

# Synthesis and Characterization of a Water-Soluble Sulfonates Copolymer of Acrylamide and *N*-Allylbenzamide as Enhanced Oil Recovery Chemical

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**ABSTRACT:** A novel water-soluble polymer was prepared by copolymerization and sulfomethylation using acrylamide (AM) and *N*-allylbenzamide (NABI) as raw materials under mild conditions. The effects of ratio of AM to NABI, initiator concentration, reaction temperature, pH, and monomer concentration on the copolymerization were studied. The sulfonates copolymer was characterized by infrared (IR) spectroscopy, <sup>1</sup>H NMR spectroscopy, elemental analysis, and atomic force microscopy (AFM). It was found that the sulfonates copolymer could achieve up to 25%, 30% retention rate of the viscosity at a high temperature (120°C) and a vigorous shear condition (1000 s<sup>-1</sup>). It was also found that the sulfonates copolymer had moderate salt tolerance (NaCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub>·6H<sub>2</sub>O) and its viscosity could be restored to the original value when the shear rate changed from 170 to 510 s<sup>-1</sup> and 510 to 170 s<sup>-1</sup>. At last, the enhanced oil recovery (EOR) of the sulfonates copolymer was tested by core flood, and with up to 10.6% EOR was afforded in presence of 5000 mg/L NaCl brine at 60°C. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** radical polymerization; synthesis and processing; synthesis; viscosity; water-soluble polymers

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## INTRODUCTION

The most widely used water-soluble enhanced oil recovery (EOR) polymer, polyacrylamide (PAM), or partially hydrolyzed polyacrylamide (HPAM) have gained immense importance with increasing worldwide demands on petroleum in recent years.<sup>1–4</sup> However, the PAM or HPAM is not suitable for the harsh conditions of high salinity, temperature and long injections at present in most oil reservoirs due to the hydrolysis, degradation and others.<sup>5–13</sup> With the deepening of the world's oil production, the water-soluble polymers, which have the heat resistance, resistance to salt and shear aiming to deeper oil wells, are a challenge to the oil filed chemists.<sup>6,12</sup>

Recently, many research works have indicated that functional polyacrylamide or acrylamide (AM) copolymerized with a suitable organic monomer could yield a better product which may be temperature resistance, salt tolerance, shear resistance, or thermal stability under the reservoir conditions of heat and salinity at least for a longer period than PAM or

HPAM.<sup>14,15</sup> These pioneer's works indicated that the copolymers containing —SO<sub>3</sub><sup>-</sup> groups could offer higher stability for their stronger hydrogen bonding than copolymers containing —COO<sup>-</sup> groups.<sup>12,15–20</sup> Normally, these were synthesized by free radical polymerization using functional monomer containing —SO<sub>3</sub><sup>-</sup> groups, such as vinyl sulfonate (VS), *p*-styrenesulfonate (SS), 2-acrylamido-2-methylpropanesulfonate (AMPS), sodium (acrylamido) methanesulfonate (SAM) etc.<sup>6,21–26</sup> However, these functional monomers are neither cheap nor easy to obtain, posing a potential barrier to extensive use.

More recently, we reported a water-soluble sulfonates copolymer using AM and *N*-phenylmaleimide (*N*-PMI) as raw materials, and moderate to good temperature resistance, salt tolerance, shear resistance obtained.<sup>27</sup> Inspired by the results, herein, we continued to search for a new highly efficient EOR chemical using AM and *N*-allylbenzamide (NABI) to achieve structural diversity by copolymerization and sulfomethylation aiming to reach the level of practicability.<sup>28–31</sup>

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## EXPERIMENTAL

## Materials

The chemicals, acrylamide (AM,  $\geq 99.0\%$ , AR), sodium hydrogen sulfite ( $\text{NaHSO}_3$ ,  $\geq 58.5\%$ , AR), ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $\geq 98.0\%$ , AR), formaldehyde (HCHO, 37% aqueous), polyoxyethylene (10) octylphenyl ether (OP-10, used as emulsifier,  $\geq 99.0\%$ , AR), sodium chloride ( $\text{NaCl}$ ,  $\geq 99.5$ , AR), magnesium chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\geq 98.0\%$ , AR), calcium chloride anhydrous ( $\text{CaCl}_2$ ,  $\geq 96.0\%$ , AR) were purchased from Chengdu Kelong Chemical Reagent Factory (Sichuan, China). *N*-allylbenzamide (NABI) was synthesized by the condensation reaction of allylamine and benzenecarbonyl chloride according to the reported method.<sup>32</sup> Other reagents were analytical grade and used without further purification. Water was doubly distilled and deionized by passing through an ion-exchange column.

## Preparation of the AM/NABI Copolymer

The AM/NABI copolymer was synthesized by using free radical copolymerization. Monomers in appropriate feed composition, OP-10 (0.3 wt %, used as emulsifier), and  $\text{NaHSO}_3$ - $(\text{NH}_4)_2\text{S}_2\text{O}_8$  initiator (indicated loading, and 1/1 mol ratio) were taken along with deionized water in a three necked flask assembled with a nitrogen inlet. The reactor was kept in a water bath with magnetic stirring unless otherwise indicated. Copolymerization was carried out at  $40^\circ\text{C}$  under  $\text{N}_2$  atmosphere for 8 h. The copolymer was then isolated by precipitation with fresh ethanol and dried in vacuum oven at  $40^\circ\text{C}$  for 7 h to yield the corresponding AM/NABI copolymer.

