

## Modification of a Nicotinic Acid Functionalized Water-Soluble Acrylamide Sulfonate Copolymer for Chemically Enhanced Oil Recovery

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**ABSTRACT:** *N,N*-Diallyl nicotinamide (DANA) and acrylic acid (AA) were used to react with acrylamide (AM) and synthesize a novel nicotinic acid functionalized water-soluble copolymer AM/AA/DANA by redox free-radical polymerization. Then, the acrylamide/sodium acrylamido methanesulfonate/acrylic acid/*N,N*-diallyl nicotinamide (AM/AMS/AA/DANA) was obtained by the introduction of the  $-\text{SO}_3^-$  group into AM/AA/DANA after sulfomethylation. The optimal reaction conditions, such as the monomer ratio, initiator concentration, reaction temperature, and pH of the copolymerization or sulfomethylation, were investigated. Both AM/AA/DANA and AM/AMS/AA/DANA were characterized by IR spectroscopy, <sup>1</sup>H-NMR, scanning electron microscopy, and intrinsic viscosity testing. We found that the AM/AMS/AA/DANA had a remarkable temperature tolerance (120°C, viscosity retention rate = 39.8%), shear tolerance (1000 s<sup>-1</sup>, viscosity retention rate = 23.3%), and salt tolerance (10 g/L NaCl, 1.5 g/L MgCl<sub>2</sub>, 1.5 g/L CaCl<sub>2</sub>, viscosity retention rates = 37.4, 27.5, and 21.6%). In addition, the result of the core flood test showed that the about 13.1% oil recovery could be enhanced by 2.0 g/L AM/AMS/AA/DANA at 70°C. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40166.

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### INTRODUCTION

The development of new chemicals to increase oil production is the mainstream in oil field for complicated geologic reservoirs, heavy oil pools, and high-temperature and high-salinity reservoirs.<sup>1–5</sup> Chemical flooding, such as surfactant flooding, polymer flooding, and alkali flooding, is an efficient way to get enhanced oil recovery (EOR) according to various studies.<sup>6,7</sup> Because of its feasible and economical operation and its ability to efficiently reduce the mobility ratio, polymer flooding has shown significant adaptability to existing reservoir conditions.<sup>8–10</sup>

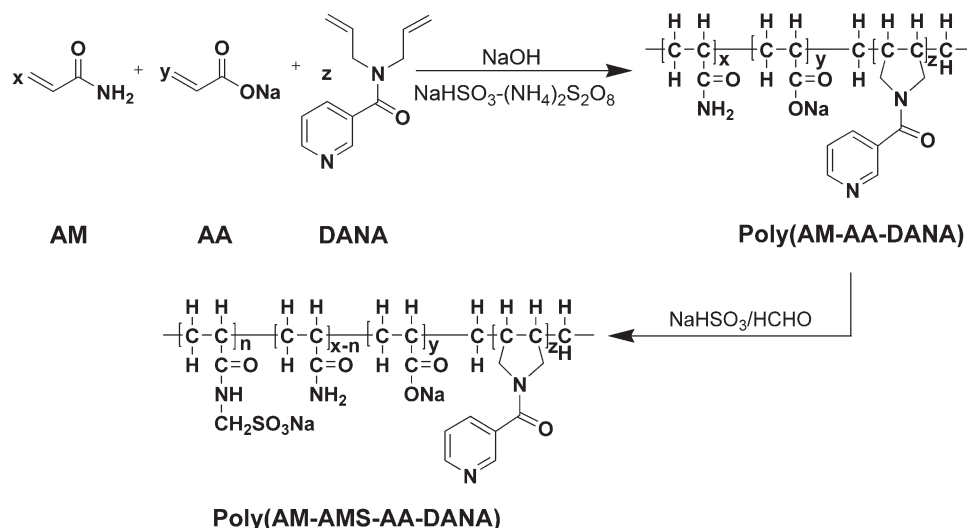
Partially hydrolyzed polyacrylamide (HPAM), one of the most widely used thickeners or modifiers in EOR, has been reported by many researchers.<sup>11,12</sup> However, the poor salt tolerance, temperature tolerance, and anti-shear ability of HPAM have seriously confined its application in oil fields.<sup>13</sup> Some studies have indicated that functional polyacrylamide or a copolymer of acrylamide (AM) with a suitable organic monomer has better performances in temperature, salt, and shear resisting.<sup>14,15</sup>

Recently, polymers with a nicotinic acid structure unit, which is primarily composed of a pyridine ring, have been reported as materials used in aviation, spaceflight, machinery, electronics,

and so on and exhibit remarkable properties<sup>16–19</sup> because the pyridine ring possesses extraordinary rigidity and thermal and chemical stability. This considerably improves the salt and temperature tolerance of polymers.<sup>20</sup> Nevertheless, as far as we know, there have been few reports of polymers with nicotinic acid structure units applied in EOR.

In addition, polymers with  $-\text{SO}_3^-$  groups attract great interest in EOR and are not only stable at high temperatures and high salt concentrations but also extraordinary dissolvable.<sup>21–23</sup> However, these functional monomers with  $-\text{SO}_3^-$  groups, such as 2-acrylamido-2-methyl propane sulfonic acid, sodium (acrylamido) methane sulfonate, or vinyl sulfonate, are neither cheap nor easy to obtain.<sup>24–28</sup> Previous studies in our laboratory confirmed that sulfomethylation is an efficient way to introduce the  $-\text{SO}_3^-$  group into copolymers because it can give the copolymer remarkable antishearing ability, temperature resistance, and salt tolerance with simple operation and economic feasibility.<sup>29,30</sup>

Hence, in this study, *N,N*-diallyl nicotinamide (DANA) was synthesized as described in the literature;<sup>31,32</sup> it was copolymerized with sodium acrylate (NaAA) and AM to obtain an AM/AA/DANA copolymer. Furthermore, the  $-\text{SO}_3^-$  group was used in AM/AA/DANA via sulfomethylation with the aim of improving



