A double-tailed acrylamide hydrophobically associating polymer: Synthesis, characterization, and solution properties

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ABSTRACT: In order to improve the salt resistant, temperature tolerance, and stability of the acrylamide-based copolymer, the double-tailed hydrophobically associating copolymer (DTHAP) was synthesized. The chemical and spatial network structures of the copolymer were characterized by Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR), and environmental scanning electron microscope (ESEM). The salt, temperature, aging resistance, and rheological behavior of the copolymer were investigated in detail. The experimental results showed that the performance of DTHAP were influenced by the amount of AA, PETMAM, SDS, and NaCl in the reaction system. Compared with HPAM, DTHAP solution showed excellent temperature resistance and salt tolerance. No matter in the solution varying NaCl or $CaCl_2$ concentration from 8 to 80 and 1 to 1.8 g/L, respectively, DTHAP behaved an obvious salt-thickening phenomenon. The simulative tertiary oil recovery tests at 80°C indicated that DTHAP can remarkably enhance 16.9% of the oil recovery ratio. Even at 100 g/L salt solution, DTHAP exhibited an excellent performance which can also enhance 9.9% of oil recovery ratio. The experiment results indicated that DTHAP was superior to HPAM as a kind of oil displacement agent for enhanced oil recovery, especially in high-temperature and high-mineralization oil fields. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42569.

INTRODUCTION

In recent years, water soluble polymers have received the considerable interest of scientists and engineers working on environmental and industrial problems, in particular, in many oilfield exploitations including chemical flooding, profile modification, drilling fluids, and hydraulic fracturing. As a type of chemical flooding, polymer flooding should boost the ultimate recovery for the field to more than 50% of original oil in place (OOIP), which is 10% OOIP more than from water flooding.[1] Among the applied water soluble polymers, polyacrylamide (PAM), and partially hydrolyzed polyacrylamide (HPAM) are used widely for improving mobility ratio and reducing permeability contrast.[2] Although HPAM exhibits a good property of thickening, viscoelasticity, and rheological behavior in polymer flooding process, there are still inconvenient defects existing. For instance, the viscosity of PAM and HPAM solution get a sharp decrease when the solution are used at high temperature or high mineralization.[3] More seriously, PAM and HPAM hydrolyze at high temperature and beyond a certain point are subject to precipitation by divalent cations,[3,4] which leads to formation damages. Therefore, PAM and HPAM are not appropriate for high temperature or high mineralization reservoir. A new type of polymers needs to be developed to improve the salt resistant, temperature tolerance, and stability of the acrylamide-based copolymer.

The performance of PAM and HPAM can be improved to some extent by grafting a certain amount of functional monomers, such as 2-acrylamide-2-methylpropane sulfonate (AMPS),[3] N-vinyl pyrrolidone (NVP),[5] sodium acrylamide-tertiary-butyl sulfonate (ATBS),[6] itaconic acid,[7] etc. In order to tolerate the more severe reservoir conditions, many new polymers were designed and synthesized to get the properties better, including hydrophobically associating polymers, hyperbranched polymers,[8] amphoteric polymers, and star polymers, etc. However, both traditional polymers (PAM and HAPM) and new polymers, their properties, especially thickening property, salt resistance and shearing resistance, can be further improved by hydrophobic modification.[9,10] For example, a branched hydrophobically modified polyacrylamide is synthesized, which can meet the property requirements for EOR polymer.[10] Thus, hydrophobically associating water soluble polymers (HAP) with small amounts of hydrophobic segments (generally less than 2 mol

%[11–14]) is expected to replace PAM and HPAM as chemical additives for its excellent thickening, viscoelasticity, and antisalt properties.[15,16] Meanwhile, the intermolecular association of the hydrophobic groups in the backbone of HAP leads to the formation of reversible three-dimensional network structures,[17,18] showing excellent antishearing property.

Actually, the structure of the hydrophobic monomer plays an important part on the performance of HAP. An appropriate hydrophobic monomer is the key to preparing HAP with excellent properties. To date, many kinds of hydrophobic monomer have been applied to prepare HAP,[19] which can be sorted into several types according to spacer group between double bond and hydrophobic chain, such as —COO—,[20–22] —NHCO—,[14,23–25] and —C$_6$H$_4$—,[17,26] etc. However, ester and amide groups, especially ester group, are easily hydrolyzed in an unneutral aqueous solution or in high temperature. While the structure of hydrophobic monomer with amide group is similar to acrylamide, and for this reason, the monomer is easy to copolymerize with acrylamide, which is beneficial to preparing HAP with high molecular weight. The allyl type hydrophobic monomer, in contrast, is hard to copolymerize with acrylamide for the polymerization retardation. From this point, as a kind of spacer group, —NHCO— is conductive to preparing HAP. Meanwhile, the introduction of benzene ring in the hydrophobic monomer can improve the heat resistance and hydrophobic association performance. Therefore, it is a good choice to design a kind of hydrophobic monomer with —NHCO— and benzene ring.

In this paper, a double-tailed hydrophobic monomer (N-phenethyl-N-tetradecylmethacrylamide, PETMAM) was synthesized because (1) it contained —NHCO— and benzene ring which combined the advantages of several types of hydrophobic monomers to improve the antihydrolysis property and thermostability. (2) It has been reported for hydrophobically modified polyacrylamide that for a similar hydrophobe level, double-chain hydrophobes considerably enhance the thickening efficiency with respect to single-chain hydrophobes.[27,28] This indicated that there was a much stronger hydrophobic interaction between acrylamide derivatives containing two alkyl chains than those containing only one alkyl chain. The structure of PETMAM was determined by FTIR and NMR spectra. After that, a double-tailed hydrophobically associating polymer (DTHAP) was prepared by free radical micellar polymerization with acrylamide (AM), acrylic acid (AA), 1-acrylamido-2-methylpropanesulfonic acid (AMPS) and PETMAM. Finally, on the basis of the characterization of polymer structure, the solution properties of DTHAP were evaluated, including viscosification, temperature resistance, salt tolerance, rheological, and antiageing properties. The simulative tertiary oil recovery tests were also conducted to evaluate the displacement performance.

