_2S_2O_8$(wt %)	amount of NaCl (nmol/L)	N_{agg}	$[\eta]$
B-1	96.3	3.5	0.2	0.1	0	12.1	653.7
B-2	96.2	3.5	0.3	0.1	0	12.1	659.6
B-3	96.1	3.5	0.4	0.1	0	12.1	642.3
B-4	96.0	3.5	0.5	0.1	0	12.2	641.5
C-1	96.3	3.5	0.2	0.1	0	12.1	653.7
C-2	96.3	3.5	0.2	0.1	5	13.8	634.8
C-3	96.3	3.5	0.2	0.1	10	15.6	643.3
C-4	96.3	3.5	0.2	0.1	15	17.5	639.1

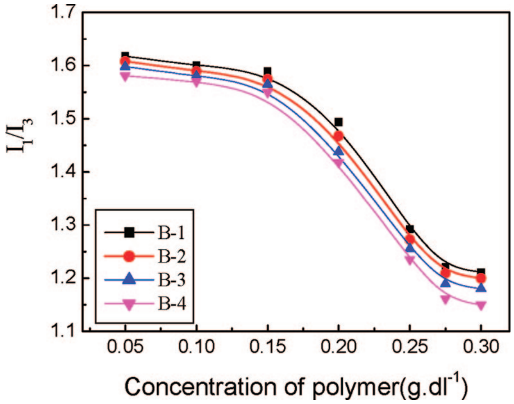


Figure 11. Variation of the I_1/I_3 value with copolymer concentration for series B.

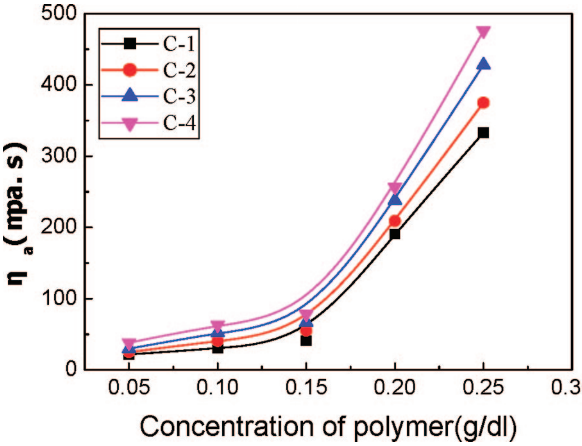


Figure 12. Apparent viscosity of aqueous solution as a function of copolymer concentration for series C. Temperature: 30.0 ± 0.5 °C. Shear rate: 6 s^{-1}.

lecular association. Intermolecular association leads to the formation of hydrophobic microdomains, and oil-soluble pyrene molecules will enter into these domains, resulting in abruptly decreasing values of I_1/I_3 due to the polarity weakening of the microenvironment around pyrene. (2) At the same concentration for the four copolymers, the higher the hydrophobe content, the lower the value of I_1/I_3. Especially beyond C^*, among the four copolymers, the value of I_1/I_3 for B-4 has a maximum decrease from 1.60 to 1.15. There is the highest hydrophobe content in the macromolecular chains of B-4, so the strongest intermolecular hydrophobic association will be produced among the four copolymers, and larger and denser physically cross-linking networks will be formed in the aqueous solution. It is not easy for water molecules to infiltrate into the larger and denser physically cross-linking networks, so the nonpolarity of hydrophobic microdomains for B-4 solution is the strongest, resulting in the lowest value of I_1/I_3.

