# A Water-Soluble Acrylamide Hydrophobically Associating Polymer: Synthesis, Characterization, and Properties as EOR Chemical

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**ABSTRACT**: A water-soluble acrylamide hydrophobically associating terpolymer for polymer flooding was successfully synthesized via free radical polymerization using acrylamide (AM), acrylic acid (AA), and *N*,*N*-divinylnonadeca-1,10-dien-2-amine (DNDA) as raw materials. The terpolymer was characterized by IR spectroscopy and fluorescence spectra. Compared with partially hydrolyzed polya-cryamide (HPAM), the terpolymer showed a stronger link and better dimensional network structure under the environmental scanning electron microscope (ESEM). The results of rheology indicated that the terpolymer (AM-NaAA-DNDA) showed an excellent shear-resistance in high shear rate (1000 s<sup>-1</sup>) and remarkable temperature-tolerance (above 110°C). The salt-resisting experiment revealed that this terpolymer had a better anti-salt ability. According to the core flooding test, it could be obtained that oil recovery was enhanced more than 15% under conditions of 2000 mg/L terpolymer in the mineralization of 8000 mg/L at 60°C. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1888–1896, 2013

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### INTRODUCTION

Water-soluble polymers are used in many oilfield operations including polymer-augmented water flooding, chemical flooding and profile modification. The role of the polymer in most enhanced oil recovery (EOR) field applications is to increase the viscosity of the aqueous phase. This increase in viscosity can improve the sweep efficiency during the process of enhanced oil recovery. The use of water-soluble polymers for improved oil recovery has thus been extensively reviewed.<sup>1–5</sup>

Polyacrylamides (PAM) and copolymer, the most widely used water-soluble enhanced oil recovery (EOR) polymer, which can yield a significant increase in oil recovery when compared with water flooding, have gained immense importance with the increasing worldwide demands on petroleum in recent years.<sup>6–10</sup> These traditional polymers rely on chain extension and physical entanglement of solvated chains for viscosity enhancement. The viscosity of a solution of PAM increases as its molecular weight increases. As a result, the solution viscosity increases at a given polymer concentration when oilfield operations use high molecular weight PAM. However, high molecular weight PAM is irreversibly degraded by high shear rates due to the breakage

of the polymer backbone caused by the high shear rates. The higher the molecular weights of PAM, the easier it is shear degraded.<sup>11</sup> In addition, the viscosity of PAM decreases rapidly as salinity or hardness increases.<sup>12</sup> The polymer will precipitate in the presence of high concentrations of divalent ions. In a word, PAM is unsuitable given the harsh conditions of high salinity, high temperature, high heterogeneity, and long-time injections which commonly exist in most oil reservoirs due to the hydrolysis, degradation, and others.<sup>13,14</sup>

Compared with polyacrylamide, xanthan gum is a rigid polysaccharide that is not readily shear degraded, and is not sensitive to an increase in salinity or divalent ion concentration.<sup>15</sup> Nevertheless, the disadvantages of xanthan also include higher cost, high susceptibility to biodegradation, and potential for injectivity problems due to the cellular debris remaining from the manufacturing process. Solutions of both PAM and xanthan exhibit decreasing viscosity as temperature increases. Nowadays, the heterogeneity is getting worse and worse after being long time water-flooded, the water-soluble polymers, which has the heat resistance, salt resistance and shear resistance, aimed to deeper oil wells, is a challenge to the oil field chemists.<sup>16–19</sup>

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Scheme 1. The synthesis of poly(AM-NaAA-DNDA).

Recently, many research works have indicated that functional polyacrylamide or acrylamide (AM) copolymerized with a suitable hydrophobic monomer, can yield a better production which may be temperature resistance, salt tolerance, shear resistance, or thermal stability under the reservoir conditions of temperature and salinity at least for a longer period than PAM.<sup>20,21</sup> Inspired by the predecessors' methods, the N,N-divinylnonadeca-1,10dien-2-amine (DNDA) was adopted as the hydrophobic monomer by achieve structural diversity to search for a new highly efficient EOR chemical based on AM copolymer aim to reach the level of practicability (see Scheme 1). The distribution of DNDA in the solution viscosity behaviors of polymers prepared by varying aqueous phase pH, ratio of hydrophobic monomer to template and hydrophobic monomer content were investigated. Effects of polymer concentration and inorganic salt concentration on hydrophobic associating behavior were examined. And the feasibility of the terpolymer to enhanced oil recovery was analyzed.