MATERIALS AND METHODS

Materials
Acrylamide (AM), 1-acrylamido-2-methylpropanesulfonic acid (AMPS), acrylic acid (AA), sodium dodecyl sulfate (SDS), 2,2′-azobis(2-methylpropionamidine)dihydrochloride (AIBA), were purchased and used directly without further purification.
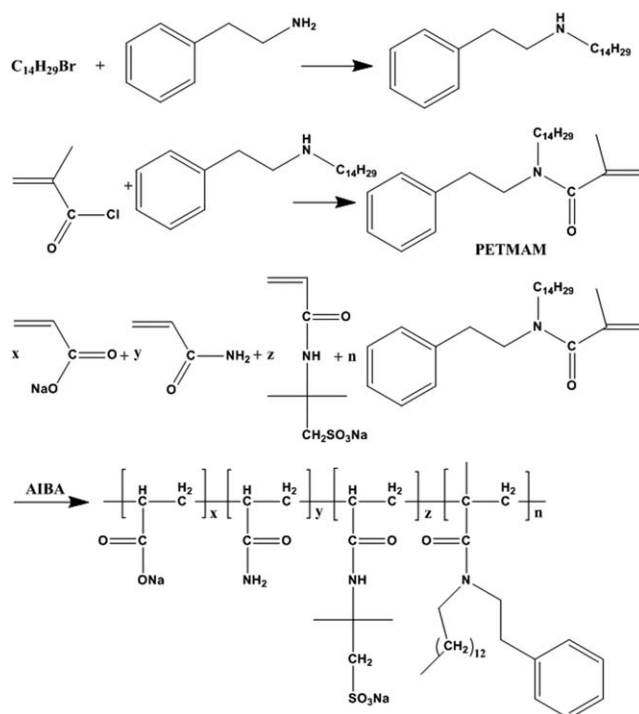
Scheme 1. The synthesis of PETMAM and DTHAP, the values of x, y, z were 80–86%, 12.0–17.0%, and 2.5%, respectively, the values of n was 1-x-y-z; the viscosity-average molecular weight of DTHAP was 5–7 million.

N-phenethyl-N-tetradecylmethacrylamide (PETMAM) was prepared in the laboratory, which synthetic routes were given in Scheme 1.

Synthesis of N-phenethyltetradecan-1-amine
N-phenethyltetradecan-1-amine was prepared by the following procedure.[29] 18.15 g of phenethylamine (0.15 mol) and 100 mL of ethyl alcohol were added into a 250 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, and a condenser. Then, 41.55 g of 1-bromotetradecane (0.15 mol) was slowly dropped into the flask from an addition funnel. After that the mixture was heated with an oil bath, and the solution was refluxed for 6 h at 80°C. Upon cooling, the resulting amine salt was filtered and extracted in methylene chloride using 5M NaOH to deprotonate the salt. The extracted methylene chloride was then concentrated on a rotary evaporator at 50°C. The concentrated solution with the color of light yellow was dried in a vacuum oven and weighed to give 61% yield.

Synthesis of PETMAM
10 g of N-phenethyltetradecan-1-amine was dissolved in 20 mL of methylene chloride, and then added into a 250 mL round-bottomed flask. Then 3.2 g of triethylamine was added into the solution as an acid-binding agent. The mixture was placed in an ice bath and agitated vigorously using a magnetic stirrer. When the temperature dropped below 10°C, methacryloyl chloride (3.6 g) in methylene chloride (20 mL) was added dropwise. After that the mixture was stirred for an additional 4 h at 20°C. Then the reaction mixture was washed once with 1M HCl, once with 1M NaOH and twice with water. The organic phase was
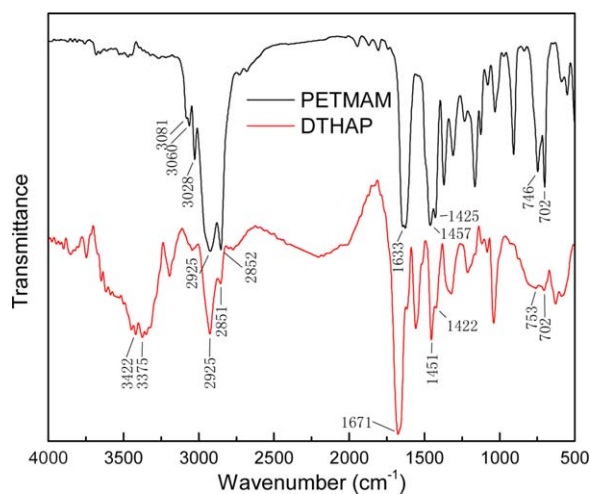
Figure 1. IR spectra of PETMAM and DTHAP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

concentrated on a rotary evaporator to yield light yellow oil (yield 92%).

Preparation of DTHAP

The DTHAP was synthesized by the photoinitiated free radical micellar copolymerization (Scheme 1). The monomers, surfactant as well as AIBA initiator in previously designed composition were taken along with deionized water in a beaker. The total weight of solution and the dosage of AIBA were constant at 50 g and 0.07 mol % of total monomers, respectively. The reactor was placed in a UV device for 4 h. The polymeric colloid was cut into pieces and soaked in ethanol for 24 h. Finally, the polymers were dried under vacuo at 50°C for 24 h.

Hydrophobic Monomer and Copolymer Characterizations

IR spectra of PETMAM and DTHAP were measured with KBr pellets in a WQF-520 infrared spectroscopy (Beijing Reili Analytical Instrument). The apparent viscosity of copolymer solution measurement was conducted by a Brookfield ULTRA DV-III rotational viscometer a shear rate of 7.34 s^{-1}. ^{1}H-NMR spectra were recorded on a Brucker AVANCE 400 MHz spectrometer at 27°C. The aggregating morphology of DTHAP in aqueous and brine solutions was observed by environmental scanning electron microscope (ESEM, Quanta 450, USA).

RESULTS AND DISCUSSION

FT-IR Spectra of the PETMAM and DTHAP

Figure 1 showed the FT-IR spectra of PETMAM and DTHAP. From the curve of PETMAM, the bands observed at 3029–3081, 2925, and 2852 cm^{-1} were attributed to the stretching vibration peaks of C—H in benzene ring, —CH$_2$— and —CH$_3$. The bands observed at 1457 and 702–746 cm^{-1} were assigned to the skeletal vibration of benzene and the bending vibration of single substituted benzene. Besides, the absorption peaks at 1633 cm^{-1} was attributed to C═O groups in the tertiary amide. In the curve of DTHAP, the characteristic absorption peaks of PETMAM at 2959, 2852, 1451, 755, and 702 cm^{-1} were present. Therefore, it can be inferred that PETMAM has been successfully incorporated into DTHAP. Moreover, it can be found that new absorptions were appeared. The absorption peak at 3375–

3422 and 1671 cm^{-1} were observed, which were associating with the stretching vibrations of the N—H and C═O bond in the —CONH$_2$. As a result, a conclusion could be reached that the structure of AM and PETMAM existed in DTHAP, and a further characterization such as ^{1}H-NMR was performed to confirm such a structure.