**Scheme 1.** Synthesis of the AM/AA/DANA and AM/AMS/AA/DANA copolymers.

the temperature tolerance and shear tolerance of the copolymer (Scheme 1).<sup>33,34</sup>

## EXPERIMENTAL

### Materials

AM [ $\geq 99.0\%$ , analytical reagent (AR)], AA ( $\geq 99.5\%$ , AR), sodium hydroxide (NaOH;  $\geq 99.5\%$ , AR), ammonium persulfate  $[(\text{NH}_4)_2\text{S}_2\text{O}_8, \geq 98.0\%$ , AR], sodium hydrogen sulfite (NaHSO<sub>3</sub>,  $\geq 58.5\%$ , AR), sodium chloride (NaCl,  $\geq 99.5\%$ , AR), magnesium chloride ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\geq 98.0\%$ , AR), anhydrous calcium chloride ( $\text{CaCl}_2$ ,  $\geq 96.0\%$ , AR), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ,  $\geq 99.5\%$ , AR), and formaldehyde (HCHO; 37% aqueous) were all commercial and were used directly without further purification. DANA was synthesized by nicotinic acid, thionyl chloride, and diallyl amine according to the reported method.<sup>31,32</sup>

### Synthesis of AM/AA/DANA

Appropriate amounts of AM, AA, and DANA were dissolved in deionized water in a beaker under a nitrogen atmosphere at a constant temperature, and then, NaOH was added to the solution to adjust pH to the indicated value. After that, the initiators  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and NaHSO<sub>3</sub> were added [ $n(\text{NH}_4)_2\text{S}_2\text{O}_8/n(\text{NaHSO}_3) = 1/1$ , amount of initiator = 0.1–0.5 wt %]. Copolymerization was carried out at 40°C under a nitrogen atmosphere for 6–8 h. The polymer was precipitated with ethanol and dried at 45°C *in vacuo* for 8 h to yield the corresponding AM/AA/DANA copolymer.

### Synthesis of AM/AMS/AA/DANA

The AM/AA/DANA solution was added to a 250-mL, three-necked flask with mechanical stirring under a nitrogen atmosphere. Then, NaHSO<sub>3</sub> and HCHO [ $n(\text{NaHSO}_3)/n(\text{HCHO}) = 1/1$ ] were added at the indicated conditions. After the reaction lasted for the indicated time, the copolymer mixture was precipitated with ethanol and dried at 50°C for 5 h to give the corresponding AM/AMS/AA/DANA sulfonate copolymer.

### Conversion Measurement

The conversion of AM was measured with high-performance liquid chromatography (HPLC; Shimadzu Co., Japan)

technology with an octadecylsilyl (ODS) column in a UV detector (210 nm, H<sub>2</sub>O/CH<sub>3</sub>OH = 90/10 v/v). The sample used in the measurement was the residual AM in ethanol, which used to precipitate the polymer. The conversion was calculated with the following equation:

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

where  $C_o$  is the concentration of a standard sample of AM;  $V$  is the solution volume of ethanol in which the polymer is precipitated;  $W$  and  $W_{\text{AM}}$  are the conversion weight of AM and the total weight of AM in the reaction, respectively;  $A_o$  is the chromatographic peak area of a standard sample of AM; and  $A$  is the chromatographic peak area of the unreacted AM.

### Characterization

AM/AA/DANA and AM/AMS/AA/DANA were individually characterized by WQF-520 IR spectroscopy with samples placed in KBr pellets. The IR spectra were obtained in the range 4500–500  $\text{cm}^{-1}$ . <sup>1</sup>H-NMR of the samples dissolved in D<sub>2</sub>O was recorded on a Bruker AVANCE III 400 spectrometer (Bruker, Switzerland). The glass-transition temperature ( $T_g$ ) was studied by a DSC 823e instrument (Mettler Toledo, The Netherlands) with a heating rate of 10°C/min. The  $T_g$  was obtained with aluminum capsules. All of the measurements were performed in a nitrogen atmosphere. The surface morphology of the copolymer solutions was determined with scanning electron microscopy (SEM; FEI Quanta 450) by the placement of several drops of polymer solution (2000 ppm) on a special glass and rapid freezing in a liquid nitrogen environment.

### Intrinsic Viscosity ( $[\eta]$ ) Measurement

The  $[\eta]$  of the copolymer was measured with an Ubbelohde viscometer at  $30 \pm 0.1^\circ\text{C}$ . The copolymer solution was dissolved and diluted to five different concentrations (0.0010, 0.00067, 0.00050, 0.00033, and 0.00025 g/L) with a 1 mol/L NaCl solution.<sup>35,36</sup> The flux time of the copolymer solution had to be accurate to  $\pm 0.2$  s. The specific viscosity ( $\eta_{\text{sp}}$ ) was calculated

**Table I.** Optimization of the Monomer Ratio and Initiator for the Copolymerization of AM/AA/DANA

Entry <sup>a</sup>	AM/AA	DANA (wt %)	Initiator (wt %)	Apparent viscosity (mPa s) <sup>b</sup>	Conversion (%) <sup>c</sup>
1	2.8	0.31	0.4	— <sup>d</sup>	— <sup>d</sup>
2	2.3	0.31	0.4	304.7	93
3	1.8	0.31	0.4	335.9	95
4	1.3	0.31	0.4	260.1	91
5	0.8	0.31	0.4	223.4	92
6	1.8	0.11	0.4	238.2	91
7	1.8	0.16	0.4	295.9	91
8	1.8	0.24	0.4	360.1	93
9	1.8	0.27	0.4	426.8	94
10	1.8	0.36	0.4	— <sup>d</sup>	— <sup>d</sup>
11	1.8	0.27	0.2	401.2	91
12	1.8	0.27	0.3	475.9	95
13	1.8	0.27	0.5	398.2	92
14	1.8	0.27	0.6	351.8	89
15	1.8	0.27	0.7	309.4	88

<sup>a</sup>The conditions were as follows: pH = 8; temperature = 45°C, and concentration = 20 wt %.

