

## Synthesis and characterizations of hydrophobically associating water-soluble polymer with nonionic surfmer

Zhongbin Ye,<sup>1,2</sup> Jinfang Jiang,<sup>2</sup> Xuan Zhang,<sup>2</sup> Hong Chen,<sup>1</sup> Lijuan Han,<sup>1,2</sup> Jiarong Song,<sup>2</sup> Ji Xian,<sup>2</sup> Wei Chen<sup>2</sup>

<sup>1</sup>State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, 610500, People's Republic of China

<sup>2</sup>School of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu, 610500, People's Republic of China  
Correspondence to: Z. B. Ye (E-mail: EORlab@swpu.com) or X. Zhang (E-mail: zx85917@hotmail.com)

**ABSTRACT:** In this article, a hydrophobically associating copolymer (2-acrylamido)-2-methylpropanesulfonic acid (AMPS)/AA-EO<sub>25</sub>C<sub>12</sub> was synthesized by AMPS and nonionic surfmer AA-EO<sub>25</sub>C<sub>12</sub> through free radical copolymerization. The structure of copolymer was characterized by FT-IR and <sup>1</sup>H-NMR. The properties of copolymer were studied and the results indicated that the copolymer exhibits good thickening ability due to intermolecular hydrophobic associations as the apparent viscosity of the copolymer solution increases sharply with increasing polymer concentration. Compared with homopolymer PAMPS, the rheological test indicates that the copolymer solution shows shear thickening behavior at low shear rate region. Besides, the copolymer exhibits interfacial activity as it can reduce the interfacial tension to 10° level, and ability to form emulsion with good stability, which is due to successfully introducing the structure of nonionic surfmer AA-EO<sub>25</sub>C<sub>12</sub> to the polymer chain. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2016, 133, 43195.

**KEYWORDS:** properties and characterization; radical polymerization; structure–property relations; surfaces and interfaces; synthesis and processing

Received 19 July 2015; accepted 2 November 2015

DOI: 10.1002/app.43195

### INTRODUCTION

Hydrophobically associating water-soluble polymers (HAWPs), containing a small amount of (generally less than 2 mol %) hydrophobic groups along the polymer backbone, have been researched extensively in the past decades.<sup>1</sup> Compared with the general water-soluble polymers, hydrophobic groups of HAWPs can form hydrophobic microdomains (intra- or intermolecular aggregates) in aqueous media. The hydrophobic groups tend to build a transient and reversible 3-D supramolecular network structure as the polymer concentration is above the critical associating concentration (*cac*), which impact a distinctive rheological properties<sup>2</sup> to the polymer solution such as good thickening capacity at high salinity and high temperature. Due to the special properties, HAWPs, as a kind of rheological control agents, have already been successfully applied in oil field.<sup>3–5</sup>

The conventional way to synthesize HAWPs is adding surfactants, which can emulsify and solubilize the hydrophobic monomers<sup>6,7</sup> that is difficult to be dissolved in water, into the reaction system. However, this can arouse some problems such

as the chain transfer during the polymerization process and the difficult to remove surfactants after reaction.<sup>8</sup> One efficient way to settle these problems is to introduce polymerizable surfactants, shortened as surfmers by academia. The surfmers both contain the amphiphilic groups and the vinyl double bonds,<sup>9</sup> which endow surfmers with the capacities of emulsification and polymerization simultaneously. According to the type of charge bore in the structure of the surfmers, it could be classified as cationic surfmers, anionic surfmers, nonionic surfmers, and zwitterionic surfmers. Many literature<sup>10–13</sup> have reported the polymers synthesized by acrylamide (AM) and acrylic acid (AA) as the backbones with cationic surfmers. However, while cationic polymer solutions are injected into the reservoirs during the enhanced oil recovery (EOR) processes, the cationic moieties of polymers are easily absorbed on the rock surface that is rich in anion. Accordingly, polymer concentration needs to be high enough to reach the target area, which results in huge loss of both time and cost. Besides, there is just a few of reports about using nonionic surfmer to synthesis of HAWP, and most of their research just focus on their thickening ability.<sup>14,15</sup>

Additional Supporting Information may be found in the online version of this article.

© 2015 Wiley Periodicals, Inc.

In this article, copolymer (2-acrylamido)-2-methylpropanesulfonic acid (AMPS)/AA-EO<sub>25</sub>C<sub>12</sub> is prepared by AMPS, a water-soluble monomer with good salt resistance and thermal stability, selected as the backbone and nonionic surfmer AA-EO<sub>25</sub>C<sub>12</sub>, a nonionic surfmer with good surface activity and hydrophobic property by free radical polymerization process in mild circumstances. The structures of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> and surfmer AA-EO<sub>25</sub>C<sub>12</sub> were confirmed by FT-IR and <sup>1</sup>H-NMR. The rheological properties of copolymer under various conditions such as polymer concentration, shear rate, temperature, and salinity, were comprehensively investigated. Additionally, the interfacial activities and emulsifying ability of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> were also studied.

## EXPERIMENTAL

### Materials

AMPS, fatty alcohol-polyoxyethylene ether (EO<sub>25</sub>C<sub>12</sub>), dichloromethane, sodium chloride, magnesium chloride hexahydrate, and calcium chloride anhydrous obtained from Chengdu Kelong Chemicals (China) were all analytical pure and used without further purification. 2,2'-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (AIBI) was purchased from Sigma Aldrich. Acryloylchloride (>98%) was purchased from Xiya Reagent. Milli-Q Water was obtained by an ultrapure water system.

### Synthesis of the Nonionic Surfmer AA-EO<sub>25</sub>C<sub>12</sub>

The synthesis scheme of nonionic surfmer AA-EO<sub>25</sub>C<sub>12</sub> was shown in Figure 1. The preparation of nonionic surfmer was carried out in a 250-mL three-necked flask equipped with a stirrer, a reflux condenser, a thermometer, and a dropping funnel. Before being added into the flask, 10 mmol EO<sub>25</sub>C<sub>12</sub> and 12 mmol triethylamine were mixed with 50-mL dry CH<sub>2</sub>Cl<sub>2</sub>. Then the flask was placed in an ice bath and the mixture was stirred at the rate of 400 rpm and 50 mL of dry CH<sub>2</sub>Cl<sub>2</sub> containing 10 mmol acryloyl chloride was added into the flask by dropwise in 30 min and the mixture was stirred at 0°C for 24 h in N<sub>2</sub> atmosphere. After the accomplishment of reaction, the hydrochloride triethylamine salts were filtered out, organic phase was washed by saturated NaCl solution until organic phase's pH was at 7 and then organic phase was separated out and dried by Na<sub>2</sub>SO<sub>4</sub> in the refrigerator for 24 h. After that, the Na<sub>2</sub>SO<sub>4</sub> was filtered out, the solvent CH<sub>2</sub>Cl<sub>2</sub> was removed under reduced pressure. Finally, a light yellow viscous oil product was obtained and the yield was 79.58%.