^{1}H-NMR of PETMAM and DTHAP

The ^{1}H-NMR spectra were showed in Figure 2 and all the resonances of protons were indicated with arrows to the corresponding chemical shifts.

Figure 2(A) showed the ^{1}H-NMR spectrum of DTHAP in D$_2$O. All the resonances of protons were as follows: 0.89 (t, 22H), 1.14 (s, 6aH), 1.51 (t, $(x+y+z)$H), 2.07 (d, $2(x+y+z+n)$H), 3.30 (m, 2H), 3.93 (t, 2H), 6.90–7.24 (m, 5H).

Figure 2(B) presented ^{1}H-NMR spectrum of N-phenethyltetradecan-1-amine in CDCl$_3$. All the resonances of protons were as follows: 0.88 (t, 3H), 1.26–1.35 (m, 22H), 1.35 (s, NH), 1.45 (t, 2H), 2.60 (t, 2H), 2.80 (t, 2H), 2.87 (t, 2H), 7.16–7.19 (m, 5H).

Figure 2(C) exhibited the ^{1}H-NMR spectrum of PETMAM in CDCl$_3$. All the resonances of protons were as follows: 0.88 (t, 3H), 1.26 (m, 22H), 1.47–1.58 (m, 2H), 2.75–2.89 (m, 2H), 3.56 (m, 2H), 5.09 (s, 1H), 5.26 (s, 1H), 7.13–7.30 (m, 5H).

All results showed that the synthesized products were the targets.

Environmental Scanning Electron Microscope (ESEM) Images

ESEM is an effective technology for characterizing the microtopography of polymer solution, which can reflect the structure of polymer chains, especially for the hydrophobic associating polymer (HAP) and partially hydrolyzed polyacrylamide (HPAM). Because more compact three dimension network structure can be observed directly from the ESEM images of HAP than HPAM.[18,30] The DTHAP solutions (DTHAP concentration, 2 g/L) for ESEM were prepared by smearing a small amount of DTHAP solutions on conducting resin. Then, the samples were dried by Vacuum Freezing and Drying Technology before
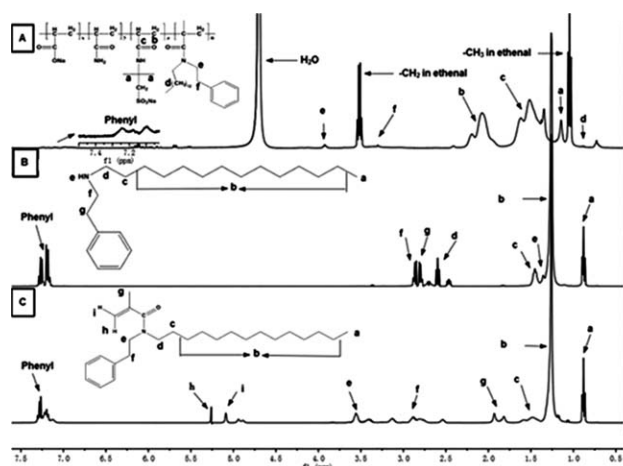

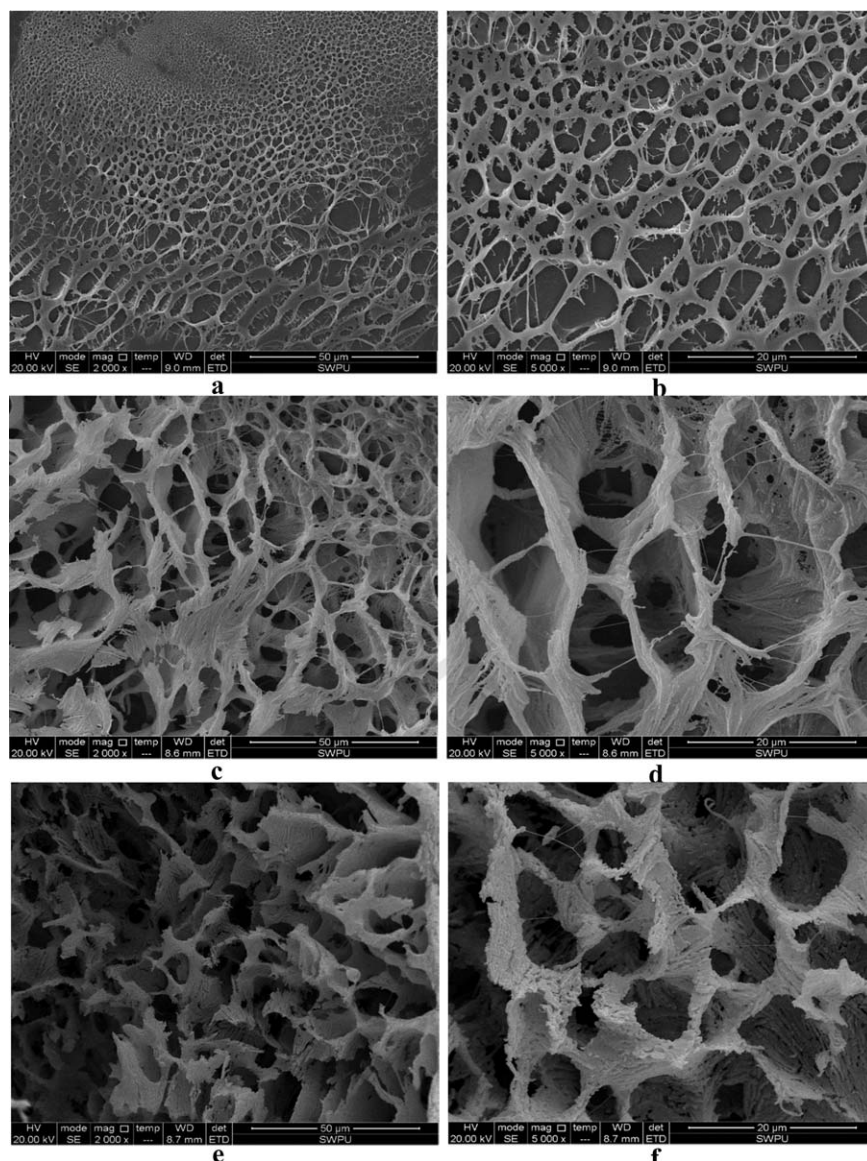**Figure 2.** ^{1}H-NMR spectra of DTHAP (A) in D$_2$O and N-phenethyltetradecan-1-amine (B), PETMAM (C) in CDCl$_3$.

