

# Synthesis and Evaluation of a Water-Soluble Acrylamide Binary Sulfonates Copolymer on MMT Crystalline Interspace and EOR

Xiang-Jun Liu,<sup>1</sup> Wen-Chao Jiang,<sup>1,2</sup> Shao-Hua Gou,<sup>1,2</sup> Zhong-Bin Ye,<sup>1,2</sup> Xiao-Dong Xie<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

Received 18 July 2010; accepted 14 July 2011

DOI 10.1002/app.35299

Published online 7 January 2012 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** A novel water-soluble polymer was prepared by binary copolymerization and sulfomethylation using acrylamide (AM) and *N*-phenylmaleimide (N-PMI) as raw materials under mild conditions. Several factors were investigated and optimized conditions were confirmed in the copolymerization and sulfomethylation. It was found that the sulfonates copolymer was afforded with up to 60% retention rate of the apparent viscosity at 85°C; 30.4 mPa s apparent viscosity under 500 s<sup>-1</sup> shear rate with 5.028 min; 3.3 times relativity viscosity (compared with polyacryl-

amides) was obtained in 80 g/L NaCl brine; up to 9.5% enhance oil recovery in presence of 5000 ppm NaCl brine by core flood tests; and it was also found that the polymer **4a**, which combine with 10 wt % of KCl or NaCl brine could significantly affect the crystalline interspace of sodium montmorillonite (from 18.9 to 15.3 Å). © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1252–1260, 2012

**Key words:** crystalline interspace; sodium montmorillonite; salt-resisting; temperature-tolerance; enhanced oil recovery

## INTRODUCTION

The most widely used water-soluble polymers, polyacrylamides (PAM), have gained immense importance in recent years in the field of enhanced oil recovery (EOR) chemical, drilling fluid/completion fluid, water-shutoff/profile modification, coagulant, etc.<sup>1–11</sup> Although the PAM, especially partially hydrolyzed polyacrylamide (HPAM), is considered the best mobility control agent in surfactant-polymer and polymer-augmented water flooding processes for EOR, it is not suitable for high-temperature reservoirs (>90°C) and/or high-density brine fluids.<sup>8</sup> Many research works has indicated that substituted PAM or acrylamide (AM) copolymerized with a suitable functional monomer, can offer a better polymer that may be temperature resistant, salt tolerance, and shear resistance and has thermal stability under the reservoir conditions of temperature and salinity at least for a period.<sup>11–15</sup>

It is well known, PAM is not thermally stable because the —CONH<sub>2</sub> group is easily hydrolyzed and

degraded at polymer chain.<sup>14–18</sup> If the hydrogen of the amide group (—CONH<sub>2</sub>) are replaced by SO<sub>3</sub><sup>-</sup> groups or coordinated with other group, such as C=O, it might be could offer higher stability in solution, on account of their stronger hydrogen bonding between —NH<sub>2</sub> with SO<sub>3</sub><sup>-</sup> or C=O group.<sup>12,18–20</sup> Keeping in mind all above points, we wish to report here a copolymers sulfonates engenders a more effective EOR agents among oilfield chemists from AM and *N*-phenylmaleimide (N-PMI) by binary copolymerization and sulfomethylation (see Scheme 1).

## EXPERIMENTAL

### Materials

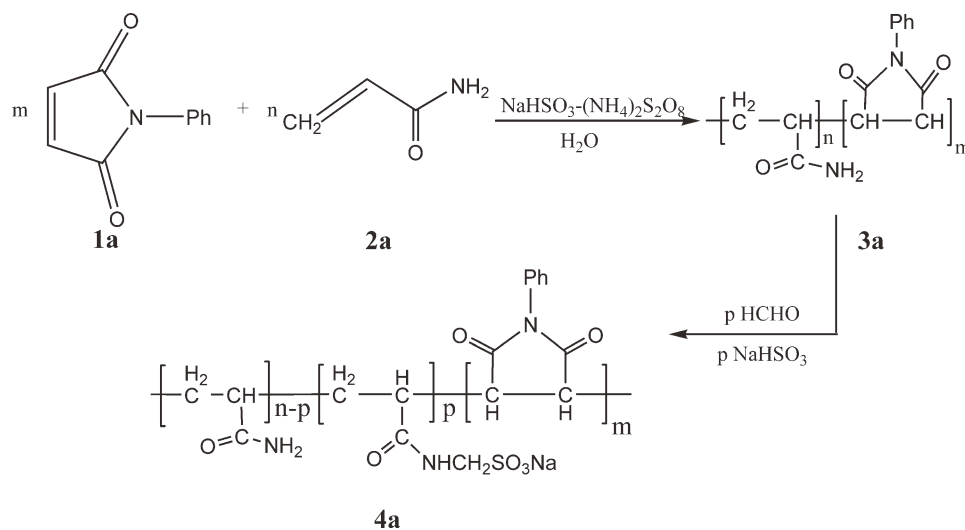
Acrylamide (AM, Analytical reagent), obtained from commercially and was recrystallized from a water-ethanol mixture. *N*-phenylmaleimide (N-PMI, analytical reagent), sodium sulfite (NaHSO<sub>3</sub>), ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), HCHO (37% aqueous), OP-10(used as emulsifier) and other chemicals were commercially available, and used directly without further purification; sodium montmorillonite (Xinjiang Xiazijie Bentonite).

### Preparation of the binary copolymers (3a)

AM and N-PMI monomers were dissolved in degassed and distilled water in the indicated ratio to

Correspondence to: S.-H. Gou (shaohuagou@swpu.edu.cn).

Contract grant sponsor: Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University; contract grant number: PLN0908.

