Research Article

Synthesis, Characterization, and Aqueous Properties of an Amphiphilic Terpolymer with a Novel Nonionic Surfermer

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A series of surfactive amphiphilic polymer PAADs were prepared from the copolymerization of sodium acrylate, dodecyl polyoxyethylene acrylate (DPA, a surfmer), and acrylamide under the action of a mixed initiating agent consisting of ammonium persulfate-sodium bisulfite/2,2′-azobis[2-(2-imidazolin-2-yl) propane] dihydrochloride. The aggregative behaviors of PAADs were explored by 13C nuclear magnetic resonance, a viscometer, and a surface tension instrument. It was found that the apparent viscosity and surface activity of PAADs were significantly improved by the increase of average sequence length of hydrophobic micro blocks, strong intermolecular hydrophobic association, or the formation of mixed micelles between hydrophobic micro blocks and micromolecular surface-active agent. The introduction of long-chain alkyls on molecular chains prolonged the average sequence length of hydrophobic micro blocks in molecular chains and enhanced the hydrophobic association between molecular chains and the tight arrangement of molecular chains on water surfaces, thereby increasing the surface activity. Moreover, the anionic monomer sodium acrylate on molecular chains, via electrostatic repulsion, promoted the conversion from intrachain association to intermolecular association and thereby facilitated the formation of dense interfacial films, enhancing the surface activity of water solutions. Then, the anion surfermer sodium dodecylbenzenesulfonate interacted with the hydrophobic micro blocks on the molecular chains to form mixed micelles, which accelerated the interchain association and enhanced the polymer surface activity. The novel polymeric micelle with higher viscosifying ability and surface activity was expected to be a promising oil drive agent for tertiary oil recovery.

1. Introduction

Amphiphilic water-soluble polymer molecules contain incompatible hydrophilic chain segments and hydrophobic chain segments. The higher viscosifying ability [1] and lower molecular surface activity [2] of polymers are mainly induced by the intramolecular association and intermolecular association generated by weak intermolecular forces, such as hydrophobic interaction of hydrophobic groups in aqueous solutions [3]. Especially, the hydrophobic association polymers containing long-chain hydrophobic alkyls are prone to generating intermolecular association and significant surface activity under low concentrations [4]. Thus, amphiphilic water-soluble polymers can be widely used as thermal-resistant and antisalt oil displacement agents in tertiary oil recovery [5–7], watercraft painting polymer dispersing agents [8], drug-controlled release [9–11], and other technical fields [12]. In the past decade, such polymers have received wide attention from both the academia and industry fields.

The properties of hydrophobically associated polymers in water solutions are closely related to their molecular structures, especially the structures, concentrations, and distribution of hydrophobic groups. Generally, a hydrophobic monomer, such as N-alkyl acrylamide (C4-12) [13, 14], N,N-dialkylacrylamide (C 4-12) [15, 16], styrene derivatives [17], or F-containing acrylate [18–20], was used to react with anionic monomer (e.g., acrylamide, sodium acrylate, or 2-methyl-2-acylamide propyl sulfonic sodium) via ternary copolymerization to form a polymer aqueous solution with...
The preparation of polymers P(AM/NaAA/DPA) is illustrated in Table 1. Specifically, into a jar containing 100 ml of distilled water, solutions containing different proportions of AM, NaAAA, and DPA were added. Then, 2.6% urea and 50 mg/l EDTA were added and mixed well. Then, the initiating agent was added at 25°C, followed by nitrogen ventilation for 30 min. After that, the jar was sealed with rubber and placed in a water bath at 45 ± 1°C, followed by reaction for 12 h. The final conversion rate was above 97%. The specific reactions are illustrated in Figure 1.

2. Characterization

2.3. Measurement of PAAD Surfactivity. Surface tension (γ) of polymer solutions was measured by a ring method (Shanghai Zhongchen Digital Technology Equipment Co. Ltd., China) at room temperature. In volumetric flasks, a series of polymer solutions at different concentrations were prepared.

2.3.2. Measurement of the Apparent Viscosity of PAAD Polymer. The apparent viscosity was measured by a DV-II viscometer (Brookfield, America) at 45°C and cut speed of 0.6 s⁻¹.
2.3.3. Structural Characterization of PAAD Polymer. $^{13}$C NMR spectra in D$_2$O and solid-state $^{13}$C NMR were measured on a Bruker Avance III spectrometer 500 Mhz (Bruker, Swiss) and a Bruker Avance 400 spectrometer 400 Mhz (Bruker, Swiss) at constant temperature (25°C), respectively.