Figure 3. The SEM images of DTHAP: (a) DTHAP solution at 50 μm in fresh water, 2000×; (b) DTHAP solution at 20 μm in fresh water, 5000×; (c) DTHAP solution at 50 μm in 40 g/L saline water, 2000×; (d) DTHAP solution at 20 μm in 40 g/L saline water, 5000×; (e) DTHAP solution at 50 μm in 80 g/L saline water, 2000×; (f) DTHAP solution at 20 μm in 80 g/L saline water, 2000×.

observation. Figure 3 showed the micromorphology of DTHAP in aqueous and brine solutions.

Among these images, Figure 3(a,b), (c,d), and (e–f) were DTHAP in fresh water, 40 and 80 g/L saline water at different scan sizes (50 μm, 2000×; 20 μm, 5000×). It can be seen clearly from the images, the mainly shapes of the structure of DTHAP solution were irregular pentagon and oval. Compared with HPAM,[18] much denser networks could be found in DTHAP, which could be the proof of higher thickening ability of DTHAP. Even at high salinity, significant reticular structures could be found in Figure 3(c–f). And more importantly, with the increasing of salinity, the structure became more compact which was consistent with the result of salt thickening performance (Figure 7). Meanwhile, NaCl crystallized at the surface of the backbone of DTHAP, which could be found obviously in Figure 3(f).

The remarkable and compact structures of DTHAP solution made it possible to be excellent EOR chemicals by increasing the apparent viscosity of aqueous solution for the synthesized copolymers. The salt-thickening ability of DTHAP in brine solution made it possible to overcome the difficult problems of traditional polymer with poor salt resistance.

The Optimization of the Synthesis Conditions
The Optimization of AA, PETMAM, SDS in Preparing DTHAP. In this paper, the factors were investigated, including the dosages of AA, PETMAM, and SDS, which had an important influence on the properties of DTHAP. The mother liquors were prepared by dissolving the polymers in water at concentration of 5 g/L. The process of dissolution can be divided into three parts: dispersed by stirring for 1 h, swelling overnight and

Table I. The Optimization of AA, SDS, PETMAM, and NaCl in Preparing DTHAP

Entry	AM (g)	AA (g)	AMPS (g)	PETMAM (g)	SDS (g)	NaCl (g)	η_{app} (mPas)
1	10.1	1.4	1	0.29	0.7	0	326.7
2	9.9	1.6	1	0.29	0.7	0	359.0
3	9.7	1.8	1	0.29	0.7	0	332.5
4	9.5	2.0	1	0.29	0.7	0	346.7
5	9.9	1.6	1	0.29	0.5	0	287.8
6	9.9	1.6	1	0.29	0.6	0	340.6
7	9.9	1.6	1	0.29	0.8	0	413.2
8	9.9	1.6	1	0.29	0.9	0	363.8
9	9.9	1.6	1	0.16	0.8	0	311.8
10	9.9	1.6	1	0.22	0.8	0	375.4
11	9.9	1.6	1	0.35	0.8	0	323.3
12	9.9	1.6	1	0.42	0.8	0	358.6
13	11	1.5	0	0.29	0.7	0.3	283.7
14	11	1.5	0	0.29	0.7	0.6	313.9
15	11	1.5	0	0.29	0.7	0.9	332.3
16	11	1.5	0	0.29	0.7	1.2	299.2
17	11	1.5	0	0.29	0.7	1.5	232.5
18	11	1.5	0	0.29	0.7	1.8	191.6

then stirred for 1 h. Then, the viscosity of polymer solution was tested at concentration of 2 g/L.

It was found from entries 1 to 4 in Table I, the viscosity of DTHAP solution reached 359.0 mPa s, when the dosage of AA was 1.6 g. Once the mass exceeded or lacked 1.6 g, the viscosity would decrease. The relationship between hydrophobic association and electrostatic repulsion was competing with each other. Electrostatic repulsion would promote the formation of association structure when the dosage of AA below 1.6 g. It was because the polymer chains stretched and disentangled by electrostatic repulsion. However, with the increase of content of AA, the rigidity of polymer chains was strengthened for the electrostatic repulsion, which hindered the formation of association structure.[31] Actually, the viscosity of DTHAP solution depended on the strength of electrostatic repulsion and hydrophobic association. The impact of the two factors depended on the relative amount of AA and PETMAM.

The relationship between the content of SDS or hydrophobic monomer and the thickening property of copolymer solution can be explained by the following equation:

$$N_H = ([H] \times N_{agg})/([SDS] - cmc_{SDS}) \qquad (1)$$

where N_H, $[H]$, N_{agg}, $[SDS]$, cmc_{SDS} are the number of hydrophobes per micelle, the hydrophobe content in the polymers, its aggregation number, the molar concentration of the surfactant, and its critical micellar concentration, respectively. The content of SDS and hydrophobic monomer effect the value of N_H, and then change the length of microblock in copolymer chains. To be specific, the two factors exhibit an opposite effect: the increase of the content of SDS will decrease the value of N_H

and by contrast, the increase of the content of hydrophobic monomer will increase the value of N_H.

According to the above relationship, the data from entries 5 to 12 in Table I can be explained as follow. The value of N_H would rise obviously in case of increasing the content of SDS or hydrophobic monomer. However, in aqueous phase, a large amount of hydrophobic monomer were existed instead of locating in micelles if the content of SDS were too low or the content of hydrophobic monomer were too high, which would reduce the value of N_H. As shown in the Table I, the viscosity of copolymer solution rose with the increase of content of SDS or hydrophobic monomer. However, the viscosity dropped when the content of SDS or hydrophobic monomer increased continually, which contributed to the decrease of N_H or solubility. Eventually, the appropriate formula was confirmed and the viscosity of copolymer solution (2 g/L, entry 7) reached 413.2 mPa s, showing a good thickening property.