## Preparation of the Sulfonates AM/SAM/NABI Copolymer

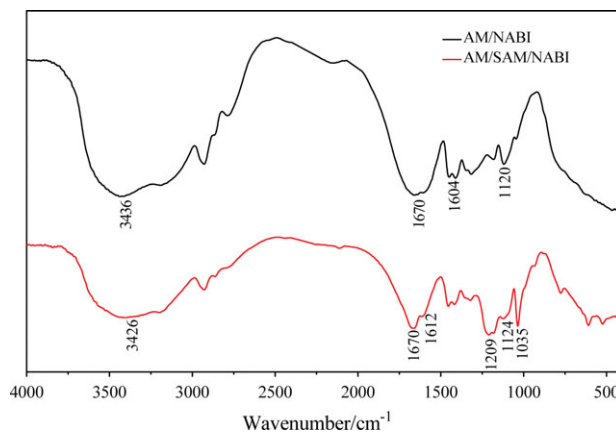
HCHO (33 wt % aqueous) and  $\text{NaHSO}_3$  ( $\text{NaHSO}_3/\text{HCHO} = 1/1$  mole ratio) were added into a solution of AM/NABI (10.0 g) in 50 mL deionized water at indicated conditions under atmosphere of nitrogen with magnetic stirring unless otherwise indicated. The mixture was isolated by precipitation with fresh ethanol and dried in vacuum at  $50^\circ\text{C}$  for 6–10 h to give the corresponding sulfonates copolymer AM/SAM/NABI.

## Characterization

IR spectra of the samples were measured with KBr pellets in a Perkin Elmer RX-1 spectrophotometer (Beijing Reili Analytical Instrument). The  $^1\text{H}$  NMR spectra of the samples were recorded by a 400 MHz BRUKER FT-NMR spectrometer by dissolving the samples in  $\text{D}_2\text{O}$ . Elemental analyses were performed using VarioEL-III elemental analyzer (Elementary Analyze System GmbH, Germany). Monomer conversion of AM was determined by high performance liquid chromatography technology (Shimadzu company, Japan) using ODS column at UV detector (210 nm),  $\text{H}_2\text{O}/\text{CH}_3\text{OH} = 90/10$  (v/v). The conversion of AM was calculated with the following equation:

$$W\% = \frac{W_{\text{AM}} - \frac{A_{\text{C}_0}}{A_0} \times V}{W_{\text{AM}}} \times 100\% \quad (1)$$

Here,  $W$  is the conversion of AM,  $W_{\text{AM}}$  is the total weight of AM in the reaction,  $C_0$  is the concentration of standard sample of AM,  $A_0$  is the chromatographic peak area of standard sample of AM,  $A$  is the chromatographic peak area of the unreacted



**Figure 1.** IR spectra of AM/NABI and AM/SAM/NABI. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

AM, and  $V$  is the solution volume of ethanol in which the copolymer was isolated by precipitation.

## Intrinsic Viscosity Measurement

The intrinsic viscosity  $[\eta]$  was measured with Ubbelohde viscometer (the diameter: 0.3 mm, length: 12.15 cm) at  $30^\circ\text{C}$ .<sup>33,34</sup> The solvent efflux time was  $>100$  s, therefore no kinetic energy corrections were made on the observed data. The temperature was controlled using a Cannon constant-temperature bath. Three measurements were made at each concentration using a stopwatch accurate to 0.2 s. Efflux time was reproducible to 0.2 s. The intrinsic viscosity  $[\eta]$  was determined by extrapolating to zero concentration a plot of reduced specific viscosity ( $\eta_{\text{sp}}/c$ ) vs. concentration (g/mL).

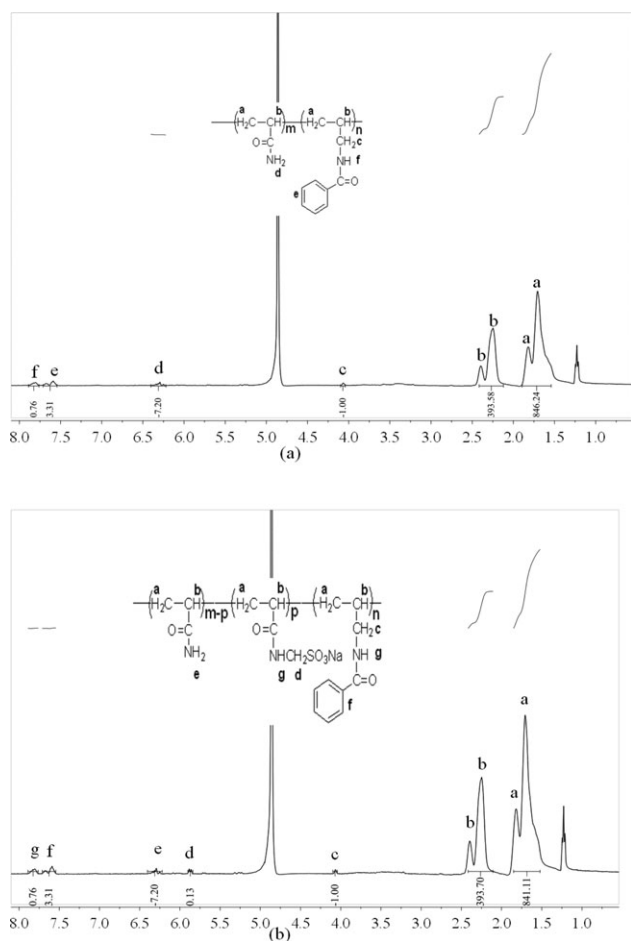
## Rheology Experiments

Rheological measurements were conducted on a HAAKE RS 600 Rotational Rheometer (Germany). Steady and dynamic shear measurements were conducted by using a set of 35 mm diameter parallel plates with a sample thickness of about 0.88 mm. In all of the dynamic oscillatory shear measurements, the strain deformation was fixed at 0.05, which is small enough to avoid nonlinear response even at elevated temperature. The temperature dependence of steady shear viscosity was obtained with shear rate of  $170 \text{ s}^{-1}$  and in temperature range  $40$ – $120^\circ\text{C}$  with a heating rate of  $2^\circ\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