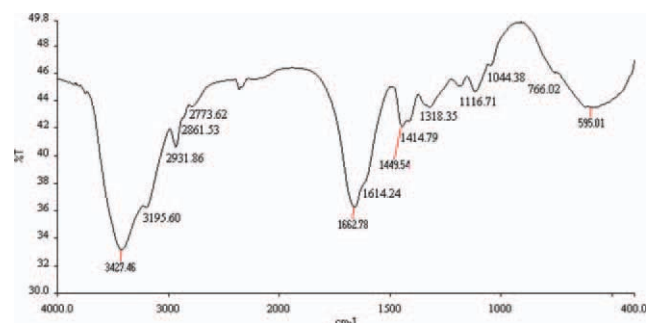


**Scheme 1** The synthesis of the binary copolymers sulfonates **4a**.

obtain an aqueous solution. Residual oxygen was removed by nitrogen being bubbled through the solution for 30 min under constant stirring at 25°C. To the mixture, OP-10(2 wt %), NaHSO<sub>3</sub>–(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (indicated loading, and 1/1 mol ratio) solutions were added slowly. The reaction was then allowed to occur at indicated times under indicated conditions. The final solution was clear and highly viscous. The polymer was then isolated by precipitation with acetone or water-ethanol and dried in vacuum for 6–10 h to yield the corresponding binary copolymer **3a**.

#### Preparation of the binary copolymers sulfonates **4a**

To a solution of AM binary copolymers **3a** (10.0 g) in 50 mL distilled water were added HCHO (37% aqueous) and NaHSO<sub>3</sub> ( $n(\text{NaHSO}_3)/n(\text{HCHO}) = 1/1$  mol ratio) at indicated conditions under atmosphere of nitrogen. And then, the mixture was stirred at indicated times. The mixture was isolated by precipitation with acetone or water-ethanol and dried in vacuum at 50°C for 6–10 h to give the corresponding copolymers sulfonates **4a**.



**Figure 1** IR spectra of binary copolymers **3a**. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

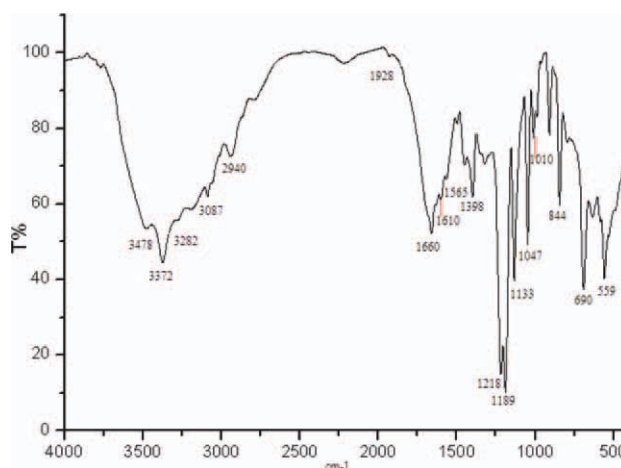
#### General remarks

All reactions were carried out under an atmosphere of with magnetic stirring unless otherwise indicated. IR spectra are taken in KBr pellets. Solution apparent viscosity is measured with the help of a rotational viscometer having a maximum shear rate of 2028 s<sup>-1</sup> at 15 wt % solution at room temperature. The salts effect and temperature effect were determined at 2000 mg/L concentration of corresponding copolymer solution.

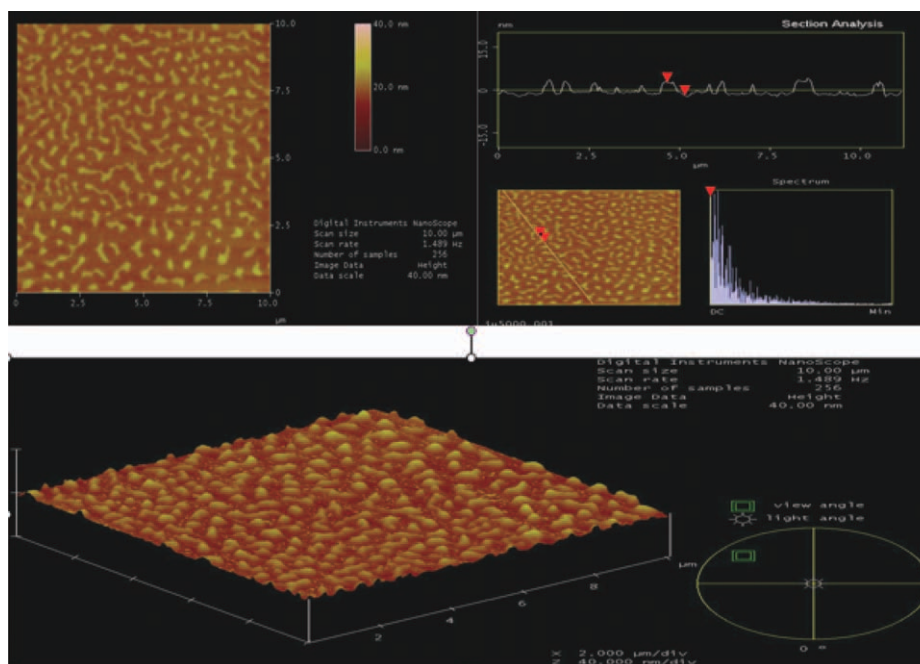
## RESULTS AND DISCUSSION

#### IR spectras analysis

The structure of the copolymers **3a** and **4a** was confirmed by FTIR spectroscopy as shown in Figures 1 and 2. The copolymer **4a** was prepared using HCHO