The Effect of NaCl on Micellar Copolymerization. The critical micelle concentration (CMC) of ionic surfactant can be reduced by adding NaCl to aqueous solution. The copolymers with different lengths of hydrophobic blocks can be synthesized by varying the amount of NaCl in the reaction system.[32] It was the combination of the two aspects that made a great influence on the performance of DTHAP.

The data from entries 13 to 18 in Table I showed that adding NaCl to the reaction system changed the viscosity of polymer solution. In the micellar copolymerization process, the hydrophobic monomer located within the micelles which showed a microblock distributing in polymer chains. The structure of microblock endowed the excellent thickening property of copolymer solution. While a small amount of the hydrophobic
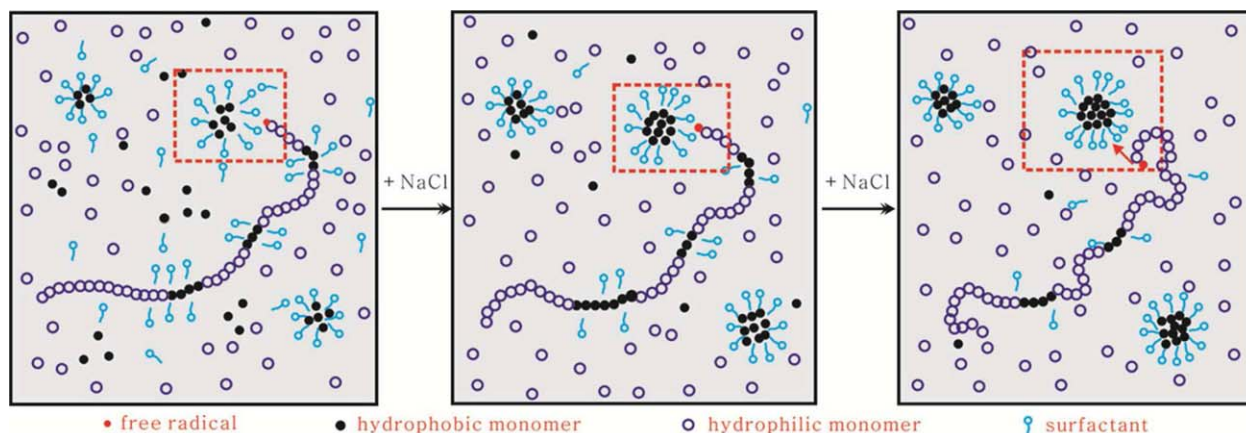
Figure 4. Schematic representation of the reaction medium for the micellar copolymerization by adding NaCl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

monomer were always existed in the aqueous phase, leading to the incorporation of single hydrophobe units into the copolymer chains.[33] Meanwhile, the amount of hydrophobic monomer in the micelles reduced relatively and then lowered the length of microblock which would result in the reduction of viscosity of copolymer solution. The amount of hydrophobic monomer in aqueous phase can be reduced by adding NaCl to the reaction system (Figure 4). The more NaCl added, the greater the influence was. However, with the content of NaCl increasing continually, the macromolecular radicals became curly on account of the electrostatic shielding which hindered radical head group diffusing into the interfacial layer region of the micelles. This effect will reduce the molecular weight of copolymer and the length of the hydrophobic block and then result in the reduction of viscosity.

The Solution Properties of DTHAP
Viscosification Property of HAP and HPAM. Viscosity is an important index for evaluating the property of polymers. The mobility ratio can be improved by increasing the viscosity of displacing phase (eq. 2) which is beneficial to improve the sweep efficiency. Actually, a good thickening property can also reduce the dosage of polymers as oil displacement agents.

$$M = \lambda_D / \lambda_d = \left(\frac{K_D}{\mu_D}\right) / \left(\frac{K_d}{\mu_d}\right) \tag{2}$$

Where M is mobility ratio. D and d are displacing phase and displaced phase, respectively. λ, K and μ are mobility, permeability and viscosity, respectively.

It can be seen from Figure 5, the viscosity of DTHAP solution was higher than HPAM. Especially, the viscosity difference became more obvious when the concentration of polymers solution reached 0.75 g/L. The difference reached 177.5 mPa s at 2 g/L. As is well known, hydrophobic associating polymer is different from the traditional polymer, which exists a critical association concentration (CAC). Once the concentration reached CAC, the space reticular structure was formed by intermolecular association. Then, the viscosity of HAP solution increased sharply. Therefore, from the view of viscosity improvement, DTHAP was superior to HPAM as a kind of oil displacement agent for enhanced oil recovery.

Salt Tolerance of DTHAP. HPAM and DTHAP (Table I, entry 1) salt solution of 2 g/L were prepared with NaCl and CaCl₂, respectively. Then, the salt tolerance of each solution was measured by viscometer at a temperature of 20°C and a shear rate of 7.34 s⁻¹.

Figure 6 illustrated the relationship of polymer apparent viscosity versus salinity. Compared with HPAM, the trend of the viscosity of DTHAP with the increase of the salinity showed great differences which can be divided into three parts. Less than 8 g/L, the viscosity dropped quickly with the increase of concentration of NaCl solution. However, the viscosity rose from 189.9 to 237.4 mPa s between 8 and 80 g/L which showed an obvious salt thickening phenomenon attributed to the hydrophobic association.[34] It was also important to note that the scope of salt thicken was wider than other literature reports[35] which showed an excellent property of salt resistance. After that the size of polymer chains were reduced by electrostatic shield and the salt thickening phenomenon disappeared after increasing the concentration of NaCl solution further. Similar to NaCl, the influence of CaCl₂ on the viscosity of DTHAP (Figure 7) can be
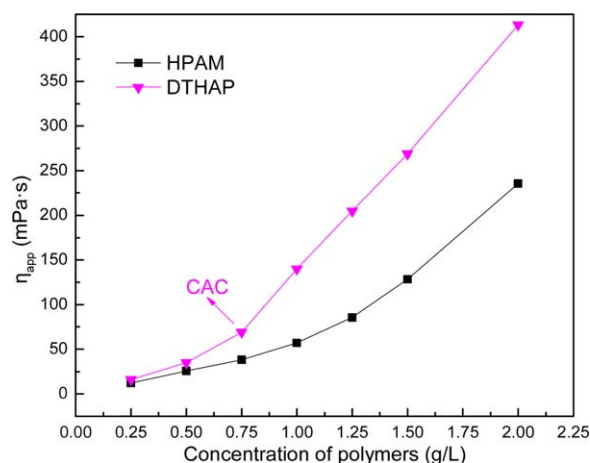