<sup>b</sup>Tested at 0.2 wt % with a Brookfield DV-II+ Pro viscometer at 30°C.

<sup>c</sup>Conversion (wt %): AM, tested by HPLC with an ODS column in a UV detector (210 nm), H<sub>2</sub>O/CH<sub>3</sub>OH = 90/10 v/v.

<sup>d</sup>Copolymer insoluble.

according to the flux time. Extrapolation of the fitted curve of the reduced specific viscosity  $\eta_{sp}/c$  ( $c$  is the concentration of polymer solution) to zero concentration would lead to a unique  $y$  intercept, which is known as  $[\eta]$  of the copolymer.

### Rheology Experiment

The rheological parameters of the copolymer were measured by a Haake RheoStress 6000 rotational rheometer with a scanning frequency ranging from 0.1 to 10 Hz. We obtained the relationship between the temperature and apparent viscosity by changing the temperature from 30 to 120°C under a constant shear rate of 170 s<sup>-1</sup>, and we investigated the relationship between the shear rate and apparent viscosity at 30°C by varying the shear rate at a range of 7.34–1000 s<sup>-1</sup>.

### Salt Tolerance Test

The salt tolerance of the copolymers was explored by measurement of the apparent viscosity at different concentrations of NaCl, MgCl<sub>2</sub>, and CaCl<sub>2</sub>. The apparent viscosity of the copolymers was determined at 0.2 wt % by a Brookfield DV-II+Pro viscometer (Brookfield) with a 62# rotor at 30°C.

### Core Flooding Test

The core used in the core flooding tests was stainless steel (25 cm in length and 2.5 cm in inner diameter) and packed with sand. The sand was washed with an 18% hydrochloric acid solution and then with a massive amount of water until the pH value reached 7. The simulation crude oil was collected

from Shengli oil field (China) with a density of 0.90 g/cm<sup>3</sup> and an apparent viscosity of 75 mPa s at 25°C. Each polymer flooding test was preceded by water flooding and followed by subsequent water flooding at 70°C. The water flooding was conducted with brine at 0.3 mL/min until the water content exceeded 98%. The oil recovery was determined by the following equation:

$$\text{EOR} = H_1 - H_2 \quad (2)$$

where  $H_1$  is the oil recovery of polymer flooding and  $H_2$  is the oil recovery of water flooding.

## RESULTS AND DISCUSSION

### Optimal Copolymerization Conditions for AM/AA/DANA

The effect of different ratios of AM to AA was investigated in the copolymerization in Table I (entries 1–10). It was found that the optimal ratio of AM to AA was 1.8 wt % (Table I, entry 3). Neither an increase nor a decrease in the ratio of AM to AA improved the apparent viscosity (Table I, entries 1, 2, and 4–5).

Different loadings of DANA were also investigated (Table I, entries 6–10). The best apparent viscosity was obtained with a loading of DANA of 0.27 wt % (Table I, entry 9). A lower apparent viscosity could be obtained whether the ratio of DANA was more or less (Table I, entries 6–8 and 10).

The initiator concentration was also examined (Table I, entries 11–15). The best result could be afforded when the loading of initiator was 0.3 wt % of the total monomer weight (Table I, entry 12). However, as the loading increased or decreased, the results could not be improved in the copolymerization (Table I, entries 11 and 13–15).

**Table II.** Optimization of the pH and Temperature for the Copolymerization of AM/AA/DANA

Entry <sup>a</sup>	pH	Temperature (°C)	Apparent viscosity (mPa s) <sup>b</sup>	Conversion (%) <sup>c</sup>
1	3	45	212.4	89
2	5	45	365.7	90
3	7	45	525.8	96
4	8	45	475.9	95
5	9	45	403.3	92
6	11	45	273.8	87
7	7	35	465.9	90
8	7	40	574.6	96
9	7	50	471.4	93
10	7	55	405.3	93
11	7	60	376.8	91

<sup>a</sup>The conditions were as follows: initiator loading = 0.3 wt %, AM/AA = 1.8 (wt %), DANA = 0.27 wt %, and concentration = 20 wt %.

<sup>b</sup>Tested at 0.2 wt % with a Brookfield DV-II+ Pro viscometer at 30°C.

<sup>c</sup>Conversion (wt %): AM, tested by HPLC with an ODS column in a UV detector (210 nm), H<sub>2</sub>O/CH<sub>3</sub>OH = 90/10 v/v.

**Table III.** Optimal Sulfomethylation Conditions for AM/AMS/AA/DANA

Entry <sup>a</sup>	(NaHSO <sub>3</sub> + HCHO)/ AM/AA/DANA (wt %) <sup>b</sup>	Temperature (°C)	pH	Apparent viscosity (mPa s) <sup>c</sup>
1	6	55	11	238
2	10	55	11	470
3	14	55	11	608
4	18	55	11	447
5	22	55	11	318
6	14	50	11	398
7	14	60	11	624
8	14	65	11	698
9	14	70	11	412
10	14	65	5	72
11	14	65	7	117
12	14	65	9	311
13	14	65	12	436
14	14	65	13	298

<sup>a</sup>The conditions were as follows: AM/AA/DANA concentration = 0.8 wt % and reaction time = 4 h.

<sup>b</sup>The mass ratio of NaHSO<sub>3</sub> + HCHO to AM/AMS/AA/DANA is shown. The molar ratio of NaHSO<sub>3</sub> to HCHO was 1:1.

<sup>c</sup>All copolymer solutions were tested at 0.2 wt % with a Brookfield DV-II+ Pro viscometer at 25°C.

The result (Table II, entries 1–6) demonstrated that the best pH value for the copolymerization was 7 (Table II, entry 3). Meanwhile, other pH values (Table II, entries 1, 2, and 4–6) led to a lower apparent viscosity in the copolymerization.