**Figure 2** IR spectra of binary copolymers sulfonates **4a**. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3** AFM images of **4a** casting films (scan size = 10.00  $\mu\text{m}$ , data scale = 40 nm). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

and  $\text{NaHSO}_3$  by sulfomethylation, which was confirmed by strong absorptions at  $1189\text{ cm}^{-1}$  in Figure 2. The characteristic absorptions of  $\text{C}=\text{O}$  stretch ( $1660\text{ cm}^{-1}$ ) and  $\text{C}=\text{C}$  stretching vibrations ( $1610\text{ cm}^{-1}$  in Fig. 1 and  $1610\text{ cm}^{-1}$  in Fig. 2) of aromatic ring in the spectrum of **3a** and **4a** were clearly presented. The disappearance of the characteristic absorption of  $\text{NH}$  (sharp peak at  $3427\text{ cm}^{-1}$  in Fig. 1 and sharp peak around  $3478$  and  $3372\text{ cm}^{-1}$  in Fig. 2) and the appearance of new characteristic absorptions of  $\text{N}-\text{H}$  ( $3183\text{ cm}^{-1}$ , Fig. 2) indicated the  $-\text{CONH}_2$  of the copolymer **3a** was partly replaced by  $-\text{CH}_2\text{SO}_3^-$  groups by sulfomethylation. As expected, the IR spectras confirmed the presence of different monomers in the copolymers **3a** and **4a**.

#### Elementary analysis of copolymer **4a**

The analysis conducted in this section was carried on by VarioEL-III elemental analyzer. In condition of high temperature and catalyst, the sample of **4a** was decomposed by oxidizing reaction. The gases which had been generated in the reaction were reduced by reducer at high temperature. Having flowed 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: 1.0% (S%), 44.12% (C%), 4.66% (H%); Found value: 0.83% (S%), 43.23% (C%), and 4.27% (H%).

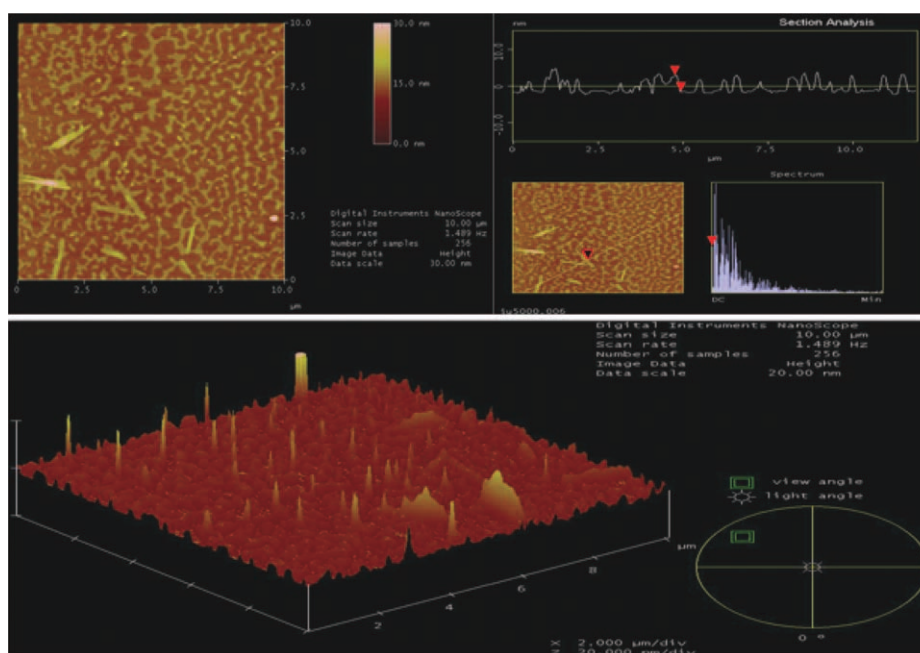
#### AFM images of **4a**

To observe a phase separation, **4a** was dissolved in degassed and distilled water as a solution (wt % = 5000 ppm). The solution was slowly evaporated to promote the phase separation, and the resulting film was annealed at room temperature for three days under reduced pressure. The surface profile of the specimen was investigated using atomic force microscopy (AFM).

Figures 3–5 shows an AFM tapping-mode phase contrast image, where the bright and dark parts represent **4a** domains. From Figure 3, many bulges could be observed under the conditions of scan size = 10.00  $\mu\text{m}$ , data scale = 40 nm. And some sharply peaks obviously could be observed when the condition changed to the scan size = 3.00  $\mu\text{m}$ , data scale = 30.00 nm (Fig. 4), Further changing the conditions to the scan size = 3.00  $\mu\text{m}$ , data scale = 40.00 nm (Fig. 5), partially cross-linked phenomenon of the copolymer **4a** could be clearly observed and the microstructure of **4a** appears in reticular shape. All the results show that the cross-link reaction was might caused by the extra addition of  $\text{HCHO}$  which was often used as cross-linker. Thus, this side reaction leads to the slight decrease of the solubility of polymer **4a**.

#### The ratio of AM to N-PMI in binary copolymeration

We investigated the effect of different ratio of AM to N-PMI in synthesis of binary copolymer **3a** (Table I).