#### **EXPERIMENTAL**

### **General Remarks**

All reactions were carried out under an atmosphere of nitrogen in flame glassware with magnetic stirring unless otherwise indicated. IR spectra of the samples measured with KBr pellets in a Perkin Elemer RX-1 Spectrophotometer (Beijing Reili Analytical Instrument Co). <sup>1</sup>H NMR spectrum was measured with 400 MHz using D<sub>2</sub>O as the solvent. Monomer conversion of AM was determined by high performance liquid chromatography technology (Shimadzu company, Japan) using ODS column at UV detector (210 nm), H<sub>2</sub>O/CH<sub>3</sub>OH = 90/10(v/v). The apparent viscosities of copolymer solutions measurement was conducted by a Brookfield LVTDV III rotational viscometer (Brookfield Asset Management Inc., Middleboro, USA) with a spindle 62 and a shear rate of 7.34 s<sup>-1</sup>. Rheological measurements were carried out on a HAAKE RS6000 Rotational Rheometer (Germany).

### Materials

Acrylamide (AM) was purchased and purified by crystallization from a water–ethanol mixture sodium hydrate (NaOH). While acrylic acid (AA), NaHSO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, OP-10, NaCl, MgCl<sub>2</sub>·6H<sub>2</sub>O, CaCl<sub>2</sub>, and other chemicals were purchased and used directly without further purification. DNDA was prepared according to the literatures.<sup>22–24</sup> Water was doubly distilled and deionized by passing through an ion exchange column. All other chemicals were of analytical grades, unless otherwise noted.

### Calculation of Intrinsic Viscosity

The intrinsic viscosity  $[\eta]$  was measured with Ubbelohde's viscometer (the diameter: 0.3 mm, length: 12.15 cm) at 30°C. The solvent efflux time was greater than 100 s; therefore no kinetic energy corrections were made on the observed data. The temperature was controlled using a Cannon constant-temperature bath. Triplicate reading were taken at each concentration using a stopwatch accurate to 0.2 s. Efflux times were 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).

### Preparation of N,N-divinylnonadeca-1,10-dien-2-amine (DNDA)

Raw material oleoyl chloride was synthesized by (E)-octadec-9enoic acid and phosphorus trichloride according to the literature.<sup>25</sup> The comonomer, N,N-divinylnonadeca-1,10-dien-2amine (DNDA) was prepared oleoyl chloride and diallylamine according to the following method: dichloromethane solution(20 ml) with diallulamine(4.6 ml,0.04 mol) and triethylamine(6 ml, 4 mol) were added to a round bottom flask, cooled by ice-water bath and purged with nitrogen at the same time. Then dichloromethane solution (20 ml) with predissolved oleoyl chloride (12.7 ml, 0.04 mol) was titrated slowly. The temperature was kept below 5°C. After titration, the system was kept still for 5 h at the room temperature. Then the organic phase was washed twice with water and aqueous phase was extracted with dichloromethane after adding excessive sodium chloride. The solvents were removed by vacuum distillation, and liquid product was obtained (yield 86%).

The monomer DNDA was determined by <sup>1</sup>H NMR spectroscopy of the samples measured in D<sub>2</sub>O. The observed <sup>1</sup>H NMR (400 MHz) shifts  $\delta$ (mg/L) of DNDA are: 2H (=CH of side chain), 4.61; 4H (=CH<sub>2</sub>), 4.09; 2H (=CH of main chain), 3.76; 4H (-CH<sub>2</sub> of N), 3.23; 2H (-CH<sub>2</sub> of carbonyl), 2.26; 4H (-CH<sub>2</sub> of ethylene), 2.14; 22H (-CH<sub>2</sub> of the main chain), 1.67; 3H (-CH<sub>3</sub>), 0.96.

### Preparation of the Copolymers AM-NaAA-DNDA

Copolymerization of the AM-NaAA-DNDA was carried out by free radical polymerization. The monomers in previously





Figure 1. IR spectra of the base polymers and copolymer AM-NaAA-DNDA (a) AM; (b) AA; (c) DNDA; (d) *co*-AM-NaAA-DNDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

designed composition, emulsifier (0.3 wt%) as well as NaHSO<sub>3</sub>– (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 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 arrangement. Copolymerization was carried out at indicated temperature under N<sub>2</sub> atmosphere for indicated time. The polymer was then isolated by precipitation with acetone or water–ethanol and dried in vacuum oven at 40°C for 7 h to yield the corresponding copolymer.