## IR Spectra Analysis

The structures of the copolymers (AM/NABI and AM/SAM/NABI) were confirmed by IR spectra as shown in Figure 1. The AM/SAM/NABI which was prepared through using HCHO and  $\text{NaHSO}_3$  by sulfomethylation was confirmed by strong absorptions at  $1209$ ,  $1035 \text{ cm}^{-1}$  in the spectra of AM/SAM/NABI.<sup>13</sup> The characteristic absorptions of  $\text{C}=\text{O}$  stretch ( $1670 \text{ cm}^{-1}$ ), and aromatic ring groups stretching vibration ( $1604 \text{ cm}^{-1}$  in the spectra of AM/NABI,  $1612 \text{ cm}^{-1}$  in the spectra of AM/SAM/NABI) in Figure 1 were clearly presented. As expected, IR spectra confirmed the presence of different monomers in the copolymers AM/NABI and AM/SAM/NABI.



**Figure 2.**  $^1\text{H}$  NMR spectra of AM/NABI (a) and AM/SAM/NABI (b) in  $\text{D}_2\text{O}$ .

### $^1\text{H}$ NMR Analysis

The  $^1\text{H}$  NMR spectra of AM/NABI and AM/SAM/NABI were shown in Figure 2(a, b), respectively. The chemical shift value at 7.8 ppm was assigned to the NH protons of  $[-\text{CONHPh}]$ . Different aromatic protons appeared in the range of 7.6–7.7 ppm. The chemical shift value at 6.3 ppm is due to the NH protons of  $[-\text{CONH}_2]$ . The protons of the aliphatic  $-\text{CH}_2-$  of  $[-\text{CH}_2\text{NHCOPh}]$  exhibited two signals at 4.06 ppm. The protons of the aliphatic  $-\text{CH}_2-$  of polymeric chain appeared at 2.1–2.5 ppm. The proton of the aliphatic  $-\text{CH}-$  of polymeric chain appeared at 1.6–1.9 ppm. A characteristic peak due to the aliphatic  $-\text{CH}_2-$  of  $[-\text{NHCH}_2\text{SO}_3\text{Na}]$  was observed at 5.8 ppm in Figure 2(b) of AM/SAM/NABI.

### Elementary Analysis of AM/SAM/NABI

The analysis conducted in this section was carried out by Vario EL-III elemental analyzer. In condition of high temperature and catalyst, the sample of AM/SAM/NABI was decomposed by oxidizing reaction at high temperature. Having flowing through the separator column, the product was separated into kinds of gases. These gases were detected in the thermal conductivity cell. Finally, the content of different element can be obtained. Theoretical value: 0.6% (S%), 42.2% (C%), 9.0% (H%); Found value: 0.4% (S%), 39.8% (C%), 8.18% (H%).

### AFM Images of AM/SAM/NABI

To observe a phase separation, AM/SAM/NABI was dissolved in the degassed and distilled water as a solution (wt % = 300 mg/L). The solution was slowly evaporated to promote the phase separation, and the resulting film was annealed at room temperature for 72 h under reduced pressure. The surface profile of specimen was investigated using atomic force microscopy (AFM) scanned at following conditions:  $1 \times 1$  and  $3 \times 3 \mu\text{m}^2$  size, 1.489 Hz scan rate using a silicon cantilever tip with a length of 200  $\mu\text{m}$  and v-shaped in configuration with a spring constant of 20 N/m and a resonant frequency of 300 kHz. Both amplitude and height single images were captured, and the diameters were measured from different images captured at several locations. Figures 3 and 4 showed the AFM tapping-mode phase contrast image of AM/SAM/NABI domains. Based on the attractive and repulsive contributions to the tip-sample interaction and indentation of the soft domains,<sup>35,36</sup> some obvious highlight and rough raised portion on surface could be observed easily due to phase separation from Figures 3 and 4. It might be attributed to the enrichment of the hydrophobic components (such as NABI and its polymer) in surface and the partially crosslink of AM/SAM/NABI caused by the HCHO.

### Intrinsic Viscosity of Copolymers

All solutions were prepared by dissolving a amount of copolymers in brine (1 mol/L),<sup>37</sup> and the copolymer concentration was adjusted by adding salt solution to the flask in a constant temperature bath at 30°C. The  $\eta_{sp}/C$  (concentration) relationships are plotted in Figure 5. It was apparent from Figure 5 that the intrinsic viscosity ( $[\eta]$ ) of AM/NABI and AM/SAM/NABI value was 117, 294 mL/g, respectively.