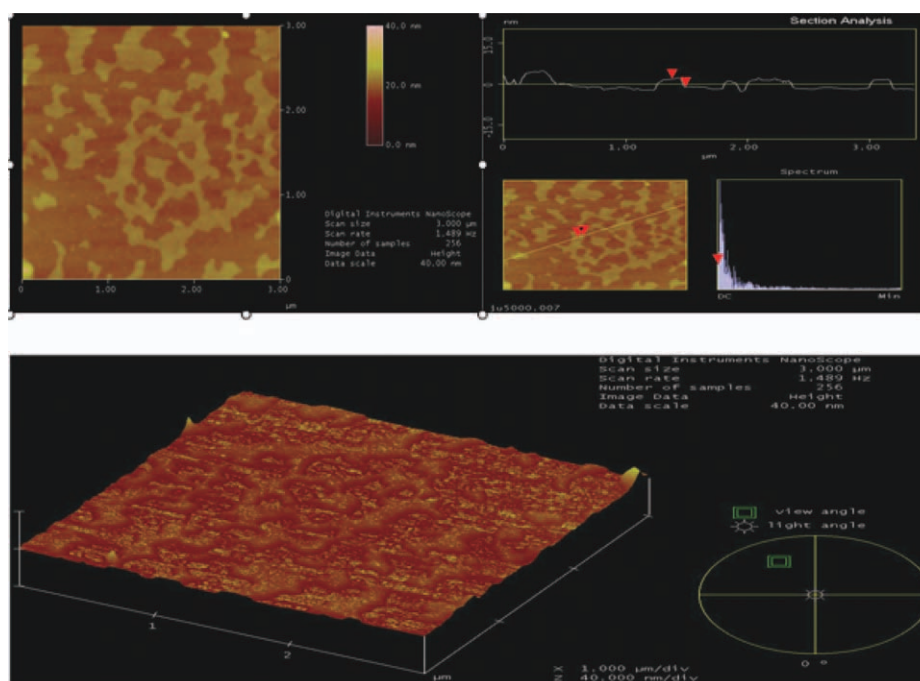


**Figure 4** AFM images of **4a** casting films (scan size = 10.00  $\mu\text{m}$ , data scale = 30.00 nm). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

It was found that the best results could be obtained by the ratios of AM to N-PMI was 8/1 (wt %), and the corresponding apparent viscosity up to 8100  $\text{mPa}/\text{s}^{-1}$  with 94% conversion (Table I, entry 5). Other ratios could give highly conversion with 1000–7200  $\text{mPa}/\text{s}^{-1}$  apparent viscosity (Table I, entries 1–4, 6–7).

#### The optimization of initiator in binary copolymeration

Having realized the most promising ratio of AM to N-PMI in the binary copolymeration, different types of initiator and loading were investigated (Table II, entries 1–6). It was found that the best initiator was  $\text{NaHSO}_3-(\text{NH}_4)_2\text{S}_2\text{O}_8$  system (Table II, entry 3) and



**Figure 5** AFM images of **4a** casting films (scan size = 3.00  $\mu\text{m}$ , data scale = 40.00 nm). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE I**  
Optimization the Ratio of AM to N-PMI in Binary Copolymerization

Entry <sup>a</sup>	AM (wt %)	N-PMI (wt %)	Apparent viscosity (mPa/s <sup>-1</sup> ) <sup>b</sup>	Conversion (%) <sup>c</sup>
1	4	1	1000	90
2	5	1	3500	90
3	6	1	5500	92
4	7	1	6900	93
5	8	1	8100	94
6	10	1	7200	95
7	15	1	7100	95

<sup>a</sup> Conditions: pH = 9.0, OP-10: 2% (wt %), initiator (NaHSO<sub>3</sub>-(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>): 0.2 wt %, Temperature 40°C, concentration of AM and N-PMI: 15% (wt %), reaction time: 4 h.

<sup>b</sup> Apparent viscosity: at room temperature.

<sup>c</sup> Conversion (wt %): AM.

other initiator systems gave dissatisfactory results under same conditions in the binary copolymerization (Table II, entries 1, 2, and 5). The best loading of NaHSO<sub>3</sub>-(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> could be obtained when the loading was 0.2 wt % (Table II, entries 3), with increased or decreased loading of the initiator could not improve the results (Table II, entries 5 and 6).

### The pH effect in binary copolymerizing and sulfomethylation

And then, the pH effect of binary copolymerizing and sulfomethylation were investigated, the results summarized in Table III. The best results could be afforded when the pH changed to 10.0 with highest apparent viscosity (Table III, entry 4), when increasing or decreasing the pH value could not improve the results in the binary copolymerization (Table III, entries 1–3, and 5). Similarly results also occurred in the sulfomethylation, the best pH value was 11.0 with highly conversion (Table IV, entry 2), others conditions gave bad results (Table IV, entries 1 and 3).

**TABLE II**  
Optimization the Initiator in Binary Copolymerization

Entry <sup>a</sup>	Initiator system	Loading (wt %)	Time (h)	Apparent viscosity (mPa/s <sup>-1</sup> ) <sup>b</sup>	Conversion <sup>c</sup> (%)
1	H <sub>2</sub> O <sub>2</sub>	0.2	10	1500	73
2	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.2	8	2300	76
3	NaHSO <sub>3</sub> -(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.2	4	8100	94
4	H <sub>2</sub> O <sub>2</sub> -FeSO <sub>4</sub>	0.2	7	3600	79
5	NaHSO <sub>3</sub> -(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.3	5	7600	93
6	NaHSO <sub>3</sub> -(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.1	5	7800	91

<sup>a</sup> Conditions: pH = 9.0, OP-10: 2% (wt %), AM/N-PMI: 8/1(wt %), Temperature 40°C, concentration of AM and N-PMI: 15% (wt %).

<sup>b</sup> Apparent viscosity: at room temperature.

<sup>c</sup> Conversion (wt %): AM.