The mass fractions of APS, NaHSO$_3$, and AIBA. 2HCl were 0.36%, 0.36%, and 0.18%, respectively. The mass fractions of monomers were all 30%.

3. Results and Discussion

3.1. Nuclear Magnetic Characterization. Figure 2 shows the $^{13}$C NMR images of monomers and their copolymers. As showed in Figure 2(a), the peaks at 171.95, 136.29, and 126.64 ppm are characteristic of COO, the unsaturated -CH$_2$=CH-, alkoxy, and saturated alkyl, respectively. As showed in Figure 2(b), the characteristic peak of -CH$_2$=CH- (at 136.29 and 126.64 ppm) disappeared, but instead, characteristic peaks of COONa (sharp peak at 180 ppm), CONH$_2$ (sharp peak at 180 ppm), and carbon atom on PAM macromolecules at 42.41 ppm appeared. It is confirmed that acrylamide, NPAAD, and DPA have copolymerized.

3.2. Effect of Surfactant DPA Concentration on Intrinsic Viscosity. The intrinsic viscosity of polymers was enhanced by the increasing dose of DPA (Table 1). This was mainly because the hydrophilic and hydrophobic groups of DPA could induce hydrophobic association in solutions, forming dynamic network structures, which enlarged the macromolecular hydrodynamic volume. Thus, the intrinsic viscosity and molecular weight of polymers were increased with the increasing dose of DPA.

3.3. Effect of NaAA Concentration on Intrinsic Viscosity. The molecular weight of polymers significantly increased with the rise in dose of the ion monomer, but declined when the acrylic dose exceeded 20%. This was due to the effect of the electrostatic repulsion on the hydrodynamic volume. When sodium acrylate in water solutions was ionized into -COO-, the electrostatic repulsion between ion groups in the macromolecular chain was gradually intensified and the interchain hydrodynamic volume and molecular weight increased accordingly with the rise of ion group dose. However, the excessive addition of -COO- led to a significant salt effect, and the cations in water solution shielded the static repulsion between anions, which thereby decreased the interchain hydrodynamic volume and intrinsic viscosity.

3.4. Effects of SDS Concentration on Intrinsic Viscosity. The intrinsic viscosity of polymers was first enhanced and then reduced by the increasing dose of SDS (Table 1). This was mainly because SDS could associate with the hydrophobic blocks of molecular chains and thereby accelerate the transition from intramolecular association to intermolecular association, which enlarged the hydrodynamic volume of macromolecular chains. However, excessive addition of SDS would shorten the hydrophobic micro blocks of mixed micelles and thereby weaken the intermolecular association and the macromolecular hydrodynamic volume.

3.5. Effect of DPA Concentration on Apparent Viscosity. The apparent viscosity of PAAD is gradually enhanced with the rise of PAAD concentration (Figure 3). The curves of PAAD-R-3, PAAD-R-4, PAAD-R-5, and PAAD-R-6 all show typical behaviors of hydrophobically associated polymer solutions and all exhibit a turning point of concentration, which is called the critical association concentration (CAC). The viscosity is intensified slowly when the concentration is below CAC, but abruptly when the concentration is above CAC. This phenomenon is related to the intramolecular and intermolecular hydrophobic associations of hydrophobic groups [28]. When the PAAD concentration is low, the hydrophobic groups are dominated by intramolecular association, which leads to molecular chain shrinkage, a decrease of hydrodynamic dimensions, and thereby a decline of apparent viscosity. When the PAAD concentration is above CAC, the intermolecular hydrophobic association is intensified, which is contributive to intermolecular association and formation of reversible physically crosslinked network structures, which result in the enlargement of hydrodynamic dimensions and apparent viscosity.

![Figure 1: Equations of polymer synthesis.](image-url)
However, apparent viscosity of PAAD declined when the DPA dose exceeded 0.5%. This was due to intramolecular association. With the monomer weight ratio, the dose of the surfmer was gradually increased to the number of micelle aggregates before copolymerization, and the length of hydrophobic micro blocks of the corresponding copolymer was prolonged after copolymerization [29]. The behaviors promoted to intermolecular association. However, too long hydrophobic micro blocks of molecular chains easily turned the amphiphilic polymers from intermolecular association to intramolecular association, leading to a reduction of viscosity.