### Synthesis of the Copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> and Homopolymer PAMPS

AMPS (15.54 g, 75 mmol) and nonionic surfmer AA-EO<sub>25</sub>C<sub>12</sub> (0.5021 g, 0.375 mmol) were dissolved with deionized water (62.68 g) in a 250-mL flask. The pH value of the solution was adjusted between 6 and 8 by adding NaHCO<sub>3</sub>. Then the system was bubbled with N<sub>2</sub> for purgation in half an hour. Under the nitrogen atmosphere, the reactive system was heated to 50°C in thermostat water bath. After adding the initiator AIBI (0.0484 g, 0.15 mmol) into the system, the polymerization process was hold for 24 h. Then, the product was precipitated with ethanol and dried in the vacuum oven at 40°C for 48 h. The synthesis scheme of copolymer was shown in Figure 2.

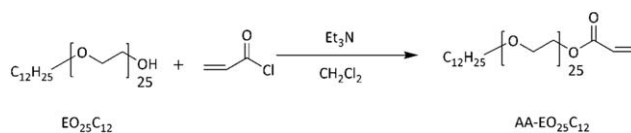


Figure 1. The synthesis route of surfmer AA-EO<sub>25</sub>C<sub>12</sub>.

Homopolymer PAMPS was synthesized without the addition of surfmer under the same conditions and used as blank sample.

### Spectroscopic Measurements

FT-IR spectra were recorded on a WQF-520 spectrometer (Beijing Rayleigh Analytical Instrument, China) by KBr disks in a range of 4000–500 cm<sup>-1</sup>. KBr pellets were prepared with the purified polymer powders.

<sup>1</sup>H-NMR spectra were performed at 400 MHz with an AM 400 (Bruker, Switzerland) spectrometer using D<sub>2</sub>O as the solvent for copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> and CDCl<sub>3</sub> as the solvent for surfmer AA-EO<sub>25</sub>C<sub>12</sub> at 25°C.

### Fluorescence Measurements

Pyrene was applied as probe for fluorescence measurement. All the measurements were carried out at ambient temperature. Polymer solutions containing pyrene with concentration of 10<sup>-6</sup> M were prepared as follows: pyrene solution (10<sup>-3</sup> M) was prepared by dissolving a certain amount of pyrene into ethanol, followed by adding 0.5 mL of 10<sup>-3</sup> M pyrene solution into a 100 mL volumetric flask, evaporating the ethanol by N<sub>2</sub> at 35°C and adding 50-mL polymer solutions. Then, these solutions were stirred in enclosed containers at room temperature for 24 h to reach the equilibrium of pyrene in the aqueous phase. Finally, fluorescence spectra of each solution were investigated through a Cary Eclipse Fluorescence Spectrophotometer. The emission spectra were obtained with an excitation wavelength 335 nm and a slit width of 2.5 nm.

### Solution Apparent Viscosity Measurements

The polymer solutions were prepared by dissolving the purified polymer in distilled water or salts (NaCl and CaCl<sub>2</sub>) solution and allowed standing at room temperature in enclosed containers for another 48 h to assure proper hydration. Then, the apparent viscosity of polymer solutions was measured by Brookfield DVIII viscometer at shear rate of 7.34 s<sup>-1</sup>.

### Rheological Measurements

Rheological characterizations of the polymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> and PAMPS solutions were investigated using HAAKE MARS III rotational rheometer. The polymer concentrations were constant at 3000 mg/L. The correlation between apparent viscosity and

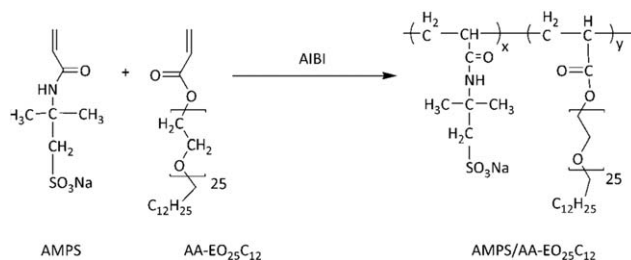


Figure 2. The synthesis route of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>.

shear rate of the polymer solutions was studied by altering shear rate from 0.01 to 500 s<sup>-1</sup>. Besides, relationship between apparent viscosity and temperature of the polymer solutions was also observed by varying temperature between 30 and 120°C at the constant shear rate of 7.34 s<sup>-1</sup>.

#### Environmental Scanning Electron Micrographs Measurements

Microstructure of the polymers in aqueous and salt solutions was observed by Quanta 450 environmental scanning electron micrographs (ESEM) (FEI, America). All samples were dissolved by deionized water and the salt solution respectively at constant polymer concentration. Then, the samples were prepared by the vacuum sublimation freezing-drying technique

#### Interfacial Tension Measurements

Interfacial tension (IFT) between *N*-heptane and the sample solution was measured by applying TX-500c spinning drop tensiometer (Bowling, Stafford, TX) at 25°C. Rotate speed is 5000 rpm and the IFT was calculated and recorded by an image acquisition software and an image pick-up device.

#### Emulsifying Ability Measurements

Emulsifying ability of polymer was studied by the following procedures: emulsions were prepared by mixing equal volume of diesel oil with polymer solution and stirred for 12 h by DF-101S magnetic stirrer. Then 10 mL of the latex was transferred into a 10-mL scaled tube and the tubes were standing for 12 h at 25°C. The emulsifying ability of polymer is evaluated by calculating the emulsifying index (EI) that is determined by the height of the divided emulsified layer (mm) versus total height of the liquid column (mm). The EI % is calculated as follows:

$$EI\% = \frac{V_e}{V_t} \times 100\% \quad (1)$$

where  $V_e$  is the volume of emulsion and  $V_t$  is the volume of total solution.

## RESULTS AND DISCUSSION

#### FI-IR Characterization Analysis of Nonionic Surfmer AA-EO<sub>25</sub>C<sub>12</sub> and Copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>

Figure 3 shows FI-IR spectrum of surfmer AA-EO<sub>25</sub>C<sub>12</sub>. Peak at 1634 cm<sup>-1</sup> is due to C=C stretching vibration and peak at 1723 cm<sup>-1</sup> is due to ester C=O stretching vibration. Bands at 2884 and 2915 cm<sup>-1</sup> are assigned to the CH<sub>2</sub> and CH<sub>3</sub> groups, at 1468 and 1343 cm<sup>-1</sup> as the bending vibration. Stretching vibration of ether —CH<sub>2</sub>CH<sub>2</sub>—O— can be obviously observed at 1111 cm<sup>-1</sup> on the spectrum. Peak at 715 cm<sup>-1</sup> is the characteristic of the long-chain alkyl group. There is no obvious peak around 3000 cm<sup>-1</sup> that is the —OH stretching vibration. The results indicate there is no residue in the surfmer.