### **RESULTS AND DISCUSSION**

# IR Spectra of the Base Polymers and Copolymer AM-NaAA-DNDA

The structures of the base polymers and copolymers AM-NaAA-DNDA were confirmed by IR spectroscopy as is shown in Figure 1. In the IR spectrum, certain groups of chemical bonding give rise to bands at or near the same frequency, regardless of the structure of the rest of the molecule. The absorption bands of N-H and C-H bonds usually dominate the spectra of about 3500–3300 cm<sup>-1</sup> typical IR spectrum. The region between 1670 and 1640 cm<sup>-1</sup> corresponds to C=O groups, and the prominent functional groups present are given in Figure 1. The major functional groups are identified on IR spectra of AM include N-H and C-H stretching vibration (3356 cm<sup>-1</sup>), C=O deformation of the saturate (1672 cm<sup>-1</sup>). The absorptions at 3415 and 1672 cm<sup>-1</sup> are due to vibration of O-H and C=O group of acrylic and was presented in the IR spectrum of AA. The peaks at 3459, 2924, and 1652 cm<sup>-1</sup> indicate the presence of C-N, C-H(-CH2-) and C=O groups stretching vibration of DNDA. As expected, IR spectra confirmed the presence of different monomers in the copolymer AM-NaAA-DNDA. The IR spectrum of the poly(AM-NaAA-DNDA) gives almost the same peak region as that of the raw materials, and the N-H stretching vibration was confirmed by characteristic absorptions of 3430 cm<sup>-1</sup>, while the characteristic

absorptions of C=O stretching vibration was in 1652 cm<sup>-1</sup>. The IR spectrum of AM, AA, DNDA and *co*-AM-NaAA-DNDA indicates that these monomers have been successfully connected to the polymer chain as expected.

**Environmental Scanning Electron Microscope (ESEM) Images** To observe a phase separation, the terpolymer AM-NaAA-DNDA was dissolved in the degassed and distilled water as a solution (wt% = 300 mg/L).<sup>26,27</sup> The scanning electron microscope images were made by S-3000 N SEM (Hitachi, Japan). The resolution of the SEM was 3  $\mu$ m, and the magnifying multiple ranges from 3 to 30,000 and analysis was achieved at 20 kV of acceleration voltage and 120–500 Pa of pressure in the sample chamber. Figure 2 shows the structure of HPAM and AM-NaAA-DNDA solution.

In Figure 2, the observation accuracy of (a) and (b) is 20  $\mu$ m, and the magnification of (a) and (b) is 5000 times. While the observation accuracy of (c) and (d) is 50  $\mu$ m, and the magnification of (c) and (d) is 2000 times. As is shown in Figure 2, the cavity structure could be observed easily from HPAM (a, c), and the copolymer AM-NaAA-DNDA showed a stronger link and better dimensional network structure than HPAM due to the association action.

### The Optimization of the Synthesis Conditions

The Optimization of AM, AA, DNDA, and Initiator in Ternary Copolymerization. It has been previously shown that the ratios of AM to AA repeat units in the final copolymer structure are critical to achieving enhanced properties.<sup>28</sup> Therefore, under fixed DNDA loading (0.0361 g), the effect of different ratios of AM to AA was investigated and summarized in Table I. All copolymer solutions were tested at 0.5 wt% for 8 h in 40°C by Brookfield LVTDV-III viscometer. It was found that when the feeding ratio of AM to AA was increased to 7:3, the apparent viscosity of poly(AM-NaAA-DNDA) increased abruptly to 278.9 mPas with 85% conversion (Table I, entry 3), which was the highest among all of the samples and other's ratios only gave 47.9-231.9 mPas in spite of highly conversion (Table I, entries 1-2, 4-7). Having realized the most promising ratio of AM to AA in the ternary copolymerization, the different loadings of DNDA were thus investigated (Table I, entries 3, 8-13). With the increase of DNDA, the viscosity of the polymer solution also continues to increase. Meanwhile the dissolving time of the polymer continues to increase. That indicated the dissolving power gradually becomes poor. What is worse is when the added amount is more than 0.1815 g the polymer cannot be dissolved in the water. The results indicated that the best loading of DNDA was 0.0361 g (Table I, entry 3). The different loadings of initiator were investigated (Table I, entries 3, 14-17). The results indicated the best loading of initiator was 0.2 wt% (Table I, entry 3). Other loadings gave dissatisfactory results under same conditions in the ternary copolymerization (Table I, entries 14-17).