The best reaction temperature for the copolymerization was 40°C with an apparent viscosity of up to 574.2 mPa s (Table II, entry 8). A lower apparent viscosity was obtained when the temperature was both too high (Table II, entries 3 and 9–11) or too low (Table II, entry 7).

#### Optimal Sulfomethylation Conditions for AM/AMS/AA/DANA

First, a different ratio of HCHO (37%) [ $n(\text{NaHSO}_3)/n(\text{HCHO}) = 1/1$ ] to AM/AA/DANA was investigated in the sulfomethylation (Table III, entries 1–5). We found that the best result was obtained when the loading of HCHO was 14 wt % (Table III, entry 3), although other ratios did not give better results (Table III, entries 1–4).

Then, the effect of the temperature on sulfomethylation was investigated (Table III, entries 6–9). The best result was obtained when the temperature changed to 60°C (Table III, entry 7). Neither increasing nor decreasing the temperature improved the result (Table III, entries 3, 6, 8, and 9).

The effect of the pH on the sulfomethylation was also investigated (Table III, entries 10–14). We found that the reaction was quite sensitive to the pH value, and the synthesized copolymer gave poor results at both low and high pH (Table III, entries 10–14 vs entry 8). The best result was obtained when the pH value was changed to 11 (Table III, entry 8).

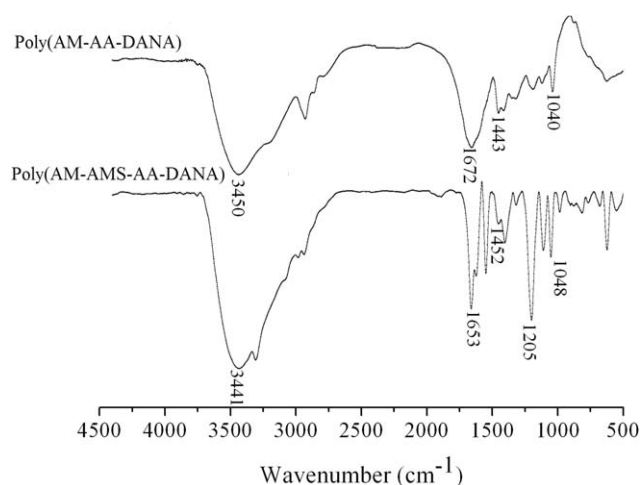
#### IR Spectral Analysis

The IR spectra of AM/AA/DANA and AM/AMS/AA/DANA are displayed in Figure 1. The strong characteristic peak (3450 cm<sup>-1</sup> in the spectra of AM/AA/DANA and 3441 cm<sup>-1</sup> in the spectra of AM/AMS/AA/DANA) was assigned to the stretching vibration of N—H. The absorption peaks appearing at 1672 cm<sup>-1</sup> in the spectra of AM/AA/DANA and 1653 cm<sup>-1</sup> in the spectra of AM/AMS/AA/DANA were due to the stretching vibrations of C=O. The stretching vibrations of the pyridine ring were observed at 1443 cm<sup>-1</sup> (AM/AA/DANA) and 1452 cm<sup>-1</sup> (AM/AMS/AA/DANA). In addition, new absorption bands around 1205 and 1048 cm<sup>-1</sup> in the spectra of AM/AMS/AA/DANA were attributed to the characteristic absorption of —SO<sub>3</sub><sup>-</sup> groups. As expected, the IR spectra confirmed the presence of different monomers in the copolymers of AM/AA/DANA and AM/AMS/AA/DANA.