Figure 4 shows result of FI-IR spectra of homopolymer PAMPS and copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>. In the spectrum of the copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>, characteristic absorption bands at 1187 and 1042 cm<sup>-1</sup> could be ascribed to —SO<sub>3</sub><sup>-</sup> stretching vibration. Absorption band at 3334 cm<sup>-1</sup> is due to the stretching vibration of —NH. Absorption peak at 2926 cm<sup>-1</sup> is ascribed to the stretching vibration of —CH<sub>2</sub>—. Peak at 1117 cm<sup>-1</sup> is due to ether —CH<sub>2</sub>CH<sub>2</sub>—O— stretching vibration. Peak at 1731 and 1664 cm<sup>-1</sup> is characteristic

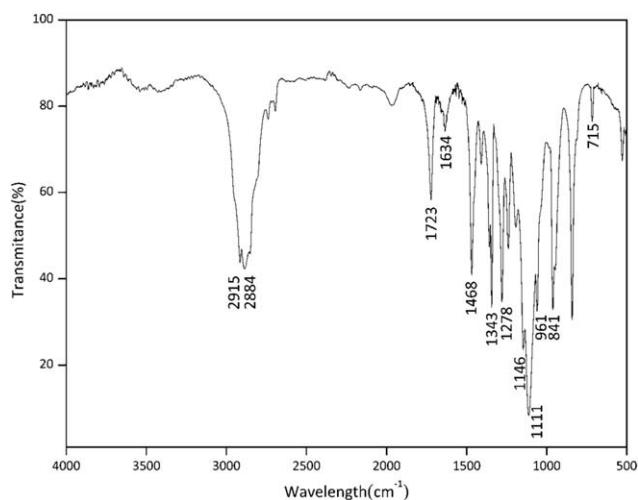


Figure 3. FI-IR spectrum of nonionic surfmer AA-EO<sub>25</sub>C<sub>12</sub>.

absorption of —CONH— group and —COO— group. However, in the spectrum of PAMPS, it only shows a broad peak at 1686 cm<sup>-1</sup> that is the characteristic absorption of the —CONH— group.

**<sup>1</sup>H-NMR Characterization Analysis of Nonionic Surfmer AA-EO<sub>25</sub>C<sub>12</sub> and Copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>.** <sup>1</sup>H-NMR spectrum of nonionic surfmer AA-EO<sub>25</sub>C<sub>12</sub> in CDCl<sub>3</sub> is shown in Figure 5: 0.88 (s, 3H, alkyl CH<sub>3</sub>), 1.27 (s, 22H, alkyl CH<sub>2</sub>), 1.57 (m, 2H, —CH<sub>2</sub>—O—), 3.64 (m, 98H, —CH<sub>2</sub>CH<sub>2</sub>O—), 4.09 (t, 2H, —CH<sub>2</sub>O—), 5.85 (m, 2H, —CH=CH<sub>2</sub>), 6.15 (m, H, —CH=CH<sub>2</sub>), 6.42 (d, 2H, —CH=CH—).

The composition of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> was determined by <sup>1</sup>H-NMR spectroscopy in deuterium oxide (D<sub>2</sub>O), shown in Figure 6: 0.739–2.508 (a, b, the alkyl in polymer main chain and side chain), 3.092–3.804 (c, d, the alkyl in EO groups). The hydrophobic content is calculated by the following equation:

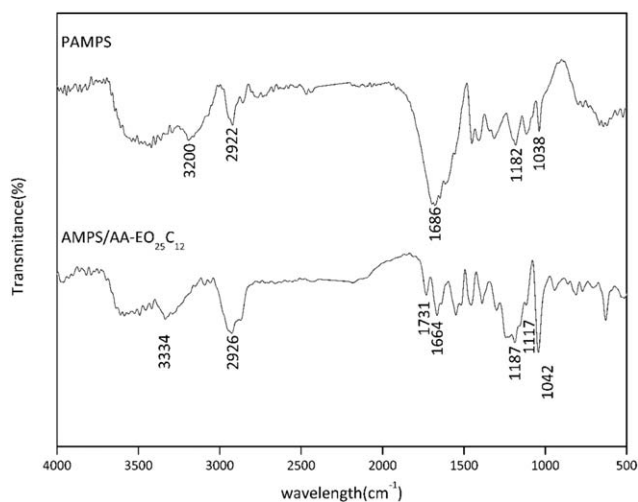


Figure 4. FI-IR spectra of homopolymer PAMPS and copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>.

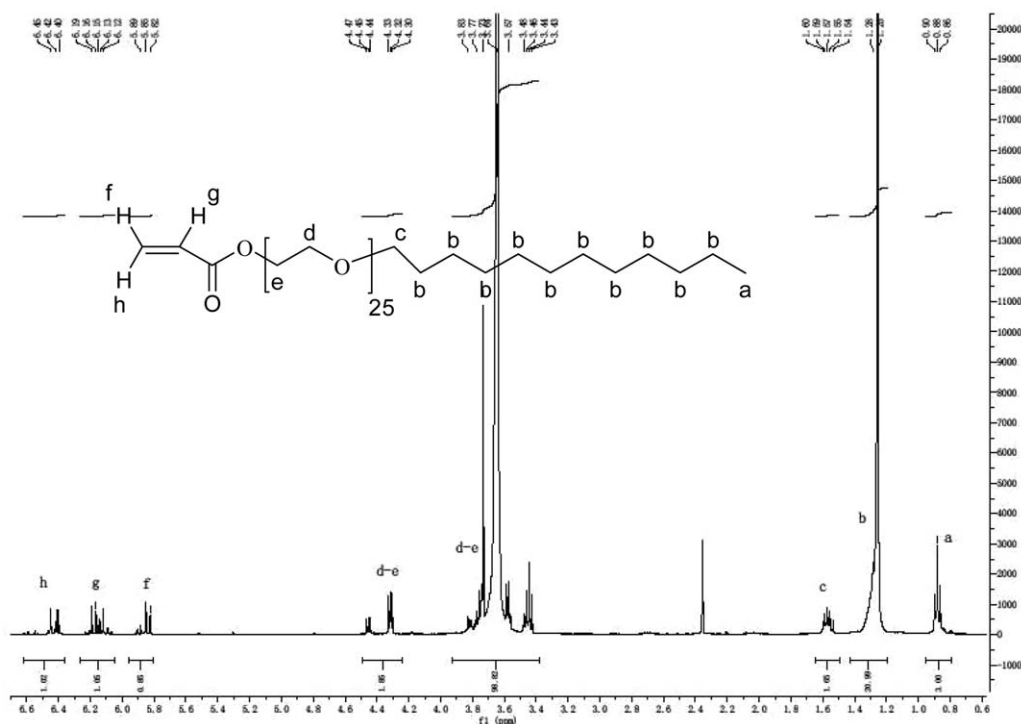


Figure 5.  $^1\text{H-NMR}$  spectrum of nonionic surfmer AA-EO<sub>25</sub>C<sub>12</sub>.