The Optimization pH, Temperature, Time in Ternary Copolymerizing. After determining the scale of AM, AA, DNDA, and initiator, the effect of pH on copolymerization was investigated. All results were summarized in Table II (entries 1–6). All copolymer solutions were tested at 0.5 wt%



Figure 2. the structure of HPAM and co-AM-NaAA-DNDA solution. (a) HPAM (×5000); (b) co-AM-NaAA-DNDA (×5000); (c) HPAM (×2000); (d) co-AM-NaAA-DNDA (×2000).

Entry	AM (g)	AA (g)	DNDA (g)	lnitiator (‰)	η (mPas)	Dissolving time (h)	Conversion (%)
1	9	1	0.0361	2	47.9	12	56
2	8	2	0.0361	2	157.9	12	72
3	7	3	0.0361	2	278.9	12	85
4	6	4	0.0361	2	231.9	12	83
5	5	5	0.0361	2	215.6	12	88
6	4	6	0.0361	2	202.6	12	81
7	3	7	0.0361	2	156.3	12	77
8	7	3	0.0181	2	205.9	8	54
9	7	3	0.0722	2	358.9	36	75
10	7	3	0.1093	2	551.9	60	79
11	7	3	0.1454	2	710.8	94	83
12	7	3	0.1815	2	-	>168	-
13	7	3	0.2176	2	-	>168	-
14	7	3	0.0361	1	132.8	12	78
15	7	3	0.0361	3	245.7	12	85
16	7	3	0.0361	4	127.9	12	81
17	7	3	0.0361	5	96.5	12	82

Table I. The Optimization of AM, AA, DNDA, and Initiator in Ternary Copolymerization



Table II. The pH and the Viscosities of Polymer Solution

Entry	pH-value	T (°C)	Time (h)	η (mPa s)	Conversion (%)
1	5	40	8	89.5	80
2	6	40	8	105.5	78
3	7	40	8	280.0	88
4	8	40	8	213.5	82
5	9	40	8	187.9	77
6	10	40	8	96.5	75
7	7	30	8	87.9	72
8	7	50	8	198.7	86
9	7	60	8	117.5	84
10	7	40	4	96.5	71
11	7	40	6	156.9	78
12	7	40	10	280.0	89
13	7	40	12	280.0	85

for 8 h in 40°C by Brookfield LVTDV-III viscometer. When the pH changes to 7.0, the highest apparent viscosity of 280.0 mPa.s could be afforded with conversion 88% (Table II, entry 3). Above or below 7, the apparent viscosity could not obviously be

improved and only gave 89.5-213.5 mPa.s, (Table II, entries 1-3, 5-6). Next, the effect of temperature on copolymerization was investigated (Table II, entries 3, 7-9). The result indicated that the best temperature was  $40^{\circ}$ C in copolymerization and the



**Figure 3.** (a) Fluorescence spectra with polymer concentration of 200~600 mg/L; (b) fluorescence spectra with polymer concentration of 800~1200 mg/L; (c) fluorescence spectra with polymer concentration of 1500~2000 mg/L; (d)  $I_3/I_1$  as a function of polymer concentration; (e) the apparent viscosity of different concentrations for poly(AM-NaAA-DNDA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

apparent viscosity could reach to 280.0 mPa.s and the conversation of 88% (Table II, entry 3). Changing the temperature to 30 °C, the apparent viscosity was only 87.9 mPa.s (Table II, entry 7). Continuously raising the reaction temperature to 50 and 60 °C, the apparent viscosity of copolymer solution could not change dramatically in spite of comparative satisfactory conversions (Table II, entries 8–9). Finally, the reaction time was examined in ternary copolymerizing under the optimized conditions (Table II, entries 10–13). While increasing directly the reaction time, it was found that the apparent viscosity was gradually rising and reached to the maximum value 280.0 mPa.s at 8 hour, and the value remained stable afterward (Table II, entries 12–13). Hence, the reaction time of copolymerizing was determined for 8 h.