**TABLE III**  
Optimization the pH in Binary Copolymerizing

Entry <sup>a</sup>	pH	Time (h)	Apparent viscosity <sup>b</sup> (mPa/s <sup>-1</sup> )	Conversion <sup>c</sup> (%)
1	7	10	1000	26
2	8	10	2600	65
3	9	4	8100	94
4	10	4	8100	95
5	11	4	7900	93

<sup>a</sup> Conditions: OP-10: 2 wt %, initiator (NaHSO<sub>3</sub>-(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>): 0.2 wt %, Temp. 40°C, AM/N-PMI: 8/1 (wt %), concentration of AM and N-PMI: 15 wt %.

<sup>b</sup> Apparent viscosity: at room temperature.

<sup>c</sup> Conversion (wt %): AM, respectively.

### The temperature effect in binary copolymerizing and sulfomethylation

It was found that the best reaction temperature was 40°C in binary copolymerization (Table V, entry 2) and 60°C in sulfomethylation (Table VI, entry 3), respectively. Other conditions could give excellent conversion with slightly lower apparent viscosities.

### Optimization the degree of sulfonylurea methylation

It was found that the degree of sulfonylurea methylation play a very important role to apparent viscosity in the copolymerization sulfonates. The best results obtained when the loading of HCHO ( $n(\text{HCHO})/n(\text{NaHSO}_3) = 1/1$ ) was 2 wt % (Table VII, entry 2). Increasing or decreasing the loading could not improve the results (Table VII, entries 1, 3, and 4), it may be attributed to the cross linking reaction between -NH<sub>2</sub> group with HCHO under same conditions.

### Fluid characteristics of the solution of binary copolymers 4a

It can be observed from Figure 6 and Table VIII that the binary copolymer 4a solutions showed strong

**TABLE IV**  
Optimization the pH in Sulfomethylation

Entry <sup>a</sup>	pH	Time (h)	Apparent viscosity <sup>b</sup> (mPa/s <sup>-1</sup> )	Conversion <sup>c</sup> (%)
1	10	4	6800	95
2	11	2	7100	96
3	12	4	6500	94

<sup>a</sup> Conditions: Temperature 60°C, concentration of **3a**: 15 wt %, concentration of HCHO and NaHSO<sub>3</sub>: 2 wt %.

<sup>b</sup> Apparent viscosity: at room temperature.

<sup>c</sup> Conversion (wt %): **3a**, respectively.

nonNewtonian behaviors which is often possessed by chemical flooding agent. And 30.4 mPa/s<sup>-1</sup> apparent viscosity was afforded under 500 s<sup>-1</sup> shear rate with up to 5.028 min; 3.3 times relativity viscosity (compared with PAM) was obtained in 80 g/L NaCl brine.

#### Comparison of **4a** with the HPAM for brine compatibility and thermal stability

Compared with HPAM which has been widely used as chemical flooding agent in EOR, this novel binary copolymer showed better brine compatibility, thermal stability.

In Figure 7, with an increasing cations concentration in the polymer solution, the stretched polyelectrolyte chain started shrinking because of a reduction in intra-anionic electrostatic repulsion. At a certain salt concentration, the amount of cations present was sufficient to complete the shrinking, making the binary copolymer behave like a nonelectrolyte.<sup>6,10</sup> Therefore, beyond that certain salt concentration, the addition of salt could not change the corresponding apparent viscosity more, and this is typical of a nonelectrolyte. The phenomena that the viscosity of **4a** solution has slightly increased with the increasing concentration of NaCl may be explained by the theory of ionic charge resonance. Polymer **4a** has amount of -CONHCH<sub>2</sub>SO<sub>3</sub><sup>-</sup> whose negative charge was resonated and dispersed on

**TABLE V**  
Optimization the Temperature in Binary Copolymerization

Entry <sup>a</sup>	Temperature (°C)	Time (h)	Apparent viscosity <sup>b</sup> (mPa/s <sup>-1</sup> )	Conversion <sup>c</sup> (%)
1	30	6	7300	93
2	40	4	8100	94
3	50	3	8000	95

<sup>a</sup> Conditions: OP-10: 2% (wt %), pH: 10.0, initiator (NaHSO<sub>3</sub>-(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>): 0.2 wt %, AM/N-PMI: 8/1 (wt %), concentration of AM and N-PMI: 15 wt %.

<sup>b</sup> Apparent viscosity: at room temperature.

<sup>c</sup> Conversion (wt %): AM, respectively.

**TABLE VI**  
Optimization the Temperature in Sulfomethylation

Entry <sup>a</sup>	Temperature (°C)	Time (h)	Apparent viscosity (mPa/s <sup>-1</sup> ) <sup>b</sup>	Conversion <sup>c</sup> (%)
1	40	4	6300	93
2	50	4	6800	95
3	60	2	6900	95
4	70	4	6700	97

<sup>a</sup> Conditions: pH: 11.0, concentration of **3a**: 15 wt %.

<sup>b</sup> Conversion (wt %): **3a**, respectively.

<sup>c</sup> Apparent viscosity: at room temperature.

three oxygen atoms. However, the negative charge of -COO<sup>-</sup> group in HPAM resonated and dispersed on two oxygen atoms. Then, the charge density of HPAM is much higher than polymer **4a**. In addition, comparing with -CONHCH<sub>2</sub>SO<sub>3</sub><sup>-</sup> groups the hydration layer formed by -COO<sup>-</sup> group is easier to damage when neutralized with counter ions. Therefore, the brine resistance of polymer **4a** is better than HPAM.

Similarly, it can be found from Figure 8 that solutions of **4a** can tolerant higher temperature than HPAM. The thermal stability of the binary copolymer **4a** solutions was studied by aging at different temperature (30–90°C, Fig. 8). It was found that the **4a** exhibited moderate thermal stability. The big loss of solution apparent viscosity for the copolymer was observed; about 60% of the solution apparent viscosity was retained at 85°C which is closed to HPAM.