### Optimization of the Reaction Conditions

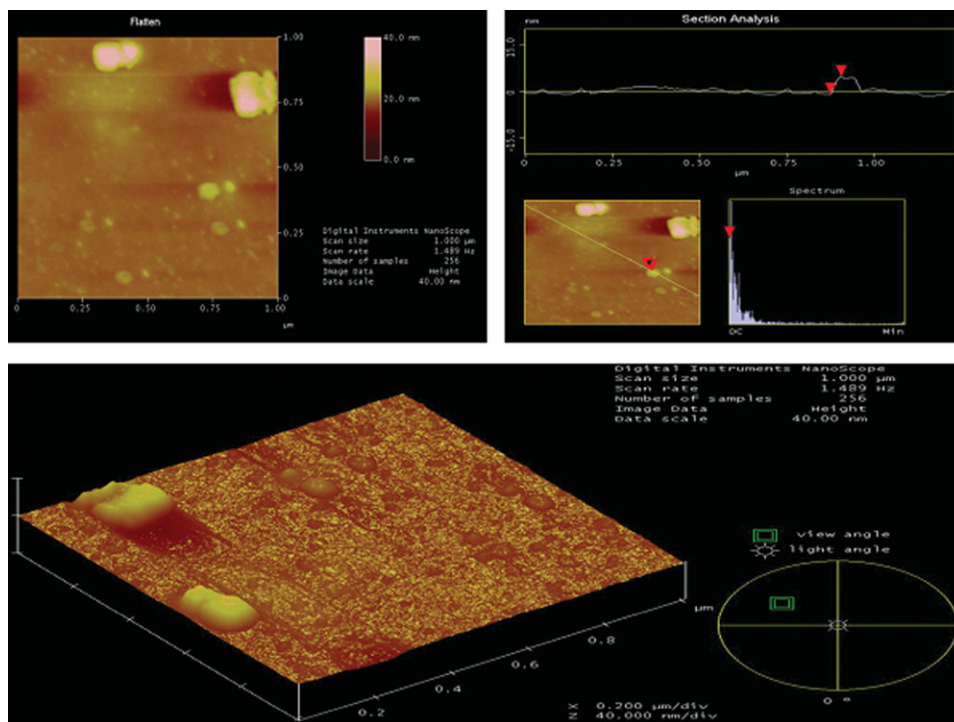
**The Ratio of AM to NABI in Copolymerization of AM/NABI.** The effect of different ratios of AM to NABI in AM/NABI (Table I) was investigated. It was found that the best results could be obtained by measuring the apparent viscosity as the ratio of AM to NABI was 99/1 wt %, and the corresponding apparent viscosity was up to 350  $\text{mPa}/\text{s}^{-1}$  with 90% conversion (Table I, entry 4). The low apparent viscosity (about 140  $\text{mPa}/\text{s}^{-1}$ ) was gained by increasing the NABI, which might be due to the steric hindrance of benzene ring in NABI (Table I, entries 1–3). Similarly, low apparent viscosity also was obtained when decreasing the NABI (Table I, entries 5, 6). Hence, the optimized ratio of AM to NABI was 99/1 wt % in the copolymerization of AM/NABI.

### Optimization the Loading of Initiator in Copolymerization of AM/NABI

Having realized the most promising ratio of AM to NABI in AM/NABI, adding different amounts of initiator was investigated (Table II, entries 1–6). It was found that the best loading of initiator was 0.25 wt % (Table II, entry 3). Decreasing or increasing the loading, low apparent viscosity (about 39–340  $\text{mPa}/\text{s}^{-1}$ ) were obtained (Table II, entries 1, 2, and 4–6).

### The Temperature Effect on Copolymerization of AM/NABI

It was found that the best reaction temperature was 40°C in AM/NABI, and the corresponding apparent viscosity was up to 350  $\text{mPa}/\text{s}^{-1}$  with 90% conversion (Table III, entry 3). The

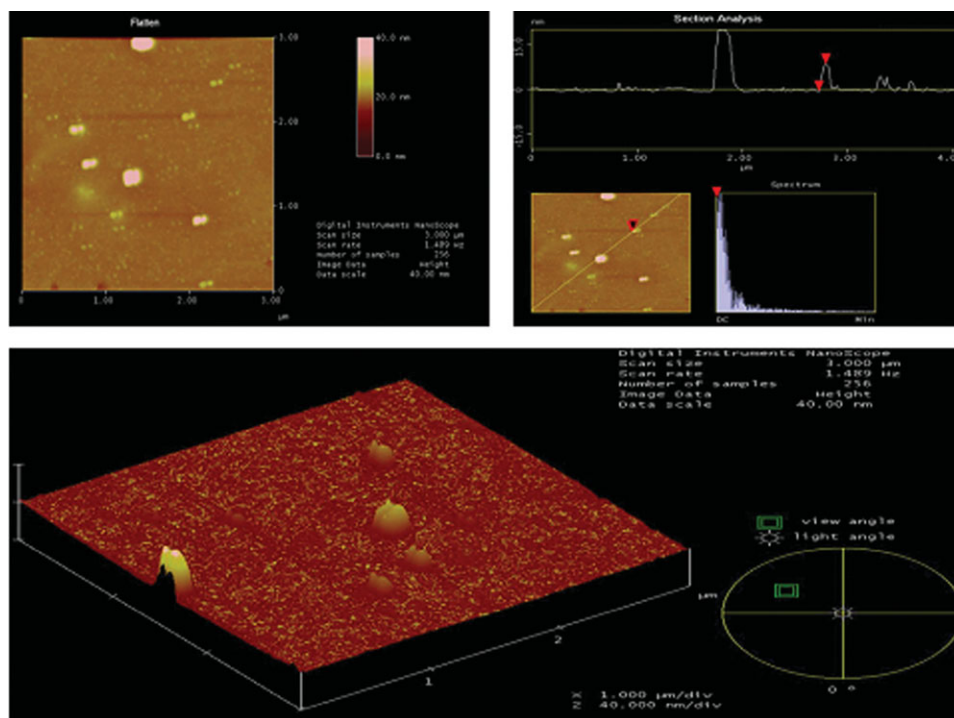


**Figure 3.** AFM images of AM/SAM/NABI casting films (scan size = 1.0  $\mu\text{m}$ , data scale = 40 nm). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

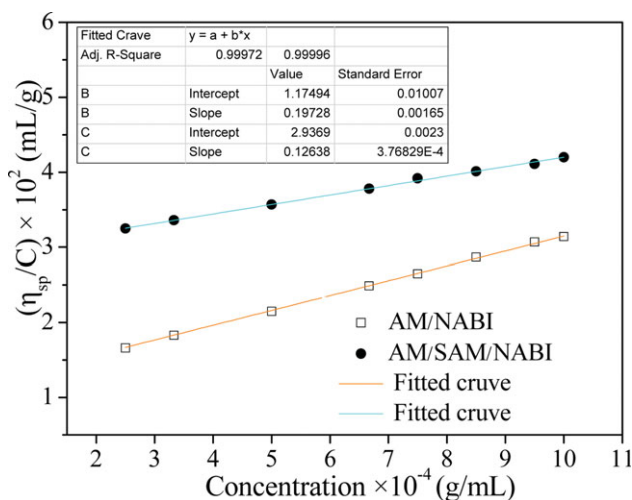
apparent viscosities were low (about 120–200  $\text{mPa}\cdot\text{s}^{-1}$ ), although better conversion could be gained under other conditions (Table III, entries 1, 2, and 4–6).