$$\text{Hydrophobe content mol \%} = \frac{y}{x+y} = \frac{9A_1 - 2A_2}{98A_2 - 19A_1} \times 100\% \quad (2)$$

where  $A_1$  is integral area for alkyl of EO group (d) and the  $-\text{CH}_2-$  linked to the  $-\text{SO}_3\text{Na}$  (c).  $A_2$  is integral area for the other alkyl (a, b). The result shown in Table I provided additional

evidence that can confirm the successful polymerization of AMPS and AA-EO<sub>25</sub>C<sub>12</sub>. Besides, the supporting information can further prove the successful polymerization as the viscosity of solution can not be dramatically changed by the mixture of PAMPS and AA-EO<sub>25</sub>C<sub>12</sub>.

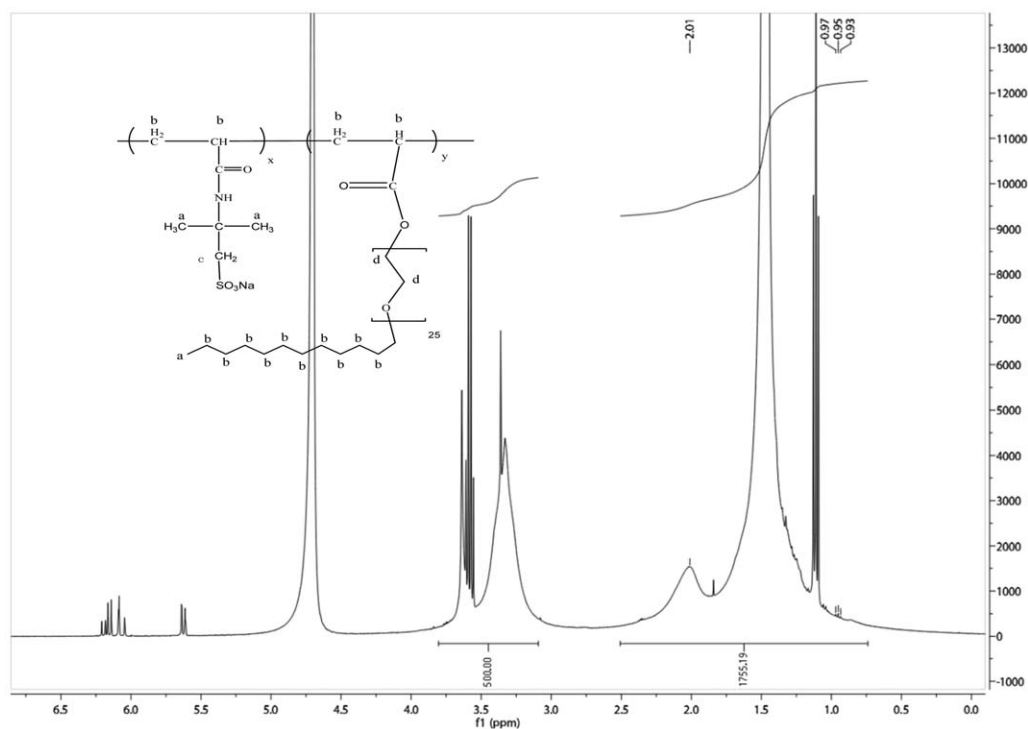


Figure 6.  $^1\text{H-NMR}$  spectrum of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>.

**Table I.** The Hydrophobe Content and the Intrinsic Viscosity of Polymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>

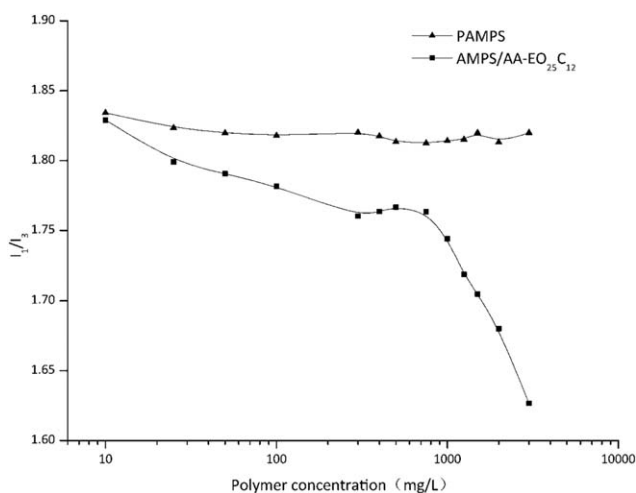
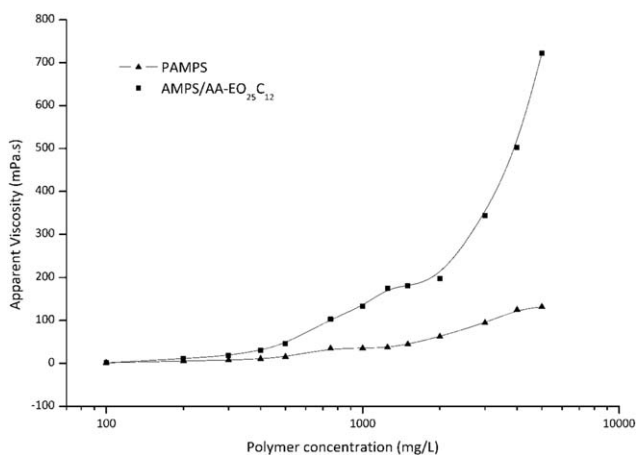
Hydrophobe content (mol %)		Hydrophobe content (wt %)	
In the feed	In the polymer	In the feed	In the polymer
0.5000	0.6089	0.6695	0.8153

### Fluorescent Results

Fluorescent emission spectra of pyrene molecules display five peaks in polymer solution. The ratio of the fluorescence intensity of the first emission peak ( $I_1$ , 373 nm) to that of the third emission peak ( $I_3$ , 384 nm) is a measure of the polarity for the microenvironment of pyrene. The smaller the value of the  $I_1/I_3$  ratio is, the weaker the polarity of the microenvironment is. Figure 7 shows the effect of polymer concentrations on the  $I_1/I_3$  ratio for copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> and homopolymer PAMPS.