#### Core flood tests

The core assembly was a stainless steel cylinder of 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.

**TABLE VII**  
Optimization the Degree of Sulfomethylation

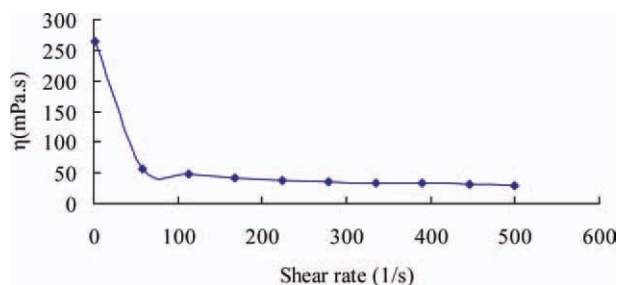
Entry <sup>a</sup>	Loading <sup>b</sup> (wt %)	Time (h)	Apparent viscosity (mPa/s <sup>-1</sup> ) <sup>c</sup>	Conversion <sup>d</sup> (%)
1	1	2	6000	90
2	2	2	6900	95
3	3	2	5200	95
4	4	2	4300	94

<sup>a</sup> Conditions: pH: 11, Temperature 60°C,  $n(\text{NaHSO}_3)/n(\text{HCHO}) = 1/1$ .

<sup>b</sup> Loading (wt %): NaHSO<sub>3</sub> and HCHO.

<sup>c</sup> Apparent viscosity: at room temperature.

<sup>d</sup> Conversion (wt %): **3a**.



**Figure 6** Fluid characteristics of the solution of copolymers **4a**. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

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, single pump flow rate of 0.01–107 mL/min; pressure sensor: range 0–0.1, 0–1, and 0–5 MPa, accuracy of 0.1% FS.

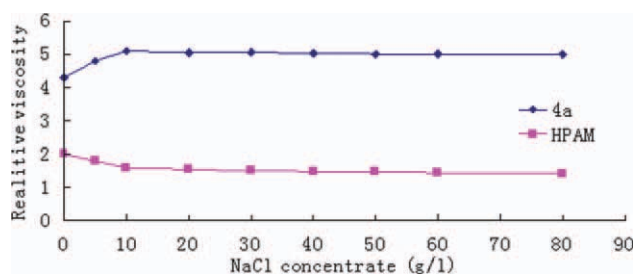
For the studies of the effect of brine on the oil recovery, the sand pack was saturated with brine instead of fresh water [see Fig. 9(a)]. It was then flooded with oil to connate water saturation after which the sand pack was flooded with brine water. Finally, it was flooded with the polymer **4a** solution. The polymer retention in the sand pack after recovery was calculated by material balance after determining the polymer concentration in solution before and after injection.<sup>7</sup>

It can be observed from Figure 9 (b–d) that the solution of copolymer **4a** can be used as an EOR chemical. It can enhance oil recovery about 7.5% in presence of 5000 ppm NaCl at 60°C compared with water flooding using 3000 ppm **4a** copolymer solution [Fig. 9(b)]. Higher enhance oil recovery (8.5%) afforded when increasing the **4a** copolymer solution to 5000 ppm [Fig. 9(c)]. Further increasing the copolymer (**4a**) concentration to 7000 ppm, with up to

**TABLE VIII**  
Fluid Characteristics Experiment of the Solution of Copolymers **4a**

Entry <sup>a</sup>	<i>T</i> (min)	Shear stress (Pa)	Shear rate (1/s)	η (mPa/s <sup>-1</sup> )
1	0.03093	0.489	1.85	264
2	0.588	3.239	57.6	56.3
3	1.14	5.341	112	47.5
4	1.695	7.053	168	41.9
5	2.252	8.617	224	38.5
6	2.808	10.07	279	36.1
7	3.363	11.3	335	33.7
8	3.916	12.8	390	32.8
9	4.473	14.07	446	31.5
10	5.028	15.2	500	30.4

<sup>a</sup> Conditions: concentration of **4a** = 5000 ppm, Temp. 60°C.



**Figure 7** The relative viscosity of salt-tolerance between **4a** and HPAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

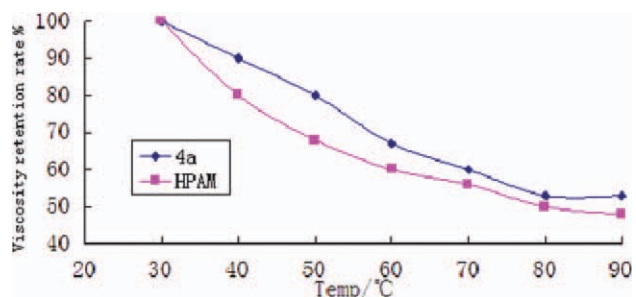
9.5% enhance oil recovery afforded [Fig. 9(d)]. The all results indicated that the copolymer has good enhance oil recovery.