#### The pH Effect on Copolymerization of AM/NABI

And then, the pH effect was investigated in AM/NABI, the result was summarized in Table IV. It was found that the best



**Figure 4.** AFM images of AM/SAM/NABI casting films (scan size = 3.0  $\mu\text{m}$ , data scale = 40 nm). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5.** The  $\eta_{sp}/C$  relationship of AM/NABI and AM/SAM/NABI. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

pH value was 3.0 (Table IV, entry 2). Increasing or decreasing pH value, the apparent viscosity of AM/NABI could not be improved, although better conversion rates could be gained (Table IV, entries 1, 3–6).

#### The Concentration of AM and NABI Effect on Copolymerization of AM/NABI

It was found that the best concentration of AM and NABI was 20 wt % in copolymerization (Table V, entry 3). Low apparent viscosity (about 50–300 mPa/s<sup>-1</sup>) was obtained as the concentration of AM and NABI decreased from 20 to 10 wt % (Table V, entries 1, 2). Besides, the results could not be improved when changing the concentration from 20 to 30 wt % (Table V, entries 4, 5).

#### Characterization for the Solution of Copolymers

**Temperature Tolerance.** The temperature tolerance of the copolymer solutions (3 wt %) was investigated between 40 and 120°C (Figure 6). It was found that the AM/NABI and AM/SAM/NABI had similar trends between 40 and 120°C, although AM/SAM/NABI had higher viscosity. However, the AM/SAM/NABI exhibited better temperature tolerance and higher

**Table I.** Optimization the Ratio of AM to NABI in Copolymerization

Entry <sup>a</sup>	AM (wt %)	NABI (wt %)	AV (mPa/s <sup>-1</sup> ) <sup>b</sup>	Conversion (%)
1	95	5	140	64
2	98	2	160	94
3	98.6	1.4	210	95
4	99	1	350	90
5	99.2	0.8	200	92
6	99.5	0.5	120	90

<sup>a</sup>Conditions: pH = 3, OP-10: 0.3 wt %, initiator (NaHSO<sub>3</sub>-(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>): 0.25 wt %, temperature: 40°C, concentration of AM and NABI: 20 wt %, reaction time: 8 h, AV: apparent viscosity, <sup>b</sup>All copolymer solution were tested at 3 wt % by NDJ-79 rotation viscometer at 344 s<sup>-1</sup> and 25°C using 1# rotor.

**Table II.** Optimization the Ration of Initiator

Entry <sup>a</sup>	NaHSO <sub>3</sub> / (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (wt %)	AV (mPa/s <sup>-1</sup> ) <sup>b</sup>	Conversion (%)
1	0.1	300	78
2	0.2	340	87
3	0.25	350	90
4	0.3	200	95
5	0.4	45	97
6	0.5	39	96

<sup>a</sup>Conditions: pH = 3, OP-10: 0.3 wt %, temperature: 40°C, AM/NABI: 99/1 (wt %), concentration of AM and NABI: 20 wt %, reaction time: 8 h, AV: apparent viscosity, <sup>b</sup>All copolymer solution were tested at 3 wt % by NDJ-79 rotation viscometer at 344 s<sup>-1</sup> and 25°C using 1# rotor.

**Table III.** Optimization the Temperature

Entry <sup>a</sup>	Temp (°C)	AV (mPa/s <sup>-1</sup> ) <sup>b</sup>	Conversion (%)
1	30	120	80
2	35	180	95
3	40	350	90
4	45	200	89
5	50	200	98
6	55	180	90

<sup>a</sup>Conditions: pH = 3, OP-10: 0.3 wt %, AM/NABI: 99/1(wt %), Temperature: 40°C, concentration of AM and NABI:20 wt %, reaction time: 8 h, AV: apparent viscosity.

<sup>b</sup>All copolymer solution were tested at 3 wt % by NDJ-79 rotation viscometer at 344 s<sup>-1</sup> and 25°C using 1# rotor.

absolute value of viscosity than AM/NABI in same conditions. And the corresponding retention rate of the viscosity of AM/SAM/NABI could be up to 25% even at 120°C. It might be attributed to the —CONHCH<sub>2</sub>SO<sub>3</sub><sup>-</sup> groups, which usually could enhance the temperature tolerance.

#### Shear Resistance

It is well known, most polymer solutions are generally classified as pseudoplastic fluids. And the pseudoplastic material is one

**Table IV.** Optimization the pH Effect

Entry <sup>a</sup>	pH <sup>b</sup>	AV (mPa/s <sup>-1</sup> ) <sup>c</sup>	Conversion (%)
1	2	180	80
2	3	350	90
3	4	220	88
4	5	200	98
5	6	160	90
6	8	100	89

<sup>a</sup>Conditions: OP-10: 0.3 wt %, AM/NABI: 99/1 (wt %), Temperature: 40°C, concentration of AM and NABI: 20 wt %, reaction time: 8 h, AV: apparent viscosity, <sup>b</sup>The pH level is controlled by HCl (10 wt %) or NaOH (20 wt %) during the copolymerization, <sup>c</sup>All copolymer solution were tested at 3 wt % by NDJ-79 rotation viscometer at 344 s<sup>-1</sup> and 25°C using 1# rotor.