In Figure 7, it can be observed that variations of  $I_1/I_3$  ratios with polymer concentration of AMPS/AA-EO<sub>25</sub>C<sub>12</sub> and PAMPS show huge differences. The curve of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> shows a characteristic sigmoidal shape, which is a typical characteristic of hydrophobic associative polymer. In diluting polymer concentration, the  $I_1/I_3$  ratios are slightly reduced, which reveals that there is little change for pyrene distributed into the nonaqueous environment. When the polymer concentration is above 750 mg/L, the polymer begins to form intermolecular aggregates and more pyrene molecules enter into these large hydrophobic aggregates. As a result, the  $I_1/I_3$  ratios reduce sharply, which indicates the low polar microenvironment.<sup>16</sup> Inflection point of the curve also indicates that *cac* of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> is about 750 mg/L that is the beginning of the intermolecular hydrophobic association.

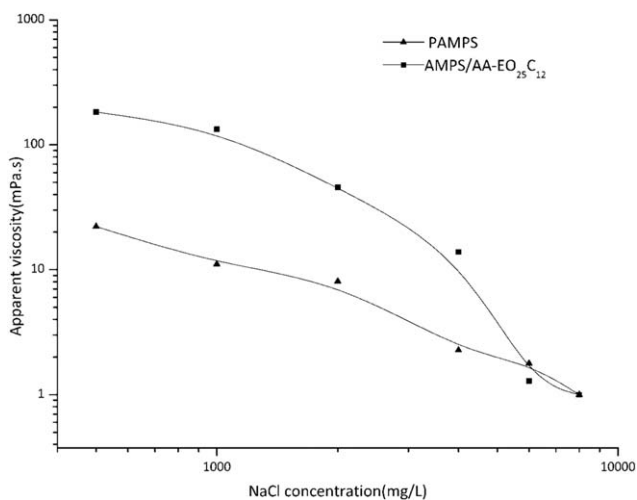
However, in the investigated scope of polymer concentrations, nearly a constant and high  $I_1/I_3$  ratio, almost equal to the  $I_1/I_3$  ratio in pure water without polymer, is observed from homopolymer PAMPS. This is due to the absence of hydrophobic groups of PAMPS. The test results further confirm the successful copolymerization of AMPS and surfmer AA-EO<sub>25</sub>C<sub>12</sub>.

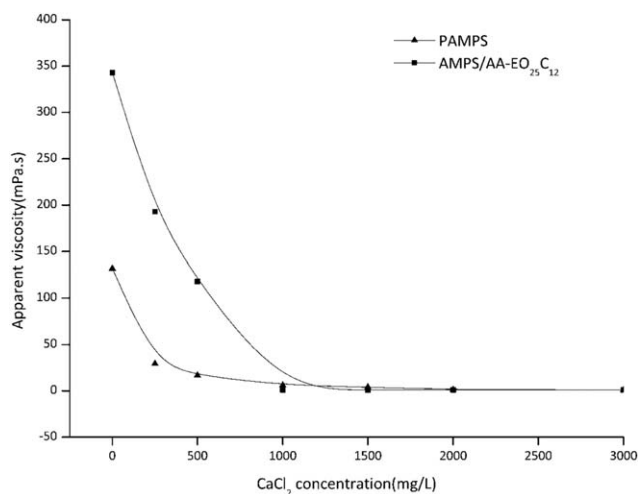
**Figure 7.** The  $I_1/I_3$  ratio against polymer concentration at 25°C.**Figure 8.** Apparent viscosity as a function of polymer concentration at 25°C.

### Effect of Copolymer Concentration on the Apparent Viscosity of Copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>

Figure 8 shows influence of copolymer concentration on apparent viscosity of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>. Homopolymer PAMPS synthesized with the same condition as copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> is also investigated as a blank sample.

In Figure 8, it is clear that both of the two kinds of polymer solutions exhibit thickening ability. But copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> can achieve a higher apparent viscosity than PAMPS solutions at the same concentration and displays a knee point at 750 mg/L, which is a typical characteristic of hydrophobic associative polymer. This is due to the formation of a physical network by intermolecular hydrophobic association, which makes a sharp increase in the apparent viscosity of copolymer as the concentration is above *cac* value. The knee point is the *cac* that is consistent with the fluorescent result. However, it can notice that PAMPS curve shows a nearly linear approximation and no knee point is existed, which can be ascribed to the absence of hydrophobic groups that can form intermolecular association aggregates to build up a tight physical network.

**Figure 9.** Effect of NaCl concentration on apparent viscosity of polymer solutions at 25°C.



**Figure 10.** Effect of  $\text{CaCl}_2$  concentration on apparent viscosity of polymer solutions at  $25^\circ\text{C}$ .

### Effect of Salts on Apparent Viscosities of Copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>

Polyelectrolyte behavior of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> was investigated through test of salt tolerance, and homopolymer PAMPS was used as blank sample. Concentrations of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> and homopolymer PAMPS were 3000 mg/L. Results are presented in Figures 9 and 10.

In Figures 9 and 10, it is obvious that apparent viscosities of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> and homopolymer PAMPS decline with elevating concentration of inorganic salt. This can be ascribed to the reduction in hydrodynamic volume of polymer chains in copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> solution, which is accounted for the formation of intramolecular association caused by effect of electrostatic screening. As the concentration of salt increases in aqueous solution, cations can screen the intra-anionic electrostatic repulsion in polymer chains and promote transformation of association from the intermolecular to intramolecular, causing the shrink of polymer chains and the

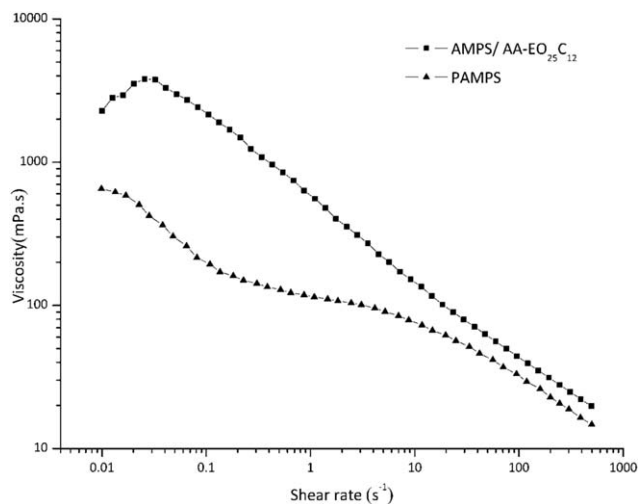
loss of apparent viscosities in salt solution. However, although similar trend with PAMPS, apparent viscosities of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> solutions are much higher than PAMPS at the same salt concentration. This is ascribed to the hydrophobic groups of surfmer AA-EO<sub>25</sub>C<sub>12</sub> that can associate in salt solution and dramatically enhance the apparent viscosities of copolymer solution.