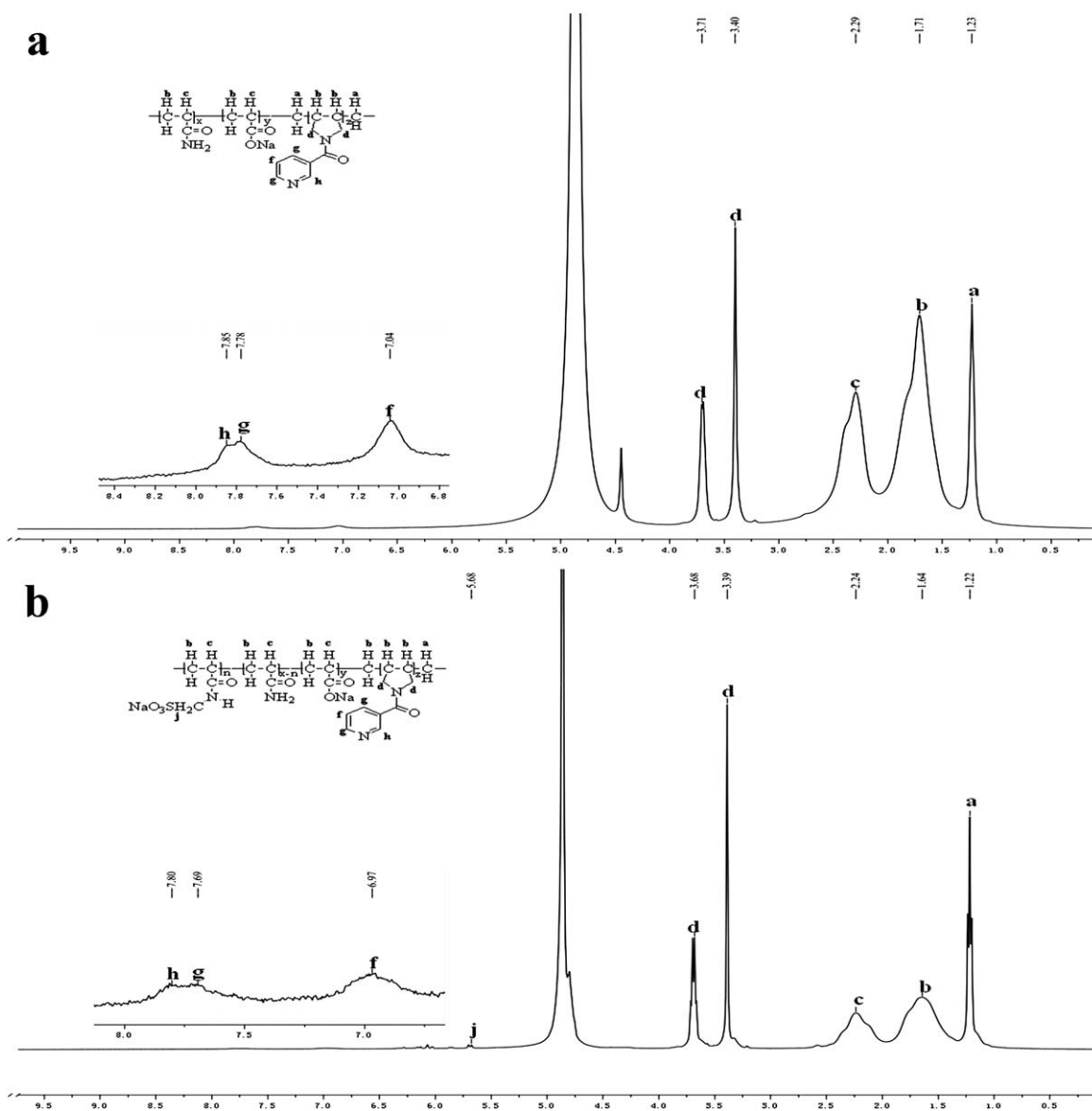
#### <sup>1</sup>H-NMR Analysis

The <sup>1</sup>H-NMR spectrum of the AM/AA/DANA copolymer is shown in Figure 2(a). In the proton spectrum, the chemical shift of aliphatic protons at 1.2 ppm (peak a) was assigned to the —CH<sub>2</sub> groups of the DANA functional monomer in the polymeric chain, and that at 1.7 ppm (peak b) was assigned to the rest of the —CH<sub>2</sub> and —CH groups of the DANA functional monomer in the polymeric chain. The protons of the aliphatic —CHCO— of the polymeric chain appeared at 2.3 ppm (peak c). The chemical shift of the aliphatic protons at 3.4–3.7 ppm (peak d) was due to the —CH<sub>2</sub> of —(CH<sub>2</sub>)<sub>2</sub>NCO. Because the loading of monomer was quite low, the typical peaks were not obvious. So in the expanded region, there were minor bands around 7.0, 7.8, and 7.9 ppm (peaks f, g, and h, respectively), which corresponded to the pyridine groups in the polymer.

Then, the <sup>1</sup>H-NMR characterization results of AM/AMS/AA/DANA were also investigated, as shown in Figure 2(b). All of the peaks assigned to the —CH<sub>2</sub> and —CH groups in the polymer backbone did not change basically, except for that of —CH<sub>2</sub> of the DANA functional monomer, whose peak changed from 1.2 ppm [peak a, Figure 2(a)] to 1.6 ppm [peak b, Figure 2(b)] compared with AM/AA/DANA. The signals at 3.4–3.7



**Figure 1.** IR spectra of AM/AA/DANA and AM/AMS/AA/DANA.



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

ppm (peak d) were due to the proton of the  $-\text{CH}_2-$  of  $[-(\text{CH}_2)_2\text{NCO}]$ . In the expanded region, minor bands around 7.0, 7.7, and 7.8 ppm (peaks f, g, and h, respectively) were associated with the pyridine groups, which were observed at the same chemical shift as AM/AA/DANA in Figure 2(a). However, a new peak representing  $-\text{CH}_2-$  of  $-\text{NHCH}_2\text{SO}_3\text{Na}$  was observed at 5.7 ppm (peak j); this indicated that the  $-\text{SO}_3^-$  group was successfully introduced into the AM/AA/DANA copolymer.

#### $T_g$ Test

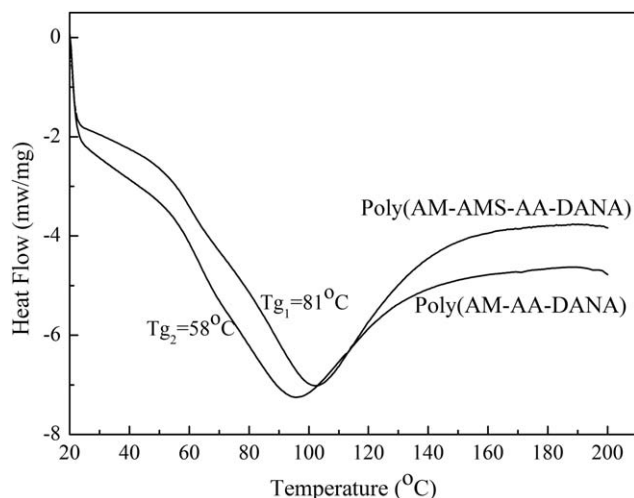
The  $T_g$  values of AM/AMS/AA/DANA and AM/AA/DANA was obtained by DSC measurement, as shown in Figure 3. In the DSC thermogram, distinct glass transitions were discernible, and only one  $T_g$  (AM/AMS/AA/DANA:  $81^\circ\text{C}$  and AM/AA/DANA:  $58^\circ\text{C}$ ) was detected for each of the two copolymers, and this indicated a single system for the copolymer.

#### $[\eta]$ Test

$[\eta]$ , which reflects the expanded extent of the polymer chain, is a measurement of the hydrodynamic volume of macromolecules.<sup>37</sup> The test of  $[\eta]$  of AM/AA/DANA and AM/AMS/AA/DANA were carried out, as shown in Figure 4. It was clear that  $[\eta]$ s of AM/AA/DANA and AM/AMS/AA/DANA were 566 and 747 mL/g, respectively.