Figure 5. The apparent viscosity of different concentrations for DTHAP and HPAM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
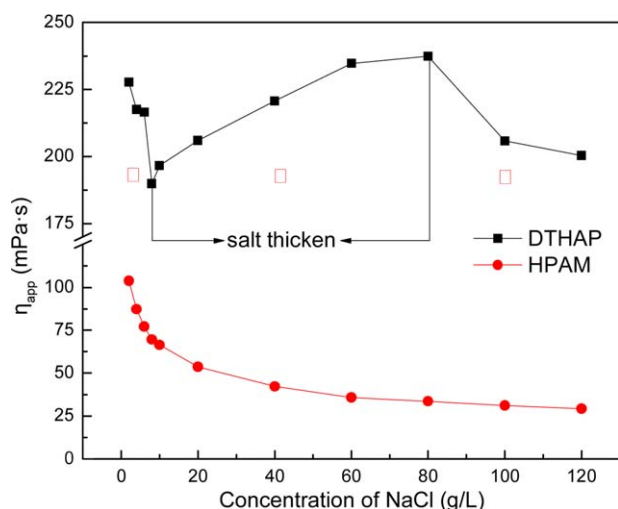
Figure 6. The effect of NaCl concentration on viscosity of DTHAP and HPAM solution with 2 g/L. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8. The effect of injected water on viscosity of DTHAP and HPAM solution with 2 g/L. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

divided into three parts as well. However, the only difference was the scope of the salt thickening section. By comparison, it can be found that $CaCl_2$ had a greater impact than the NaCl on the viscosity of DTHAP which was different from nonionic polymers. The simulated water (NaCl 171.51 g, $CaCl_2$ 28.53 g, $MgCl_2$ 4.75 g in 1 L distilled water) was diluted by distilled water to prepare polymer solution with different salinity. It can be seen from Figure 8, the salt thickening phenomenon still existed and the viscosity of DTHAP solution was much higher than HPAM. It was generally assumed that the effect of salts on the hydrophobic interactions of nonionic polymers depended only on the ionic strength but was independent of the nature of the ionic species.[34] Actually, the effects on the viscosity of ionic polymers by adding salts can be divided into two opposite aspects. The chains of ionic polymer were coiled by electrostatic shield and then hindered the hydrophobic interactions. On the
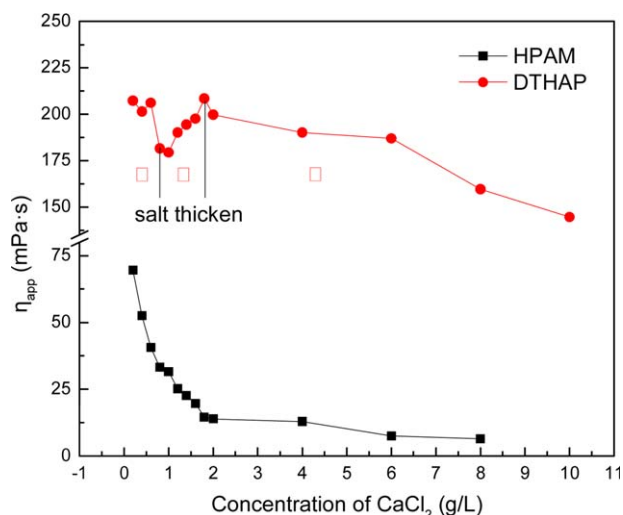
contrary, the hydrophobic association was enhanced with the increase of salinity which was consistent with nonionic polymers. The electrostatic shield made the differences between ionic and nonionic polymers.

In addition, compared with HPAM, DTHAP showed a superior antisalt ability for NaCl and $CaCl_2$ which was candidate to be used for high salinity reservoirs.

Temperature Resistance of DTHAP. The effect of temperature on DTHAP (Table I, entry 7) and HPAM solution at 2 g/L were investigated at a constant shear rate of 7.34 s^{-1}. The polymer solution was heated from 20 to 90°C and then cooled gradually to room temperature. The viscosity value was recorded at each of 5°C. The viscosity retention rate was defined as the residual viscosity divided by the initial viscosity multiplied by 100%.

It can be found from Figure 9, for HPAM, the viscosity simply decreased with increasing temperature, whereas, for DTHAP,

Figure 7. The effect of $CaCl_2$ concentration on viscosity of DTHAP and HPAM solution with 2 g/L. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
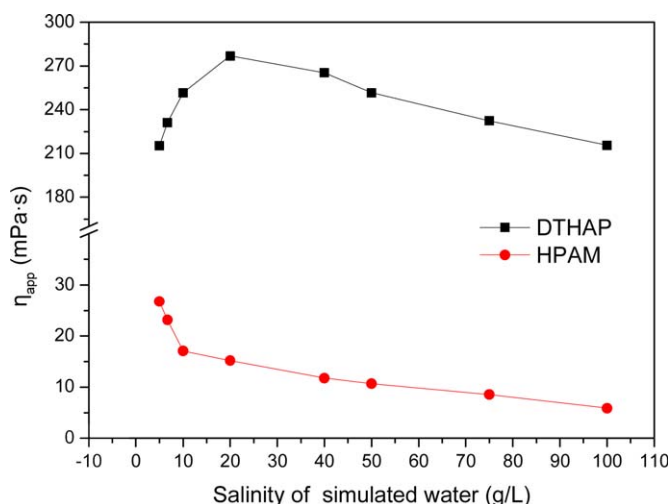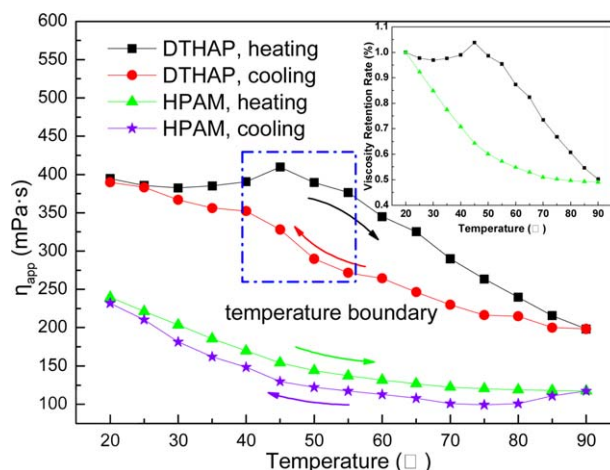