Besides, the tests of salt tolerance exhibit that the multivalent ion  $\text{Ca}^{2+}$  has a stronger impact on polymer chain than univalent ion  $\text{Na}^+$ . The apparent viscosities of the polymer solutions can be reduced significantly by adding a low concentration of multivalent ions  $\text{Ca}^{2+}$ . The reason is that multivalent ion  $\text{Ca}^{2+}$  has a stronger ionic strength and screening effect than univalent ion  $\text{Na}^+$ . Consequently, multivalent ion  $\text{Ca}^{2+}$  can shield electrostatic charges more effectively on polymer chains than that univalent ion  $\text{Na}^+$ , which leads to a stronger shrink of polymer chains and loss of apparent viscosity at last.

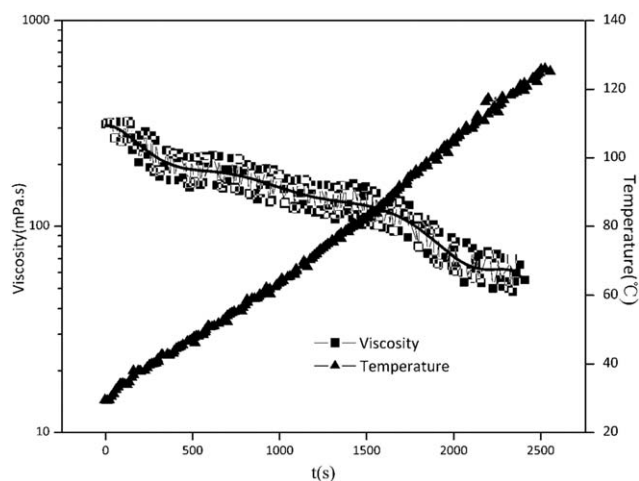
### Effect of Shear Rates on Apparent Viscosities of Copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>

Data in Figure 11 show the relationship between shear rates and apparent viscosities of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>.

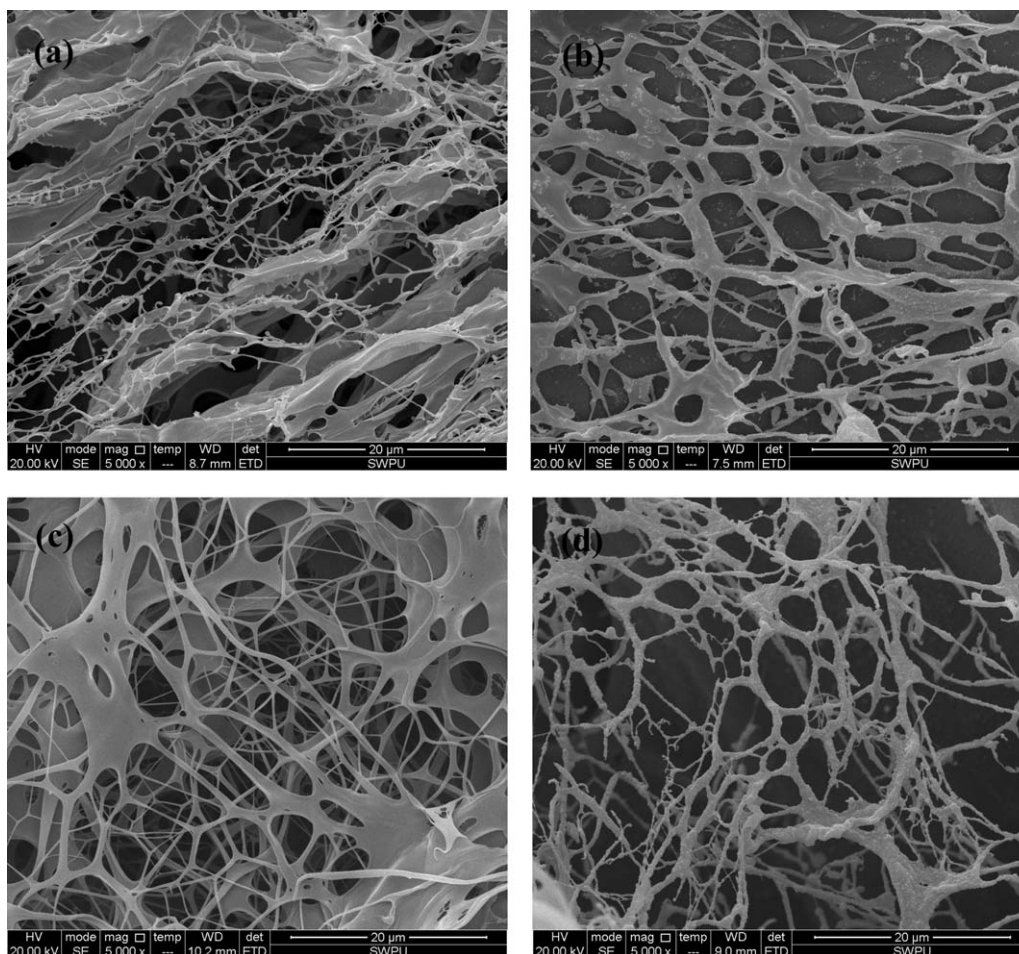
In Figure 11, the apparent viscosity of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> solutions increases up to a maximum with shear rate, which indicates shear thickening behavior of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>, and then decreases with increasing shear rate, which indicates shear thinning behavior. In shear thickening regime, intramolecular association is disrupted and the polymeric chains are much more extended, resulting in a transform of association from intramolecular to intermolecular. This can enhance the 3-D supermolecular network structure and, as a result, apparent viscosity of polymer solution obviously increases. In shear thinning regime, intermolecular association is disrupted, leading to a collapse of 3-D supermolecular network structure. Consequently, the apparent viscosity of polymer solution decreases.<sup>17,18</sup> However, PAMPS just exhibits a shear thinning behavior that the apparent viscosity decreases with increasing shear rate. This can further prove that the structure



**Figure 11.** Apparent viscosity as a function of shear rate for copolymer solution at  $25^\circ\text{C}$ .



**Figure 12.** Apparent viscosities as a function of temperature for copolymer solution ( $7.34 \text{ s}^{-1}$ ).



**Figure 13.** ESEM images for polymer (a) 3000 mg/L homopolymer PAMPS in water; (b) 3000 mg/L homopolymer PAMPS in 2000 mg/L NaCl; (c) 3000 mg/L copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> in water; (d) 3000 mg/L copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> in 2000 mg/L NaCl.

of surfmer AA-EO<sub>25</sub>C<sub>12</sub> is successfully introduced and distributed along the copolymer chain that can significantly adjust the apparent viscosity of copolymer.