**Table V.** Optimization the Concentration of AM and NABI

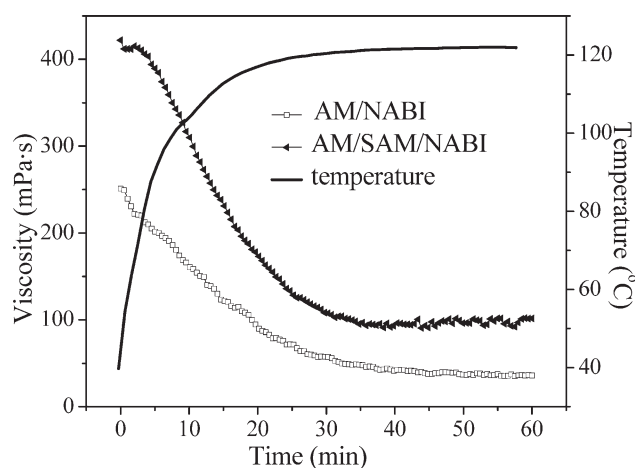
Entry <sup>a</sup>	AM and NABI (wt %)	AV (mPa/s <sup>-1</sup> ) <sup>b</sup>	Conversion (%)
1	10	50	96
2	15	200	98
3	20	350	90
4	25	300	98
5	30	230	98

<sup>a</sup>Conditions: pH = 3, OP-10: 0.3 wt %, AM/NABI:99/1(wt %), temperature: 40°C, concentration of AM and NABI: 20 wt %, reaction time: 8 h, AV: apparent viscosity, <sup>b</sup>All copolymer solution were tested at 3 wt % by NDJ-79 rotation viscometer at 344 s<sup>-1</sup> and 25°C using 1# rotor.

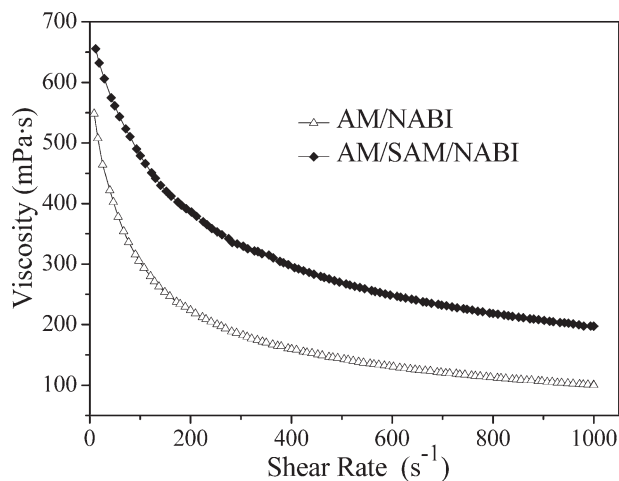
that exhibits a smaller resistance to flow as the shear rate increasing. Mathematically, the formula is known as the power-law model [eq. (2)]<sup>38</sup>:

$$\tau = K\gamma^n \quad (2)$$

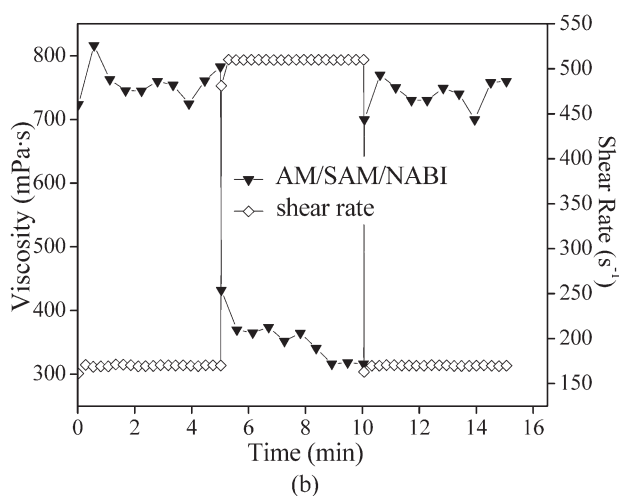
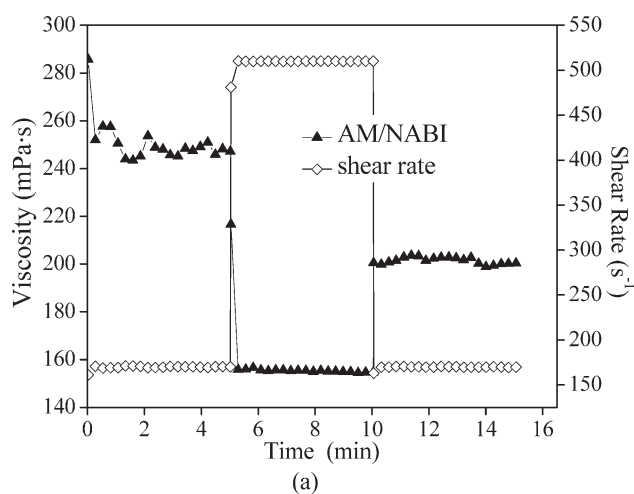
where the  $\tau$  is the shear stress (Pa),  $\gamma$  is the shear rate (s<sup>-1</sup>),  $n$  is the flow behavior index (dimensionless), and  $K$  is the consistency index (Pa/s<sup>-n</sup>). According to eq. (2),  $\eta$  and  $\gamma$  should show a straight-line relationship. The flow curves for aqueous solutions (3 wt %) of AM/NABI and AM/SAM/NABI were shown in Figure 7. In Figure 7, it was clearly found that the AM/NABI and AM/SAM/NABI showed non-Newtonian shear-thinning behavior which was often possessed by chemical flooding agent. Herein, a very obvious drop trends to viscosity could be observed by changing the shear rate from 10 to 1000 s<sup>-1</sup>. The results indicated that the AM/SAM/NABI had better shear resistance than AM/NABI, and AM/SAM/NABI had higher viscosity than AM/NABI under the same conditions. And AM/SAM/NABI had higher retention rate of the viscosity than AM/NABI at 1000 s<sup>-1</sup> shear rate (30% vs. 18%). This may support the fact that the presence of  $-\text{CONHCH}_2\text{SO}_3^-$  groups in AM/SAM/NABI could contribute to the shear resistance of aqueous polymer solution, because the strong hydrogen bonding ability of