3.6. Effect of NaAA Concentration on Apparent Viscosity. The apparent viscosity of PAAD solutions was first enhanced and then reduced with the rise of NaAA concentration; at low dose of NaAA, no CAC was observed on the curve (Figure 4). When the dose of NaAA exceeded 10%, the apparent viscosity was significantly intensified, which was a typical behavior of hydrophobically associated polymer solution. This was because at low dose of acrylic acid, the intrachain association of polymers was significant, which reduced the apparent viscosity of polymers. With the rise of NaAA dose, the static repulsion between carboxylic acid anions on macromolecular chains was significant, which accelerated the transfer from intramolecular to intermolecular association and thereby enhanced the apparent viscosity of polymer solutions and reduced their CACs [30]. However, the salt effect could shield charge and weaken intermolecular association when the dose of NaAA exceeded 20%, which led to the reducing of apparent viscosity.

3.7. Effects of SDS Concentration on Apparent Viscosity. The apparent viscosity of polymers was first enhanced and then...
reduced by the increasing surfmer dose (Figure 5). This was related to the interaction between SDS and macromolecules as well as the aggregation shapes. In water solutions, SDS and surfmer associated to form mixed micelles. With the rise of SDS dose, the number of mixed micelles was increased and the intermolecular associated aggregates were enlarged, which led to the forming of tighter space network structures in the system and the large enhancement of apparent viscosity of polymer solutions accordingly [31]. However, when the SDS dose was excessive, the number of hydrophobic side chains contained in one aggregate was less than 2; both intra-chain and interchain associations were broken and the system viscosity rapidly declined.

3.8. Effect of Surfmer Concentration on Surface Tension. The surface tension of polymers was gradually reduced and then stabilized with the rise of polymer concentration; thus, a turning point appears on each curve, namely, the critical micelle concentration (CMC) of water solutions. When the polymer concentration was equal to CMC, the surface tension was significantly reduced, minimized, and then stabilized despite further addition of polymers. This was because when the polymer concentration was low, the molecules tended to arrange on the solution surfaces; when the polymer concentration reached a certain level, the newly added polymers, under the action of hydrophobic effect, formed molecular aggregates inside the solution, while the surface polymer molecules were already full. Namely, the surfmer concentration on the solution surfaces was basically stable, so the surface tension was generally constant. The CMCs of PAAD were gradually reduced with the increasing of surfmer (Figure 6).

The surface tension of PAAD on the CMCs was firstly reduced and then increased with the increasing of DPA. The behaviors were related to the length and ratio of hydrophobic blocks. When the dose of DPA was 0.5%, the surface tension of PAAD-R-4 minimized to 28.1 mN/m. It was indicated appropriate dose of surfmer contributed to increasing the length and ratio of hydrophobic blocks and the hydrophobic association ability, tightening the water surface arrangement of polymer molecules and reducing surface tension. However, excessive DPA resulted in the forming of the long hydrophobic blocks, which were prone to intramolecular association to form monomolecular micelles.

3.9. Effect of NaAA Concentration on Surface Tension. The surface tension of polymer solutions first declined with the increase of NaAA dose (Figure 7). The behavior was jointly induced by electrostatic repulsion and hydrophobic interaction. This was because the polymer was gradually transited from intramolecular association to intermolecular association with the rise of NaAA dose, under electrostatic
Thus, intermolecular association between macromolecule led to the forming of tight interfacial films at the interface and the reducing of the surface tension in the water solutions. When the dose of PAAD was 25%, the surface tension of PAAD-ID-5 minimized to 25.9 mN/m.

3.10. Effect of SDS Concentration on Surface Tension. The surface tension of PAAD solutions first declined and then stabilized with the increase of PAAD dose (Figure 8). The surface tension first decreased with the rise of SDS dose and minimized to 26.1 mN/m when the dose was 4%. This was related to the mixed micelles formed from the SDS and DPA association. This was because the increasing of mixed micelle aggregation number and the enlarging of DPA capacity in each micelle before aggregation resulted in elongating of the hydrophobic micro blocks on copolymer molecular chains with the increasing of the SDS dose. Thus, the surface tension was reduced [32], accordingly.

4. Conclusions

A series of surfactive amphiphilic polymer PAADs were prepared from acrylic acid, dodecyl polyoxyethylene acrylate (DPA), and acrylamide under the action of a mixed initiating agent consisting of APS-NaHSO 4/2,2’-azobis[2-(imidazolin-2-yl)propane] dihydrochloride (AIBA.2HCl). The conversion rate was above 97%. The surfmer DPA, through intermolecular association, increased the molecular weights of the polymers and the viscosity and surface activity of polymer solutions. The NaAA repeated units on molecular chains, through static repulsion between carboxylic acid anions, accelerated the transfer from intramolecular to intermolecular association and thereby enhanced the molecular weights, apparent viscosity, and surface activity of polymer solutions.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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References