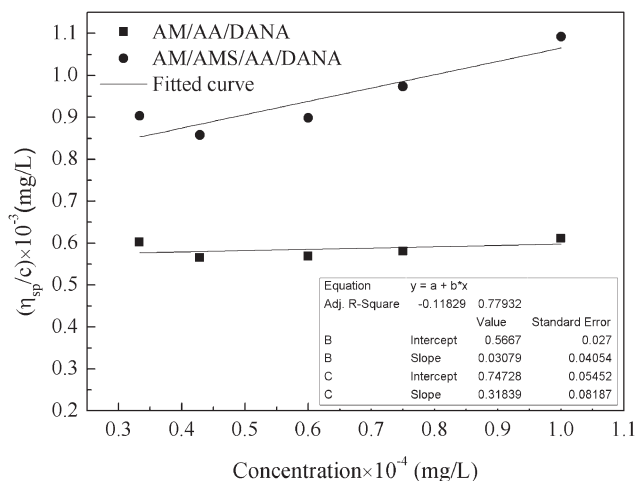
#### Microcosmic Morphological Analysis by SEM

The SEM images of HPAM, AM/AA/DANA, and AM/AMS/AA/DANA are shown in Figure 5. Figure 5(a,b) presents images of HPAM with scan sizes of  $50\ \mu\text{m}$  ( $2000\times$ ) and  $20\ \mu\text{m}$  ( $5000\times$ ), respectively. Figure 5(c,d) shows AM/AA/DANA at different sizes:  $50\ \mu\text{m}$  ( $2000\times$ ) and  $20\ \mu\text{m}$  ( $5000\times$ ). Similarly, the images of AM/AMS/AA/DANA are displayed at  $50\ \mu\text{m}$  ( $2000\times$ ) and  $20\ \mu\text{m}$  ( $5000\times$ ), as shown in Figure 5(e,f). The reticular structure of the synthesized copolymers was more complicated and denser



**Figure 3.**  $T_g$  values of AM/AA/DANA and AM/AMS/AA/DANA from DSC testing.

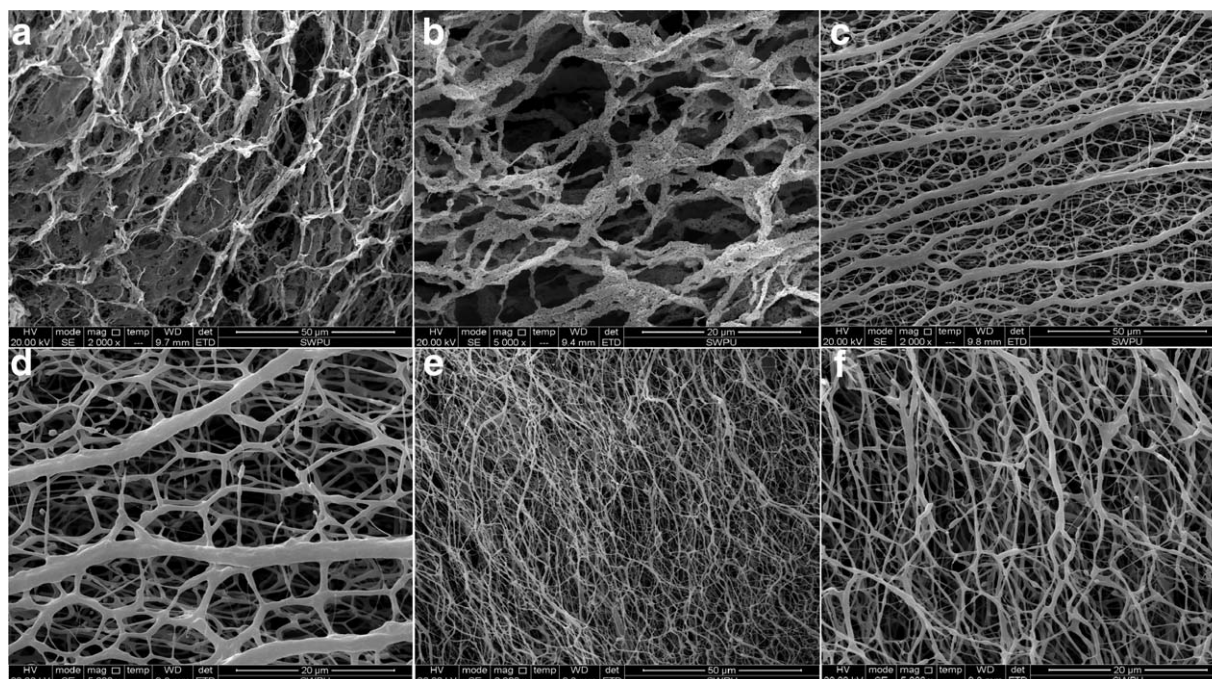
than that of HPAM under the same scanning conditions. The hexagonal mesh of AM/AA/DANA was evident among the microcosmic configuration images shown in Figure 5(c,d). Because of the partial crosslinking reaction among AM/AMS/AA/DANA caused by the excess HCHO, the AM/AMS/AA/DANA exhibited a more reticular structure compared to AM/AA/DANA at the same amplification. The reticular structure might have made it possible for the copolymers to become excellent EOR chemicals to improve the salt and temperature tolerance of the displaying fluid.<sup>37</sup>



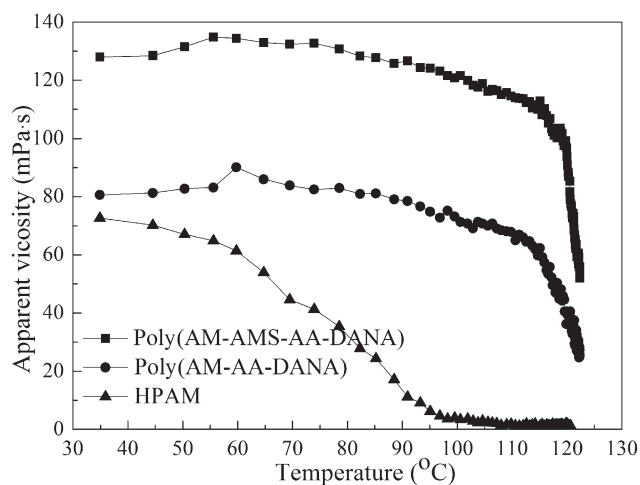
**Figure 4.**  $\eta_{sp}/c$  relationship for AM/AA/DANA and AM/AMS/AA/DANA.