### The crystal spacing between copolymer **4a** with sodium montmoduonite

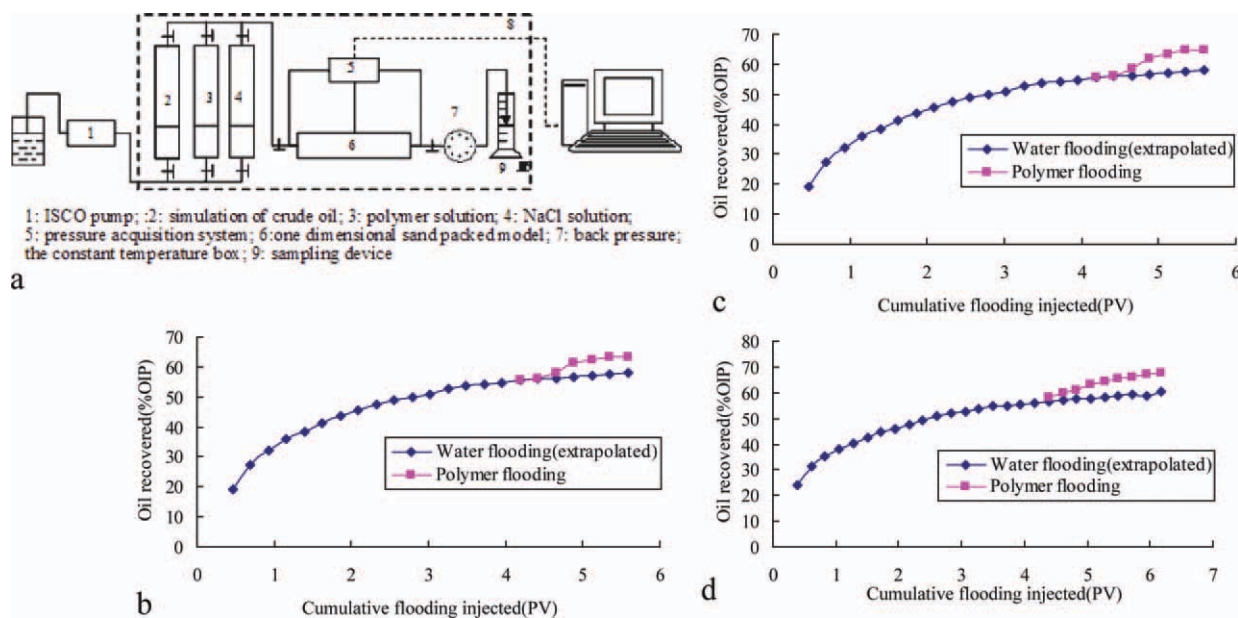
According to the previous works in the field of clay stability and EOR chemical,<sup>4,5,21</sup> generally, it is the most important internal cause that clay mineral occurs hydration expansion when the external water environment have changed leading to reduced strength of shale formation and inducing wellbore instability. To investigate the details of the effect, we choose sodium montmorillonite (MMT) which is the most common clay mineral in the stratum to study its crystalline interspace.

After drying, the MMT was prepared as 11 samples and each weight is 2 g. Then, the MMT sample was mixed with copolymer (**4a**) solution of different concentrations and different salts (10 wt %; KCl, NaCl, or/and CaCl<sub>2</sub>) and placed into a special hermetic container. Thirty minutes later, the sample was made into tablet the crystalline interspace of which would be measured by X-ray diffraction.

Firstly, the crystalline interspace of copolymer (**4a**) was investigated (Fig. 10). And then, different concentration copolymer and salts combine with MMT were also measured (Figs. 11 and 12). It was found that the copolymer (**4a**) solution has little influence



**Figure 8** Comparison of Temperature-resistant between **4a** and HPAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



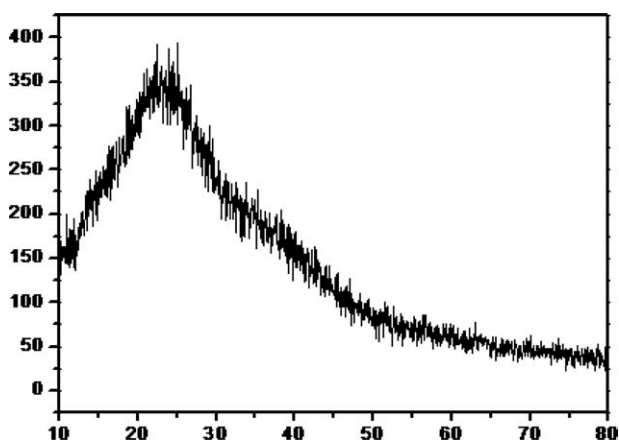
**Figure 9** Oil recovery by using water and copolymer (4a) flooding in presence of 5000 ppm NaCl at 60°C. (a) The one-dimensional sand-packed model for EOR (b) using the copolymer (4a) solution 3000 ppm (c) using the copolymer (4a) solution 5000 ppm (d) using the copolymer (4a) solution 7000 ppm. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

on the crystal spacing of MMT compared with the MMT combine with distilled water which means that copolymer solution would not lead to negative effect on the stability of well (Table IX, entries 2–7 and Fig. 11). The crystalline interspace of MMT could be obviously reduced from 18.95323 Å to 15.37453 Å when 10 wt % NaCl or KCl were be combined (Table IX, entries 9, 10, and Fig. 12). However, the bad result was obtained when 10 wt % CaCl<sub>2</sub> employed in the same conditions (Table IX, entry 8 and Fig. 12). When the 10 wt % NaCl, KCl, and CaCl<sub>2</sub> were employed in the same conditions, similar result with 10 wt % NaCl or KCl afforded (Table IX, entry 11 vs. entries 9, 10, Fig. 12, mixture sample). All of the above results indicated that the

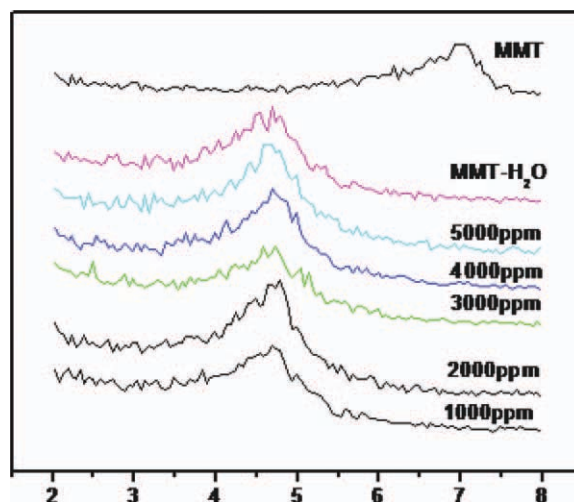
copolymer (4a) solution with salt could even help stabilizing the well environment.<sup>20</sup>