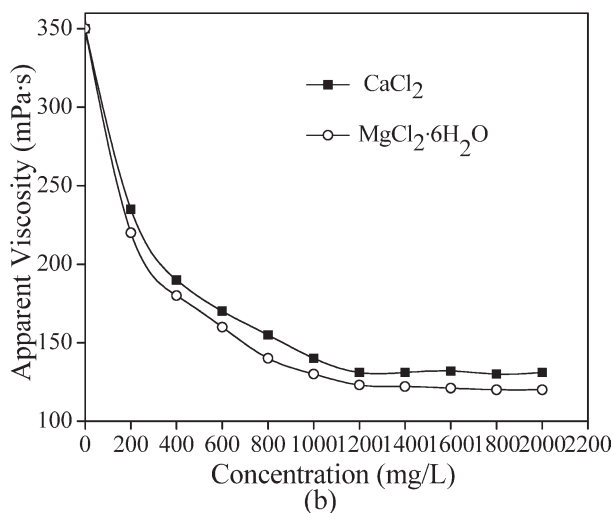
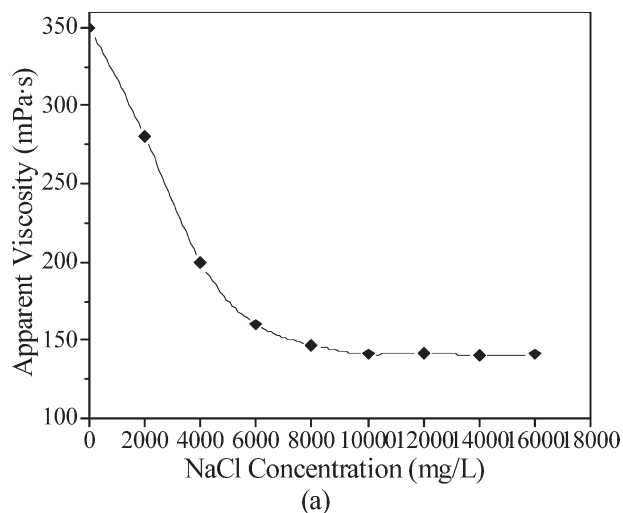
**Figure 6.** Effect of temperature on solution viscosity of 3 wt % aqueous solution of the copolymers at 170 s<sup>-1</sup>.



**Figure 7.** Viscosity vs. shear rate for AM/NABI and AM/SAM/NABI at 20°C.



**Figure 8.** Viscosity vs. shear rate for AM/NABI (a) and AM/SAM/NABI (b) at 20°C. The data were obtained that the different shear rate effect in apparent viscosity of copolymer within the same time.



**Figure 9.** Salt tolerance ((a) NaCl, (b) CaCl<sub>2</sub>, MgCl<sub>2</sub>·6H<sub>2</sub>O) of AM/NABI (3 wt %) at 344 s<sup>-1</sup> and 25°C.

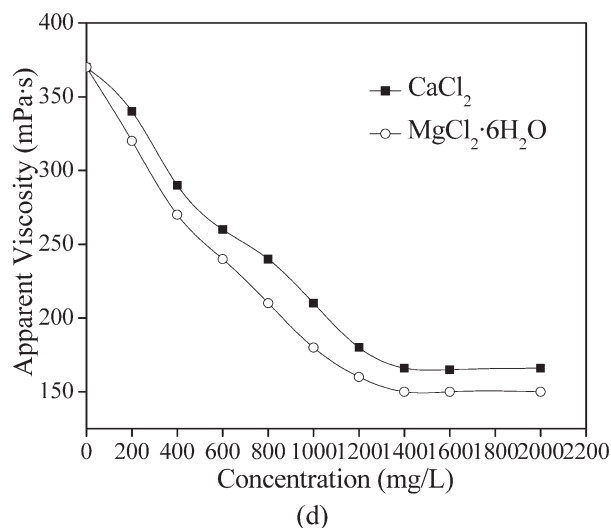
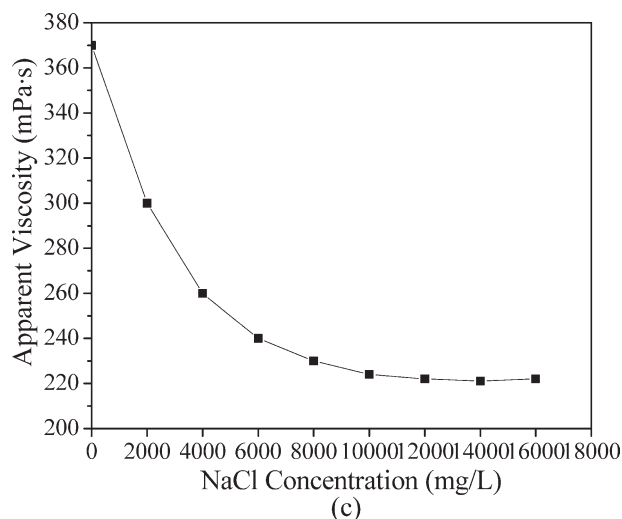
the  $-\text{SO}_3^-$  group may have helped with the reformation of the structures in AM/SAM/NABI during shearing.<sup>6</sup> It was obvious that all of the samples exhibited shear-thinning behavior.