### Temperature Tolerance of the Copolymers

The influence of the temperature on the copolymer (2.0 g/L) was investigated from 30 to 120°C under 170 s<sup>-1</sup>. We observed that the apparent viscosity decreased with increasing temperature, as shown in Figure 6. The viscosity retention rate of AM/AMS/AA/DANA (39.8%) and AM/AA/DANA (27.8%) was much better than HPAM (3.7%) at 120°C. The remarkable anti-temperature ability of AM/AMS/AA/DANA could be explained by the following aspect: on one hand, the nicotinic acid constitutional unit might lead to the difficulty rotation within the copolymer molecular chains, and the existence of crosslink structure caused by the excess of HCHO could prevent the molecular chain curling effectively. On the other hand, the



**Figure 5.** SEM images of polymers: (a) HPAM solution at 50  $\mu\text{m}$  (2000 $\times$ ), (b) HPAM solution at 20  $\mu\text{m}$  (5000 $\times$ ), (c) AM/AA/DANA solution at 50  $\mu\text{m}$  (2000 $\times$ ), (d) AM/AA/DANA solution at 20  $\mu\text{m}$  (5000 $\times$ ), (e) AM/AMS/AA/DANA solution at 50  $\mu\text{m}$  (2000 $\times$ ), and (f) AM/AMS/AA/DANA solution at 20  $\mu\text{m}$  (5000 $\times$ ).



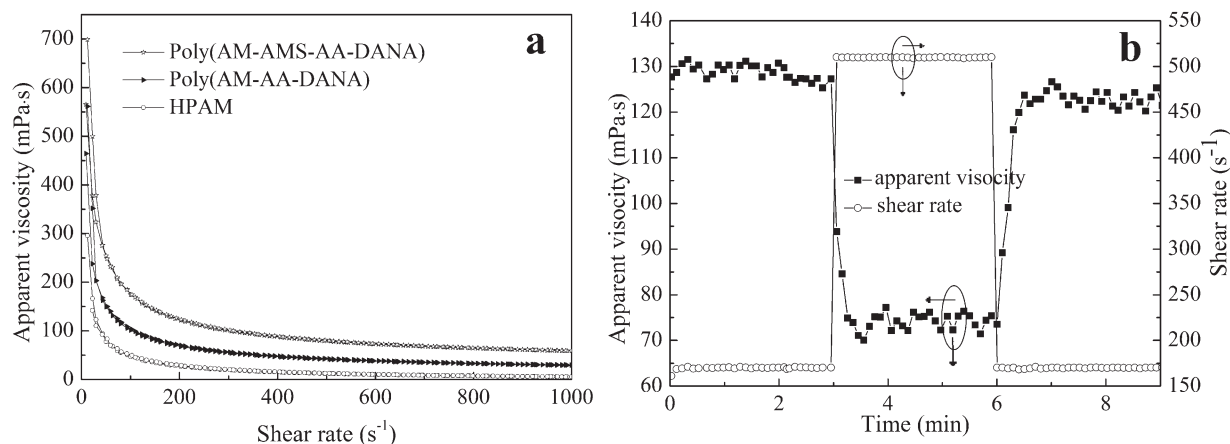
**Figure 6.** Temperature tolerance of AM/AMS/AA/DANA and AM/AA/DANA.

$-\text{CONHSO}_3^-$  groups introduced by sulfomethylation, which possessed a strong hydrogen-bonding ability, might have been beneficial to the temperature tolerance of the copolymers.<sup>30,38</sup>