## CONCLUSIONS

A novel binary copolymer was prepared and characterized by binary copolymerization and sulfomethylation using AM and N-PMI as raw materials. The replacement of the –CONH<sub>2</sub> group with a sulfonate group produced polymer that has moderate or good brine compatibility, shear resistance, and thermal stability for



**Figure 10** The crystal spacing of copolymer 4a.



**Figure 11** The crystalline interspace of MMT and copolymer (4a)-MMT. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**TABLE IX**  
**The Crystal Spacing Between Copolymer 4a Solutions**  
**with MMT**

Entry <sup>a</sup>	Sample	Crystalline interspace <sup>b</sup> (Å)
1	MMT	12.63387
2	MMT-H <sub>2</sub> O	18.95323
3	<b>4a</b> (1000 ppm) <b>4a</b> -MMT	18.89232
4	<b>4a</b> (2000 ppm) <b>4a</b> -MMT	18.80511
5	<b>4a</b> (3000 ppm) <b>4a</b> -MMT	18.84386
6	<b>4a</b> (4000 ppm)-MMT	18.7007
7	<b>4a</b> (5000 ppm)-MMT	18.87817
8	CaCl <sub>2</sub> (10 wt %) - <b>4a</b> (1000ppm)-MMT	18.1523
9	NaCl (10 wt %)-1000 ppm <b>4a</b> -MMT	15.37453
10	KCl (10 wt %)- <b>4a</b> (1000 ppm) -MMT	15.45829
11	KCl (10 wt %)-CaCl <sub>2</sub> (10 wt %)- NaCl(10 wt %)-MMT	15.66094

<sup>a</sup> Two gram scale MMT used, room temperature (25°C), concentration of **4a** = 5000 ppm, Temperature 60°C.

<sup>b</sup> Determined by XRD technology.

EOR chemical. Compared with HPAM which has been widely used as chemical flooding agent in EOR, this novel binary copolymer (**4a**) shows better brine compatibility, shear resistance, solubility, and thermal stability. And the further investigation on the applications of the corresponding copolymers is ongoing.

The authors wish to thank Dr Lanjun Nai for core flood tests.

## References

- Lipp, D.; Kozakiewicz, J. In *Encyclopedia of Chemical Technology*, 4th ed.; Grant, M. H., ed.; Wiley: New York, 1991; Vol. 1.
- Gogarty, W. B.; Tosch, W. C. *J Pet Technol* 1968, 20, 1407.
- Szabo, M. T. *J Pet Technol* 1979, 31, 553.
- Shalaby, S. W.; McCormick, C. L.; Buttler, G. B., Eds. *Water Soluble Polymers. Synthesis, Solution Properties and Applications*; ACS Symposium Series 467; American Chemical Society: Washington, DC, 1991.
- Glass, J. E., Ed. *Water Soluble Polymers: Beauty with Performance*; *Advances in Chemistry* 213; American Chemical Society: Washington, DC, 1986.
- Abdel-Alim, A. H.; Hamielec, A. E. *J Appl Polym Sci* 1973, 17, 3769.
- Borchardt, J. K. In *Encyclopedia of Polymer Science and Technology*, 2nd ed.; Kroschwitz, J. I., ed.; Wiley-Interscience: New York, 1987; Vol.10.
- van Poollen, H. K. *Fundamentals of Enhanced Oil Recovery*; PennWell: Tulsa, Okla, 1980; p 87.
- Dominguez, J. G.; Wilhite, G. P. *Soc Pet Eng J* 1977, 17, 111.
- Szabo, M. T. *Soc Pet Eng J* 1975, 15, 323.
- Hou, J.; Gong, H. J.; Xu, G.Y.; Zhu, Y. Y.; Wang, Y. J.; Wu, D.; Niu, M. Y.; Wang, L. S.; Guo, H. J.; Wang, H. B. *Energy Fuels* 2009, 23, 300.
- Doe, P. H.; Araghi, A. M.; Shaw, J. E.; Stahl, G. A. *Soc Plast Eng Res Eng* 1987, 2, 461.
- Anupom, S.; Arun, B.; Inamul, H. *J Appl Polym Sci* 2003, 87, 1869.
- Anupom, S.; Arun, B.; Inamul, H. *Energy Fuels* 2003, 17, 683.
- Smith, E. A.; Prues, S. L.; Oehme, F. W. *Ecotoxicol Environ Safety* 1997, 37, 76.
- Sutherland, G. R. J.; Haselbach, J.; Aust, S. D. *Environ Sci Pollut Res*, 1997, 4, 16.
- Suzuki, J.; Hukushima, K.; Suzuki, S. *Environ Sci Technol* 1978, 12, 1180.
- Neidlinger, H. H.; Chen, G. S.; Arai, F.; McCormick, C. L. *Polym Prepr* 1981, 22, 90.
- McCormick, C. L.; Elliot, D. L. *Macromolecules* 1986, 19, 542.
- Budd, P. M. In *Comprehensive Polymer Science*; Allen, G., Ed.; Pergamon: Elmsford, NY, 1989; Vol. 1, p 225.
- Liu, X. G.; Yuan, S. L.; Liu, H.; Wu, X. L. *Rock Soil Mech* 2011, 32, 137.