### Performance Evaluation of the New Polymer

**Fluorescence Probe Experiment.** The ratio of the intensities of the first and the third vibronic peaks in the fluorescence spectrum of pyrene (I<sub>3</sub>/I<sub>1</sub>) was used to estimate the micropolarity sensed by pyrene in its solubilization site.<sup>29,30</sup> Fluorescence spectrums of different concentrations of poly (AM-NaAA-DNDA) are shown in Figure 3(a–c). The fluorescence emission spectra of pyrene probe sequences in 375, 385, 395, and 475 nm nearby stand for  $I_1$ , I<sub>3</sub>I<sub>3</sub>, I<sub>m</sub>(monomer), and I<sub>e</sub>(excimer).  $I_3$ I<sub>3</sub>/ $I_1$ I<sub>1</sub> was used to characterize the size of their environment polarity, because the third emission peak and first emission peak intensity ratio ( $I_3$ I<sub>3</sub>/ $I_1$ I<sub>1</sub>) will increase as the polarity of the solution decreases. Figure 3d depicts the dependence of  $I_3$ I<sub>3</sub>/ $I_1$ I<sub>1</sub> values of pyrene in steady state on copolymer concentration in aqueous solution.

The  $I_3/I_1$  values increased slowly when the concentration was lower than 1000 mg/L. As the concentration increased from 1000 to 1700 mg/L, the  $I_3/I_1$  values began to increase significantly. The abrupt increase of the  $I_3/I_1$  values (Figure 3d) indicated that the pyrene molecules removed from water to the highly hydrophobic microdomains resulted from the formation of strongly hydrophobic association.<sup>31,32</sup> The results indicated that the strong hydrophobic interaction would occur when the copolymer concentration is above 1000 mg/L, which also could



Figure 4. The apparent viscosity of poly(AM-NaAA-DNDA) with 3000 mg/L in different shear rate.



**Figure 5.** The apparent viscosity of poly(AM-NaAA-DNDA) with 3000 mg/L in different temperatures.

be deduced from the relationship of viscosity and concentration in Figure 3e.

The Shearing Resistance. The rheological properties of polymer solution are closely related with its solution properties. Meanwhile polymer solution rheological is the integrated embodiment of its microphase structure and functions. The fluid characteristics of the copolymer AM-NaAA-DNDA were investigated by 0.3 wt% in aqueous at 30°C, and the shear rate was changed from 170 to 1000 s<sup>-1</sup>. The results were shown in Figure 4.

It can be found from Figure 4 that the viscosity of poly (AM-NaAA-DNDA) dropped from 270 to 107.5 mPas dramatically. After increasing the shear rate to 1000  $s^{-1}$ , no obvious change could be discovered in the value of viscosity, and the viscosity retention rate of poly(AM-NaAA-DNDA) could arrive 47.8% (500  $s^{-1}$ ) while it was 32% at 1000  $s^{-1}$ . This indicated that the copolymer solutions had a perfect property of retaining viscosity and strong non-Newtonian behaviors. From the above results, it showed that the capacity to be viscosity retention for copolymer solution was excellent under higher shear rate.

The Temperature Tolerance. The effect of temperature on poly(AM-NaAA-DNDA) solution was investigated using 0.3 wt% copolymer at shear rate constant 170 s<sup>-1</sup> (Figure 5). Interestingly, it showed that the apparent viscosity was gradually increasing little by little before 40°C, however, the general trend indicated an apparent viscosity decrease after increasing temperature further. The phenomenon may be attributed to the effect of temperature. When the temperature is lower, intramolecular hydrophobic associations are dominant, and intermolecular hydrophobic associations are slightly strengthened with rising temperature, which result in a slight viscosity increase. But a large number of associating groups aggregate together to form reversible, physical, supermolecular structures by strong van der Waal's interactions, and polymer chains entangle with each other via hydrogen-bond interactions in the aqueous solution. But the intermolecular interaction is unstable, especially under high temperature, even degradation and molecular chain fractures are likely to occur, resulting in the apparent viscosity ARTICLE

### Applied Polymer



Figure 6. The effect of NaCl concentration on apparent viscosity of polymer aqueous solution with 2000 mg/L. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reducing. At 80°C, the viscosity retention rate could reach to 94.4% (249.4 mPas), when the temperature was  $100^{\circ}$ C and it could be 86.0% (227.2 mPas). However, the apparent viscosity markedly dropped when the temperature rose to  $110^{\circ}$ C and the retention rate was 75.8%. It demonstrated that the poly(AM-NaAA-DNDA) revealed a good temperature tolerance (90– $100^{\circ}$ C).