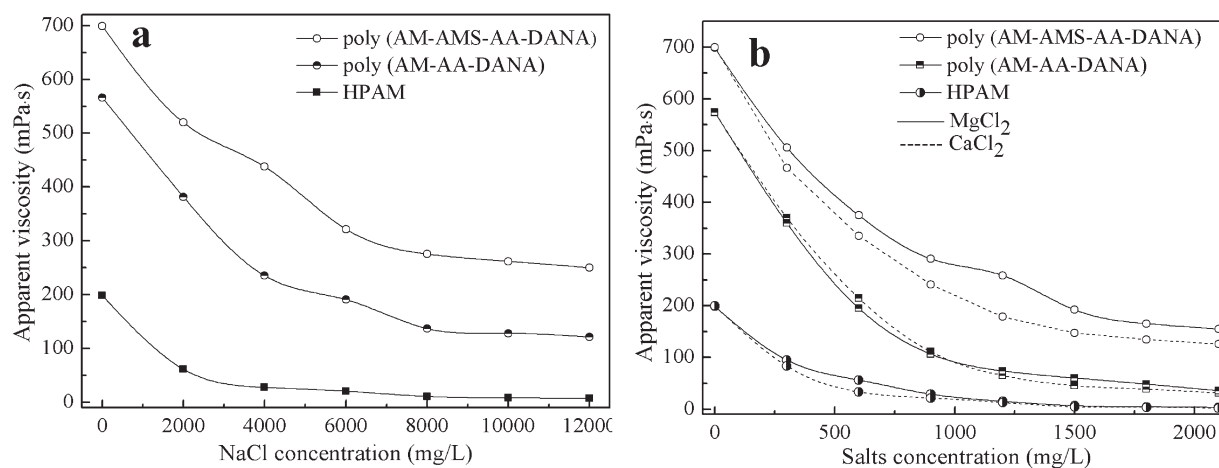
### Shear Tolerance of the Copolymers

The shear tolerance of the copolymers (2.0 g/L) was investigated, as shown in Figure 7(a). It was clear that the apparent viscosity of the copolymers decreased sharply under a shear rate of  $3.7\text{--}200\text{ s}^{-1}$ , whereas a slight alteration of the apparent viscosity was observed under a higher shear rate in  $600\text{--}1000\text{ s}^{-1}$ . The apparent viscosity and shear rate did not present a linear relationship; they exhibited an obvious pseudoplastic fluid behavior that belonged to a non-Newtonian fluid. Compared with HPAM, the synthesized copolymers AM/AMS/AA/DANA and AM/AA/DANA had better viscosity retention rates (AM/AMS/AA/DANA: 23.3%, AM/AA/DANA: 17.1%, and HPAM: 2.1%) at  $1000\text{ s}^{-1}$ . The results reveal that the obtained copolymers possessed extraordinary shear tolerance, which is important for a chemical flooding agent.

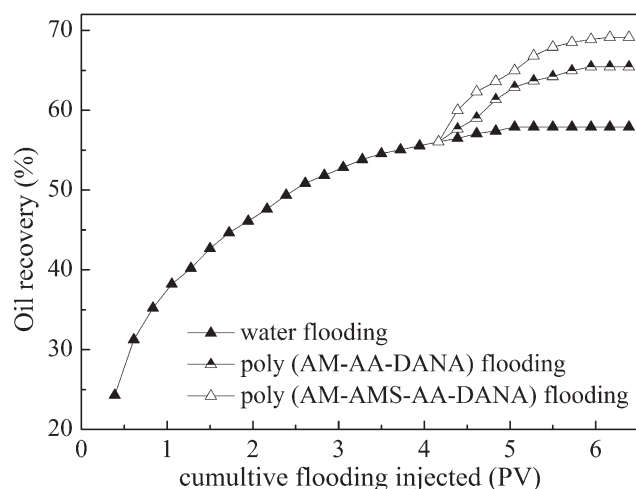
What is more, we also investigated the AM/AMS/AA/DANA solution by changing the shear rate abruptly after a constant shear rate lasted for 3 min [Figure 7(b)]. The apparent viscosity of AM/AMS/AA/DANA almost turned to the original value when the shear rate changed from  $170\text{ to }510\text{ s}^{-1}$  and then back to  $170\text{ s}^{-1}$ . This indicated that AM/AMS/AA/DANA showed a preferable recovery capability after the shear



**Figure 7.** Shear tolerance of (a) AM/AMS/AA/DANA and AM/AA/DANA and (b) AM/AMS/AA/DANA at different shear rates.



**Figure 8.** Effects of (a) NaCl, (b)  $\text{MgCl}_2$ , and  $\text{CaCl}_2$  on the copolymers at 0.2 wt % and  $30^\circ\text{C}$ .



**Figure 9.** EOR results for AM/AMS/AA/DANA and AM/AA/DANA at 70°C.

rate completed one cycle. The favorable rheological behavior of AM/AMS/AA/DANA might have been related to the strong hydrogen-bonding ability of  $-\text{SO}_3^-$ ; this was reformation assistance of the structure of AM/AMS/AA/DANA during shearing.

#### Salt Tolerance of the Copolymers

The relationship between the apparent viscosity and salt, such as NaCl,  $\text{MgCl}_2$ , and  $\text{CaCl}_2$ , was investigated (Figure 8). The solutions were tested at 2.0 g/L at 30°C. The apparent viscosity of the copolymer solutions decreased with increasing loading of salts, and it did not change when the addition of salts went beyond a certain concentration. This phenomenon could be explained by the reduction of intra-anionic electrostatic repulsion and the shrinking of the stretched polyelectrolyte chain with increasing quantities of cations. However, when the amount of cations was sufficient to complete the shrinking, the continuing addition of salt did not change the corresponding viscosity any more. The retention rates of the apparent viscosity were 37.4, 27.5, and 21.6% for AM/AMS/AA/DANA, and 22.7, 12.2, and 10.5% for AM/AA/DANA under conditions of NaCl (10 g/L),  $\text{MgCl}_2$  (1.5 g/L), and  $\text{CaCl}_2$  (1.5 g/L), respectively. However, the apparent viscosity retention rates for HPAM were only 3.5, 2.1, and 1.7% under the same conditions. AM/AMS/AA/DANA and AM/AA/DANA possessed better salt tolerances than HPAM. The hydration layer formed by the  $-\text{COO}^-$  group was easier to damage than the  $-\text{CONHCH}_2\text{SO}_3^-$  groups when neutralized with counter ions. Moreover, the partial crosslinking reaction among AM/AMS/AA/DANA caused by the excess of HCHO might have been related to a better salt tolerance.

#### Core Flooding Test

The core flooding experiments were conducted in a horizontal orientation. The relationship between the oil recovery and injected pore volume (PV) is displayed in Figure 9. Compared with water flooding, AM/AMS/AA/DANA and AM/AA/DANA could enhance the oil recovery significantly. AM/AMS/AA/DANA (EOR = 13.1%) was much better than AM/AA/DANA (EOR = 9.4%) in EOR in 2.0 g/L.

## CONCLUSIONS

Copolymers of AM/AA/DANA with AM, AA, and modular nicotinic acid were prepared by free-radical polymerization in aqueous solution. The  $-\text{SO}_3^-$  group was introduced into AM/AA/DANA to obtain the AM/AMS/AA/DANA copolymer by sulfomethylation. Compared with HPAM and AM/AA/DANA, the AM/AMS/AA/DANA exhibited better temperature tolerance, shear resistance, and salt tolerance. In addition, the core flooding test showed that the AM/AMS/AA/DANA remarkably enhanced the oil recovery by about 13.1%. Further investigation into the applications of the corresponding copolymers is ongoing.

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