Besides, the AM/NABI and AM/SAM/NABI were also investigated by changing the shear rate from 170 to 510 s<sup>-1</sup> and 510 to 170 s<sup>-1</sup> around [Figure 8(a, b)]. All the copolymer solutions exhibited time-dependent thixotropic behavior under different shear conditions. The AM/SAM/NABI could be restored to the original value of the apparent viscosity when one cycle was completed. However, the copolymer AM/NABI could not gain the original viscosity again. The phenomenon may support the strong hydrogen bonding ability of the  $-\text{SO}_3^-$  which may have helped with the reformation of the structures in AM/SAM/NABI during shearing.

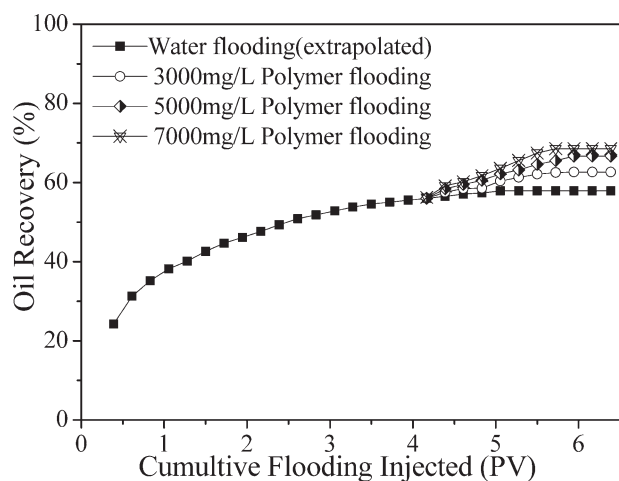
#### Salt Tolerance

In Figures 9(a, b) and 10(c, d), it could be observed that AM/NABI and AM/SAM/NABI had less satisfactory salt tolerance to Ca<sup>2+</sup> or Mg<sup>2+</sup> than Na<sup>+</sup> in same conditions. Compared with

AM/NABI, the AM/SAM/NABI showed better brine compatibility. In each case, the viscosity was decreased to a certain value by adding salts to the solution. Continuing to increase the concentration of salts in the solution, the viscosity was constantly remained constant value. This can be explained by a consideration of the polyelectrolyte behavior of the copolymers in brine-free water. As the concentration of cation was increased in the solution, the stretched polyelectrolyte chain started shrinking because of a reduction in intra-anionic electrostatic repulsion. At a certain salts concentration, the amount of cations present was sufficient to complete the shrinking, making the copolymers behavior like a nonelectrolyte. Therefore, beyond that salts concentration, the viscosity could not be reduced by increasing the concentration of salts. In addition, comparing with  $-\text{CONHCH}_2\text{SO}_3^-$  groups of AM/SAM/NABI the hydration layer formed by  $-\text{CONH}_2$  groups was easier to damage when neutralized with counter ions. Therefore, the brine resistance of copolymer AM/SAM/NABI was better than copolymer AM/NABI.



**Figure 10.** Salt tolerance ((c) NaCl, (d) CaCl<sub>2</sub>, MgCl<sub>2</sub>·6H<sub>2</sub>O) of AM/SAM/NABI (3 wt %) at 344 s<sup>-1</sup> and 25°C.



**Figure 11.** EOR results of AM/SAM/NABI in presence of 5000 mg/L NaCl at 60°C.

### Core Flood Tests

The core assembly was a stainless steel cylinder of the length 25 cm and an internal diameter 2.5 cm packed with sand. The sand was obtained by grinding iron free sandstone and further purified for iron impurities by washing with hot hydrochloric acid followed by washing with distilled water for several times. The differential pressure between the inlet and the outlet during the recovery was monitored. After the packed dry core apparatus was assembled, the sand pack was saturated with distilled water. The apparent viscosity of simulation of crude oil: 70.34 mPa/s<sup>-1</sup> at 60°C; ISCO 260D syringe pump, maximum injection pressure: 50 MPa, accuracy of 0.1% FS.

For the studies of the effect of brine on the oil recovery, the sand pack was saturated with brine instead of the fresh water.<sup>12</sup> It was then flooded with oil to connate water saturation after which the sand pack was flooded with brine water. Finally, it was flooded with AM/SAM/NABI solution. The oil recovery was determined as the following equation [eq. (3)]:

$$\text{EOR} = H_1 - H_2 \quad (3)$$

Herein,  $H_1$  is the oil recovery of polymer flooding;  $H_2$  is the oil recovery of water flooding.

It can be observed from Figure 11 that the solution of the AM/SAM/NABI can enhance oil recovery about 4.8% in presence of 5000 mg/L NaCl at 60°C compared with water flooding using 3000 mg/L AM/SAM/NABI polymer solution. Higher EOR (8.7%) was obtained with increasing the concentration of AM/SAM/NABI to 5000 mg/L. Further increasing the AM/SAM/NABI concentration to 7000 mg/L, the oil recovery was enhanced about 10.6%. All the results indicated that the copolymer had a good enhanced oil recovery.

### CONCLUSIONS

A novel binary copolymer was prepared by copolymerization and sulfomethylation using AM and NABI as raw materials. The AM/SAM/NABI was characterized by IR, <sup>1</sup>H NMR spectroscopy, elemental analysis and AFM. The solution properties of copoly-

mers were investigated under various conditions such as salinity, temperature and shear rate. The results showed that the replacement of the —CONH<sub>2</sub> group with a sulfonate group produced copolymer, which has moderate or good brine compatibility (NaCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub>·6H<sub>2</sub>O), shear resistance, and thermal stability for EOR chemical. And the further investigation on the applications of the corresponding copolymers is ongoing.

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