Figure 9. The viscosity and viscosity retention rate of DTHAP and HPAM with 2 g/L at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
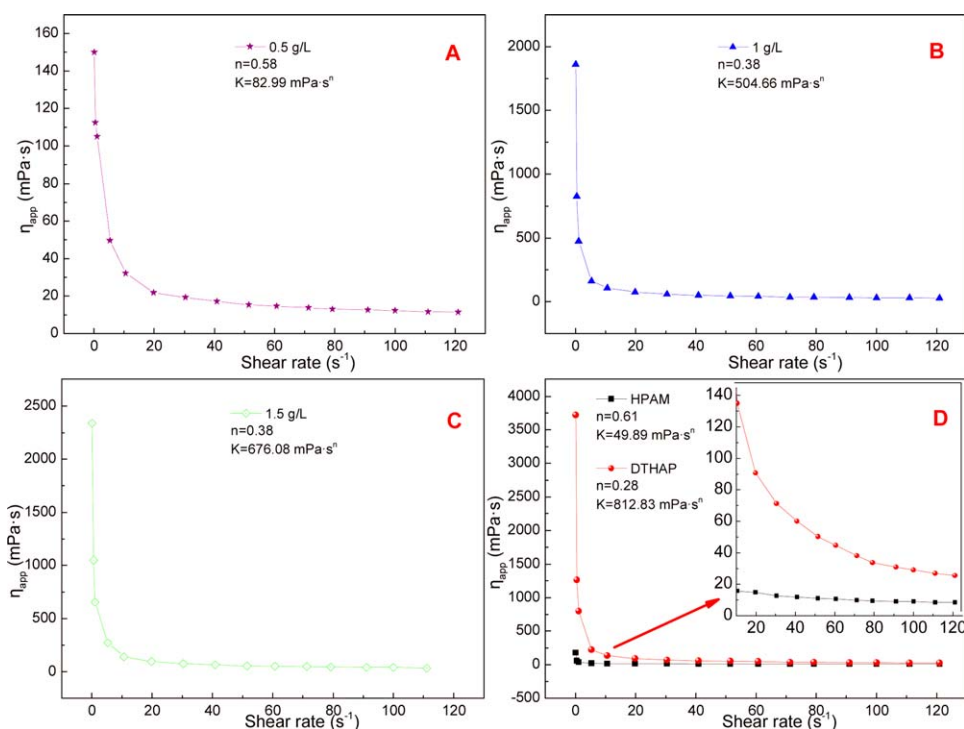
Figure 10. A, B, and C, the rheological properties of DTHAP at different concentration (0.5, 1, and 1.5 g/L) in fresh water; D, the rheological properties of DTHAP and HPAM at 1.5 g/L in 10 g/L saline solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the viscosity initially decreased then increased followed by a decrease, and it reached a maximum at 45°C. Both the viscosity and viscosity retention rate of DTHAP exceeded HPAM before 90°C which exhibited a certain temperature tolerance. With the continually rising of temperature, the viscosity retention rate of HPAM (49.0%) and DTHAP (50.2%) tended to equal. However, compared with HPAM, the viscosity of DTHAP increased 70 mPa s at 90°C. Meanwhile, differing from HPAM, on gradually cooling to the room temperature, the viscosity difference of DTHAP between cooling and heating process can be divided into two parts. The temperature between 40 and 55°C was the boundary of destruction and renewal of supermolecular structure. From 90°C to the boundary, the viscosity difference got increased and reached a maximum at 55°C. However, the viscosity difference decreased rapidly between 40 and 55°C. The experimental results may be attributed to the effect of hydrophobic association as well as the structure of the hydrophobic monomer. With the temperature increase, a large number of associating groups aggregated together to form reversible, physical, supermolecular structures by strong van der Waal's interactions.[30] The introduction of the benzene ring in the hydrophobic monomer can also improve the associating properties and temperature tolerance of DTHAP. However, the supermolecular structure formed by hydrophobic association was unstable, especially under high temperature, which resulted in the decrease of viscosity. In the process of lowing the temperature, the supermolecular structures recovered, especially at the boundary.

Rheological Property of DTHAP. DTHAP solution was prepared at different concentrations of 0.5, 1, and 1.5 g/L in fresh

water. Then, the 1.5 g/L DTHAP and HPAM solution were prepared in 10 g/L saline water, wherein the Ca^{2+} and Mg^{2+} were 0.55 g/L. The rheological properties of each solution were measured by a shear rate of 0–120 s^{-1} at 20°C.

As can be seen from Figure 10, the concentration of DTHAP solution had an obvious effect on the values of n and K. As we know, n is the symbol of pseudoplastic solution and K is the sign of the thickening ability of polymer solution. With the concentration of DTHAP solution rising, the values of n and K changed from 0.58 to 0.38 and 82.99 to 676.08 mPa s^n which
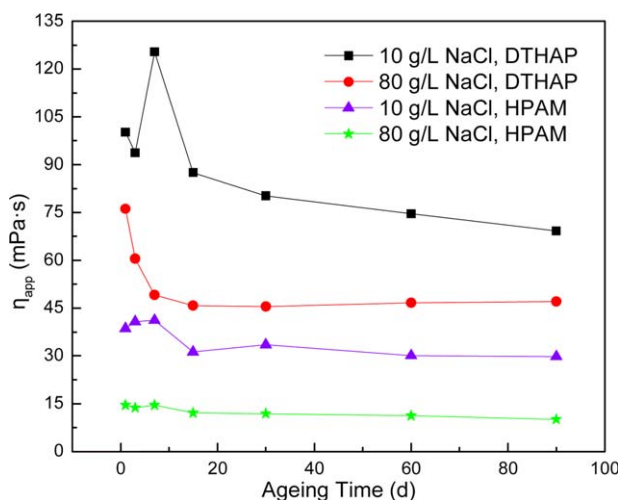

Figure 11. The antiaging properties of DTHAP and HPAM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