#### Effect of Temperature on Apparent Viscosity of Copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>

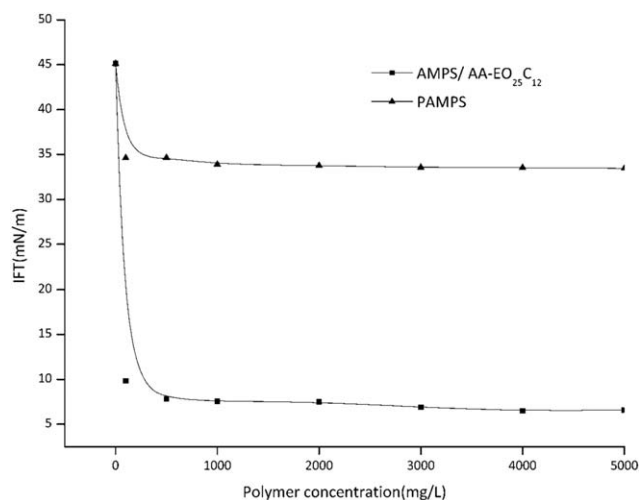
Figure 12 shows the relationship between temperature and apparent viscosity of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> in the temperature range from 30 to 125°C at shear rate of 7.34 s<sup>-1</sup>.

In Figure 12, it presents that apparent viscosities of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> solutions are gradually reduced by elevating temperature, which indicates a thermal stability of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>. Apparent viscosity is 108 mPa·s at 100°C. Gradually increasing temperature to 125°C, apparent viscosity is reduced to 55 mPa·s. The results show that temperature plays an important role in the apparent viscosity of polymer solutions. The copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> is endowed with the capacity of temperature-resistance, which can be ascribed to the motion of the polymer molecules. On account of the endothermic hydrophobic association, elevating temperature will accelerate the motion of polymer molecules, leading to the conversion of hydrophobic association from intramolecular to intermolecular and the breakage of 3-D supermolecular network structure

simultaneously. Effect of conversion can contribute to the increment of apparent viscosity and effect of breakage is just the opposite. At low temperature, effect of conversion can certainly counteract effect of breakage, and thus, apparent viscosities of polymer solution do not reduce significantly. Once the effect of breakage surpasses the effect of conversion at a certain temperature, the apparent viscosity of polymer solution begins to reduce gradually. Besides, the stable anion group —SO<sub>3</sub><sup>2-</sup> in the copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> can contribute to temperature resistance of copolymer at high temperature. As a consequence, the combined interaction of these effects makes copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> achieve a good thermal stability at high temperature.

#### ESEM Results

ESEM images of PAMPS and copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> are shown in Figure 13. In Figure 13, it can be observed that microstructure of PAMPS exhibits large open micropores and remains in dispersed state both in water and salt solution. However, microstructure of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> exhibits smaller micropores and shows more compact network structure than PAMPS. However, microstructure of copolymer is much looser in salt solution than water. This can be ascribed to the anionic structure of copolymer, which is anionic copolymer.



**Figure 14.** Effect of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> concentrations on oil-water IFTs at 25°C.

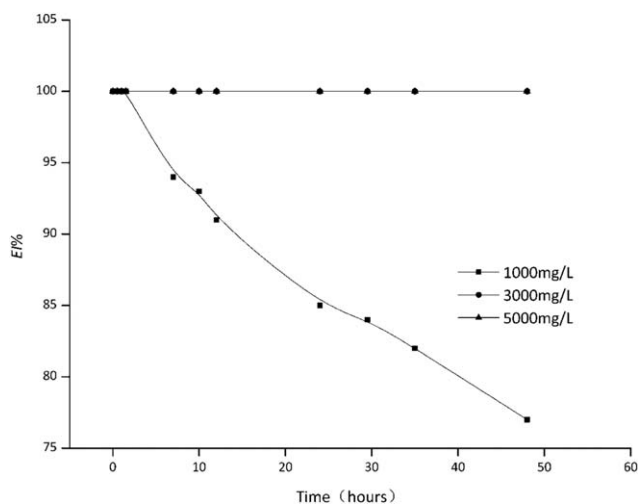
The salt can cause the polymer chain coil that results in the loss of apparent viscosity which is due to shielding the intra-anionic electrostatic repulsion in copolymer chain. As surfmer AA-EO<sub>25</sub>C<sub>12</sub> owns an amphiphilic structure, it can improve the association of copolymer in salt solution, since the polarity of the solution increases with the addition of salts. Therefore, copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> form more compact structures than PAMPS in salt solution.

#### IFTs of Copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>

Interfacial tension measurements were performed by altering concentration of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> and homopolymer PAMPS solutions. Figure 14 shows the relationship between IFT of *n*-heptane and polymer solution and polymer concentration at 25°C.

As depicted in Figure 14, for copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>, a sharp decrease in IFT is observed up to a polymer concentration of 500 mg/L after which a slightly decrease is observed. Decrease in IFT could be attributed to the increased absorption of available polymer molecules at oil–water interface as copolymer concentration increases leading to interfacial excess of polymer molecules. At low polymer concentration, polymer molecules absorb at interface so that hydrophobic moieties of polymer can avoid the unfavorable aqueous environment and escape to the oil phase because of the in-availability of enough polymers to form intermolecular aggregates. Consequently, a sharp decrease in IFTs is observed at low polymer concentration. At higher polymer concentrations, the interface becomes saturated with polymer molecules and formed intermolecular aggregates provide favorable environment for hydrophobes. Hence, a less pronounced decrease in IFTs is observed at higher copolymer concentrations.

However, for homopolymer PAMPS, a slightly decrease in IFTs is observed, which can be ascribed to scarce absorption of the polymer molecules at the oil–water interface for the absence of hydrophobic moiety. As a result, reduction in IFTs for homopolymer PAMPS is much lower than that of copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub>.