The Salt Resistance. The copolymer is finally applied in the processes of oil recovery, and the underground water contained a great amount of inorganic ions like Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> will be a vast influence on the properties of copolymer in aqueous solution. Since the added salt has a shielding effect on the electrostatic resistance among polymer ions, the polymer chains are tending to coil up. It results in a decrease of the viscosity of the polymer solution with the increase of the concentration of inorganic ions. For the hydrophobically associating polymer



**Figure 7.** The effect of  $MgCl_2$  concentration on apparent viscosity of polymer aqueous solution with 2000 mg/L. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 8. The effect of  $CaCl_2$  concentration on apparent viscosity of polymer aqueous solution with 2000 mg/L. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

synthesized in this experiment, the viscosity decrease can be partially retarded since the adding of DNDA results in the increase of the association effect of the hydrophobic groups. The salt resistance was investigated by using 0.2 wt% copolymer solution at room temperature compared with HPAM. The results are shown in Figures 6–8. Among these salts, NaCl brine appeared the best anti-salt ability (Figure 6), the apparent viscosity could be up to 79 mPas when the NaCl was 12000 mg/L. Copolymer solution also showed moderate property against MgCl<sub>2</sub> and the apparent viscosity of 66 mPas could be given when the concentration of MgCl<sub>2</sub> increased to 1200 mg/L (Figure 7). However, anti-CaCl<sub>2</sub> revealed that the apparent viscosity was only 60 mPas in 800 mg/L solution (Figure 8). In addition, compared with HPAM, poly (AM-NaAA-DNDA) showed a superior anti-salt ability for NaCl, MgCl<sub>2</sub>, and CaCl<sub>2</sub>.



**Figure 9.** The one-dimensional Sand-packed Model for EOR. 1: ISCO pump; 2: simulation of crude oil; 3: polymer solution; 4: NaCl solution; 5: pressure acquisition system; 6: one-dimensional sand packed model; 7: back pressure; 8: the constant temperature box; 9: sample device; 10: computer.

75

70

65



Figure 10. The relationship of cumulative flooding injected and oil recovered. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Flooding Experiment. To study and analyze the feasibility of the terpolymer to enhanced oil recovery, the one-dimensional sand packed model of 500 mm in length and 25 mm in diameter was used for the experiments.<sup>33</sup> Core flooding displacement process was shown in Figure 9. Difference concentration solutions of poly (AM-NaAA-DNDA) were applied in the core flood tests. All results have been shown in Figure 10. From the diagram, compared with about 58.1% of oil recovery using the brine system, it was found that under 5000 mg/L NaCl brine at 65°C, about 63.8% for recovery and 5.7% for EOR were revealed using 2000 mg/L poly (AM-NaAA-DNDA). While the result of applying HPAM in the same condition was only about 60.2% for recovery and only 2.1% for EOR. A higher EOR result (10%) could be afforded when increasing the concentration of poly (AM-NaAA-NAE) to 3500 mg/L and the oil recovery could reach to 68.1%. After increasing the concentration to 5000 mg/L, the final oil recovery stabilized at 72.4%, at the same time, with up to 14.3% EOR attained. These results indicate that the poly (AM-NaAA-DNDA) reveals a better ability of EOR than HPAM under same conditions.<sup>34,35</sup>

### CONCLUSIONS

This work has introduced a new material poly (AM-NaAA-DNDA) as a flooding polymer which has been prepared by free radical polymerization under mild conditions. Studies on the properties of water-soluble copolymer revealed that the polymer solution had an excellent capability of shearing resisting and the retention rate of the apparent viscosity could be obtained with up to 32% at a high shear rate of 1000 s<sup>-1</sup>. Meanwhile, the retention rate was 86% at high temperature (100°C). In addition, compared with HPAM, the copolymer appeared a better anti-salt ability especially for NaCl brine of 12000 mg/L. However, the viscosity of copolymer solution decreased sharply to 66 mPas in the presence of MgCl<sub>2</sub> (1200 mg/L) and was 60 mPas for CaCl<sub>2</sub> (800 mg/L). The spectra of pyrene suggested that strong hydrophobic interaction had occurred in the critical aggregate concentration of the copolymer solution being at about 1000 mg/L. In the different concentrations of poly (AM-NaAA-DNDA) solutions, the results of core flood test showed EOR was up to 14.3% under 5000 mg/L NaCl brine at 65°C. Based on the results above, poly (AM-NaAA-DNDA) might be a good candidate as an EOR chemical for hightemperature reservoirs with high density brine fluid.

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