Table II. Results of the Enhanced Oil Recovery of Polymer Flooding

Entry	Polymer	C (g/L)	Salinity (g/L)	η_{app} (mPa s)	Permeability (μm^2)	E_1 (%)	E_2 (%)	EOR (%)
1	HPAM	2	40	35.8	1.62	40.3	47.4	7.1
2	DTHAP	2	40	134.1	1.59	36.4	53.3	16.9
3	DTHAP	2	100	105.2	1.40	42.0	51.9	9.9

C, the concentration of polymer solutions; V, the pore volume of cores; E_1, the oil recovery ratio by water flooding; E_2, the total oil recovery ratio by water flooding and polymer flooding; $EOR = E_2 - E_1$.

showed an opposite trend. Therefore, according to the eq. 3, the pseudoplastic and thickening ability of were enhanced with the increase of the concentration of DTHAP solution. Then, the rheological properties of DTHAP and HPAM solution in 10 g/L saline water were investigated. By comparison, the pseudoplastic and thickening ability of DTHAP solution were much better than HPAM solution. Because of the hydrophobic association, the unique three-dimensional network structure of hydrophobic associating polymer formed and made the great difference between DTHAP and HPAM. Meanwhile, an interesting phenomenon can be found by comparing C and D. The values of n and K in saline water were higher than that in fresh water which behaved more excellent pseudoplastic and thickening ability. The phenomenon was similar to the salt thickening phenomenon which attributed to the reinforcement of association between hydrophobic chains by salt.

$$\eta = K \cdot \dot{\gamma}^{n-1} \tag{3}$$

where η, K, $\dot{\gamma}$ and n are viscosity, consistence factor, shear rate, and rheologic index, respectively.

The Antiaging Performance of DTHAP

The polymer solution of DTHAP and HPAM (2 g/L) were prepared in which the concentration of NaCl were 80 g/L. Then, the solution was placed into vials in the oven at 80°C. The viscosity was investigated at different times to evaluate the antiaging performance of polymer solution.

It can be observed from Figure 11, the curves of viscosity–aging time of DTHAP and HPAM fluctuated largely before 15 days, and then began to flatten after extending the time further. Compared with HPAM, it was found that the antiaging property of DTHAP solution was more excellent than HPAM. The experimental results showed that the viscosity of DTHAP declined from 76.1 to 47.1 mPa s and the viscosity retention rate was 61.9%, while HPAM declined from 14.5 to 10.1 mPa s and the viscosity retention rate was 69.5%. Their viscosity retention rates were similar, but the viscosity of DTHAP was higher than HPAM. Actually, the viscosity of polymer solutions should exceed crude oil in the process of polymer flooding. However, the viscosity of HPAM was too low to enhanced oil recovery in high temperature and high salinity reservoirs. Therefore, DTHAP was more suitable than HPAM as a kind of displacement agents for enhanced oil recovery.

Enhanced Oil Recovery Experiments

The procedure of the artificial sandstone core flood test was as follows. The first step was the preparation of artificial sandstone

core. The core was placed into the coreholder with casing pressure at 80°C. The second step was the establishment of initial water saturation. The cores were flooded with oil under water production ceased. The third step was the water flooding. Water flooding was conducted horizontally at a constant injection flow rate of 3 mL/min. The same injection flow rate was used for all the water displacement tests in the study. The fourth step was the tertiary polymer flooding. A 0.3 PV polymer slug was injected at the rate of 1 mL/min when the water cut reached 98%. Finally, water flooding was conducted continually until reached the economic limit (98%).

As indicated in Table II and Figure 12, the oil recovery experiments of DTHAP solution were conducted at different salinity. The oil recovery ratio of DTHAP in 40 g/L saline water was higher than the others which might attribute to the viscosity. Actually, the viscosity of DTHAP in 40 g/L saline water exceeded the others. The mobility ratio could be improved by increasing the viscosity of displacing phase (eq. 2) which was beneficial to improve the sweep efficiency and then enhance oil recovery. Compared with HPAM, DTHAP could remarkably enhance 9.8% of the oil recovery ratio. Even at a high salinity, DTHAP exhibited an excellent performance which can also enhance 2.8% of oil recovery ratio. The increased EOR was due to the thickening efficiency of the supramolecular structure formed by hydrophobic association, which could increase the molecule hydrodynamic volume.[35] The tertiary oil recovery tests
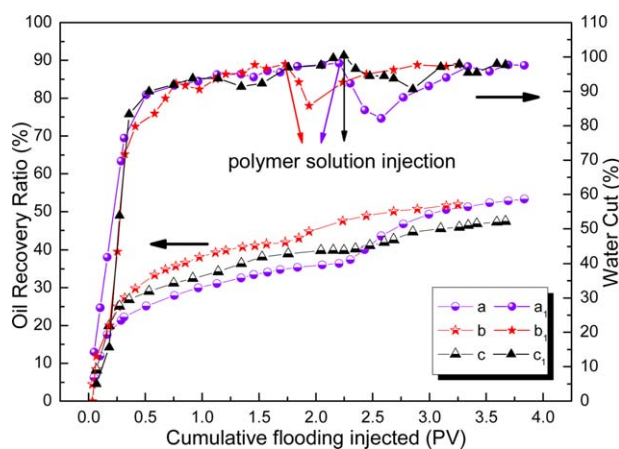

Figure 12. The relationship of cumulative flooding injection and oil recovery as well as water cut: a and a$_1$, 0.2 g/L DTHAP in 40 g/L saline water. B and b$_1$, 0.2 g/L DTHAP in 100 g/L saline water. C and c$_1$, 0.2 g/L DTHAP in 40 g/L saline water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

demonstrated that the synthetic DTHAP exhibited better flooding effectiveness certainly and had potential application for enhanced oil recovery.

CONCLUSIONS

In this work, a double-tailed acrylamide hydrophobically associating polymer was synthesized by photoinitiated free radical micellar copolymerization. The chemical and spatial network structures of the copolymer were characterized by FT-IR, NMR, and ESEM. Compared with HPAM, DTHAP exhibited superior properties on aspects of salt tolerance, temperature resistance, rheological, and antiaging properties. In addition, the simulative tertiary oil recovery tests indicated that, compared with HPAM, DTHAP could remarkably enhance 9.8% of the oil recovery ratio. The introduction of hydrophobic group as well as benzene ring improved the performance of the copolymer and made it potential to be a kind of oil displacement agent for enhanced oil recovery, especially in high-temperature and high-mineralization oil fields.

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