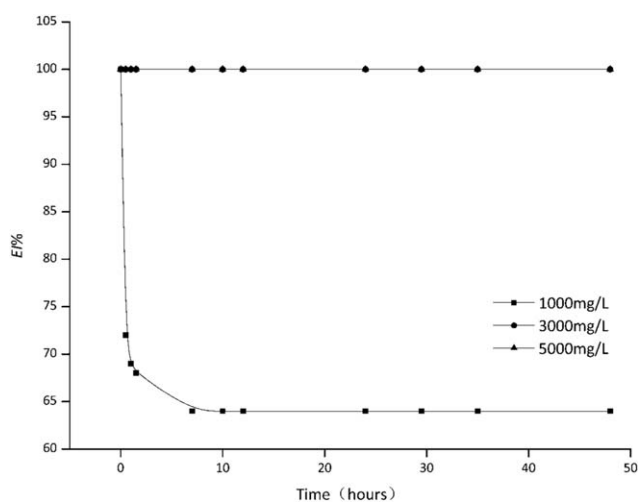


**Figure 15.** Stability of the emulsion in distilled water at 25°C.

#### Emulsifying Behaviors

Nowadays, many laboratory experiments and field applications have confirmed that polymer flooding can increase oil recovery more notably than HPAM flooding in that the former can emulsify crude oil during EOR processes.<sup>19–21</sup> Figures 15 and 16 exhibit results of the emulsifying oil phase (diesel oil) with copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> solution in the presence of 2000 mg/L NaCl or not.

In Figure 15, it shows the variation of emulsion stabilities with time without the addition of salt. Emulsifying indexes decrease within the time at 1000 mg/L polymer concentration. When polymer concentrations are 3000 and 5000 mg/L, emulsifying indexes are all 100%. That is, due to the high concentration polymer solution that can build up a tight network to prevent the coagulation of emulsion particles. In presence of salt (Figure 16), emulsifying indexes decrease within the test time at 1000 mg/L polymer concentration, but much lower than emulsion without salt at the same polymer concentration, which can be illustrated that salt can shrink polymer chain for screening effect. As a result, the polymer chain cannot spread at interface



**Figure 16.** Stability of the emulsion in 2000 mg/L NaCl at 25°C.



to reduce IFTs significantly. All the emulsifying indexes are 100% for 3000 and 5000 mg/L polymer concentrations with salt or not. Thus, polymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> presents a good capacity of stabilizing emulsion.

## CONCLUSIONS

Copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> was prepared by free radical polymerization process in aqueous media. Compared with homopolymer PAMPS, copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> achieves better thickening ability both in water and brine. Fluorescent experiments present that the copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> owns capacity to form hydrophobic association in aqueous media, which is due to the existence of surfmer structure along polymer chain. Rheological results show that the copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> solution exhibits shearing thickening ability at low shear rate, which is different with PAMPS. Environmental scanning electron microscopes further confirm hydrophobic association of the copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> which can form a tighter 3-D network structure than PAMPS both in water and brine. Besides, emulsifying experiments show that emulsion prepared by copolymer AMPS/AA-EO<sub>25</sub>C<sub>12</sub> solution with diesel has good stability.

## ACKNOWLEDGMENTS

The authors thank the State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, the Engineering Research Center of Oilfield Chemistry and Ministry of Education Key Lab for experiment condition support.

## REFERENCES

1. Gao, B. J.; Jiang, L. D.; Kong, D. L. *Colloid Polym. Sci.* **2007**, *285*, 839.
2. Lu, H. S.; Huang, Z. Y. *J. Macromol. Sci. A* **2009**, *46*, 412.
3. Wang, Y. Y.; Dai, Y. H.; Zhang, L.; Luo, L.; Chu, Y. P.; Zhao, S.; Li, M. Z.; Wang, E. J.; Yu, J. Y. *Macromolecules* **2004**, *37*, 2930.
4. Shashkina, Y. A.; Zaroslov, Y. D.; Smirnov, V. A.; Philippova, O. E.; Khokhlov, A. R.; Pryakhina, T. A.; Churochkina, N. A. *Polymer* **2003**, *44*, 2289.
5. Castelletto, V.; Hamley, I. W.; Xue, W.; Castelletto, V.; Hamley, I. W.; Xue, W.; Sommer, C.; Pedersen, J. S.; Olmsted, P. D. *Macromolecules* **2004**, *37*, 1492.
6. Lacík, I.; Selb, J.; Candau, F. *Polymer* **1995**, *36*, 3197.
7. Hill, A.; Candau, F.; Selb, J. *Macromolecules* **1993**, *26*, 4521.
8. An, H. Y.; Lu, C. G.; Wang, P. X.; Li, W. B.; Tan, Y.; Xu, K.; Liu, C. *Polym. Bull.* **2011**, *67*, 141–158.
9. Liu, R.; Pu, W. F.; Jia, H.; Shang, X. P.; Pan, Y.; Yan, Z. P. *Int. J. Polym. Sci.* **2014**, *68*.
10. Zhang, W.; Dong, G. J.; Yang, H.; Sun, J. H.; Zhou, J. Z.; Wang, J. B. *Colloids Surf. A* **2009**, *348*, 45.
11. Feng, Y. J.; Billon, L.; Grassl, B.; Khoukh, A.; Francois, J. *Polymer* **2002**, *43*, 2055.
12. Blagodatskikh, I. V.; Vasil'eva, O. V.; Ivanova, E. M.; Bykov, S. V.; Churochkina, N. A.; Pryakhina, T. A.; Smirnov, V. A.; Philippova, O. E.; Khokhlov, A. R. *Polymer* **2004**, *45*, 5897.
13. Gao, B. J.; Yu, Y. M.; Jiang, L. D. *Colloids Surf. A* **2007**, *293*, 210.
14. Ye, Z. B.; Zhang, X.; Chen, H.; Han, L. J.; Lv, C.; Su, Z.; Song, J. R. *J. Appl. Polym. Sci.* **2014**, 131.
15. Ye, Z. B.; Zhang, X.; Chen, H.; Han, L. J.; Jiang, J. F.; Song, J. R.; Yuan, J. Y. *Colloid Polym. Sci.* **2015**, *293*, 2321.
16. Chen, H.; Han, L. J.; Xu, P.; Luo, P. Y. *Acta Phys.-Chim. Sin.* **2003**, *19*, 1020.
17. Kujawa, P.; Rosiak, J. M.; Selb, J.; Candau, F. *Macromol. Chem. Phys.* **2001**, *202*, 1384.
18. Regalado, E. J.; Selb, J.; Candau, F. *Macromolecules* **1999**, *32*, 8580.
19. Sabhapondit, A.; Borthakur, A.; Haque, I. *Energy Fuels* **2003**, *17*, 683.
20. Sun, J. L.; Sun, L. X.; Liu, W. D.; Liu, X. G.; Li, X.; Shen, Q. *Colloids Surf. A* **2008**, *315*, 38.
21. Samanta, A.; Ojha, K.; Mandal, A. *Energy Fuels* **2011**, *25*, 1642.