3.5.3. Effect of Hydrophobic Microblock Length. The terpolymers of series C have varying hydrophobic microblock lengths in series but have the same hydrophobe content and basically identical molecular weight, and Figure 12 shows the relationship curves between the apparent viscosities of copolymer aqueous solutions and concentrations. It can be seen that, over C^*, at the same concentration, the apparent viscosity of the aqueous solution of the copolymer with longer hydrophobic microblock is greater. The reason for this is that the longer hydrophobic microblock in the macromolecular chains will result in a stronger intermolecular association ability and larger physical cross-linking network.[17,19,26,27] It also can be found from Figure 12 that the effect of the hydrophobic microblock length on the hydrophobic associativity of copolymer is more notable than that of the hydrophobe content. The content of hydrophobic monomers of C-4 ($DiC_{12}AM$, 0.2 mol % ; $NaAMC_{12}S$, 3.5 mol %) is the same with B-1,whose content of hydrophobic monomers is the lowest among the copolymers of series B. However, because copolymer C-4 has the longer hydrophobic microblock, the viscosity of its solution is far higher than that of B-1 solution; furthermore, the viscosity of C-4 solution is actually closed to that of the solution of B-4 whose content of hydrophobic monomers is the highest among the copolymers of series B.

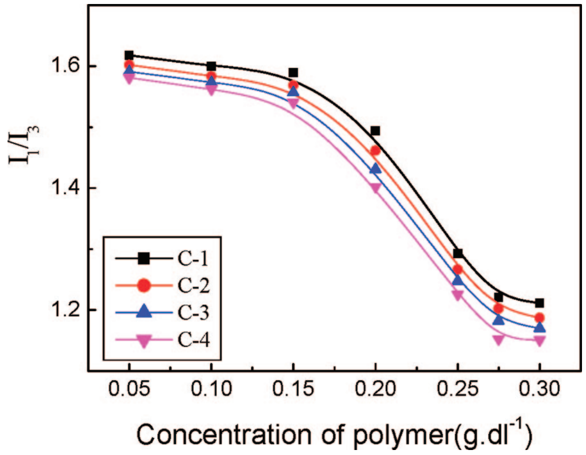


Figure 13. Variation of the I_1/I_3 value with copolymer concentration for series C.

Figure 13 displays the relationship curves between the values of I_1/I_3 and copolymer concentrations for the copolymers of series C. At the same concentration, the longer the hydrophobic block length, the lower the values of I_1/I_3. As mentioned above, the copolymer with the longer hydrophobic microblock has stronger intermolecular hydrophobic association ability, larger hydrophobic microdomains will be formed, and the inner nonpolarity inside the hydrophobic microdomains is stronger, giving the lower value of I_1/I_3. Furthermore, it can be seen that the decrease in magnitude of I_1/I_3 for copolymer C-4 (from 1.58 to 1.14) corresponds to that of B-4. This once more indicates that the effect of hydrophobic block length on the hydrophobic associativity is more notable in comparison with that of the hydrophobe content.

4. Conclusion

A new micellar copolymerization system, which combines a surface-active monomer, 2-acrylamido-dodecane sulfonate ($NaAMC_{12}S$), and a hydrophobic monomer, was constituted, and hydrophobic association polyacrylamides (HAPAM) have been prepared by the copolymerization of acrylamide and *N*-dodecylacrylamide ($C_{12}AM$) or *N*,*N*-didodecylacrylamide ($DiC_{12}AM$). Because the surface-active monomer also participates in the copolymerization, the resultant polymers are terpolymers with hydrophobic microblock structure, $C_{12}AM/NaAMC_{12}S/AM$ and $DiC_{12}AM/NaAMC_{12}S/AM$. This new micellar copolymerization system not only overcomes the drawback of complicated procedure in the conventional micellar copolymerization, but also, the formed polymers have a stronger hydrophobic association property due to the incorporation of the surface-active monomer into the copolymer backbone. Especially, the terpolymer containing twin-tail-type acrylamide, $DiC_{12}AM/NaAMC_{12}S/AM$, has an unusual thickening property due to the strong hydrophobic association property of $DiC_{12}AM$. Similar to the HAPAM prepared in the conventional micellar copolymerization system, the hydrophobe content and the length of the hydrophobe microblock are found to be the two main microstructure factors affecting the hydrophobic association behavior of HAPAM. The HAPAM with higher hydrophobe content and longer hydrophobe microblock has an expected stronger hydrophobic association property. Additionally, for the new micellar copolymerization system, the length of such hydrophobe microblock on the terpolymer chains can be controlled by varying the added amount of electrolyte.

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