

# High-Temperature Resistance Water-Soluble Copolymer Derived from Acrylamide, DMDAAC, and Functionalized Sulfonamide for Potential Application in Enhance Oil Recovery

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**ABSTRACT:** A water-soluble poly(AM-AA-DMDAAC-TCAP) was prepared using acrylamide (AM), acrylic acid (AA), diallyl dimethyl ammonium chloride (DMDAAC), and *N*-allyl-4-methylbenzenesulfonamide (TCAP), and the synthesis conditions were investigated. The obtained copolymer was characterized by FTIR, <sup>1</sup>H-NMR, SEM, TG, and XRD. The temperature resistance and thickening function of the copolymer are improved significantly compared with that of partially hydrolyzed polyacrylamide. It is found that the viscosity of copolymer could achieve up to 53.3% retention rate at 120°C compared to that at 30°C. About 16.6% for enhanced oil recovery is obtained by poly(AM-AA-DMDAAC-TCAP) brine solution at 65°C. In addition, the results of XRD show that 3000 mg/L copolymer combined with 10 wt % KCl solution could reduce the *d*-spacing of sodium montmorillonite from 18.94 to 14.86 Å exhibiting remarkable effect on inhibiting hydration of clays. All the results demonstrate that poly(AM-AA-DMDAAC-TCAP) have excellent performance for potential application in enhance oil recovery. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40727.

**KEYWORDS:** copolymers; oil and gas; properties and characterization; rheology; X-ray

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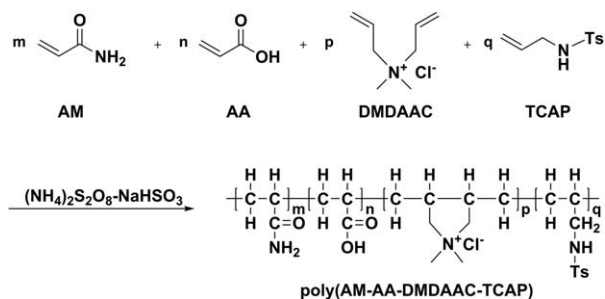
## INTRODUCTION

In recent decades, polyacrylamide (PAM) and partially hydrolyzed polyacrylamide (HPAM) have been used mostly in enhanced oil recovery (EOR).<sup>1</sup> However, given the harsh conditions present in most oil reservoirs, problems and limitations make them not fully meet the practical needs. The apparent viscosity of PAM and HPAM has greatly reduced because of the hydrolysis of —CONH<sub>2</sub> group above 60°C.<sup>2,3</sup> PAM and HPAM could not withstand high salt concentration due to the precipitation and flocculation of —COO<sup>−</sup> groups with multivalent metal ions, which could lead to the curl of the molecular chain resulting in a much lower viscosity.<sup>4</sup> In addition, PAM and HPAM could be degraded at high shear rate attributed to the linear chain structure.<sup>5</sup> Moreover, the application of the incompatible EOR chemicals might lead to swelling of the clay minerals resulting in formation damage in hydrocarbon reservoirs.<sup>6,7</sup>

Subsequently, the ultrahigh molecular weight PAM and HPAM have been applied in EOR by increasing solution viscosity at a given polymer concentration.<sup>1</sup> Nevertheless, the higher molecular weight of PAM and HPAM could not solve the problems of

mechanical degradation and salinity sensibility.<sup>5</sup> Thereupon, several studies involving the chemical structure modification of PAM and HPAM have been reported and roughly divided into two directions. One included introducing the efficient monomer like, aromatic ring,<sup>8–10</sup> sulfonic acid groups,<sup>11,12</sup> sulfonamide groups,<sup>13,14</sup> branched structure,<sup>15,16</sup> the long chain monomers,<sup>17–20</sup> and zwitterionic monomers<sup>21,22</sup> into the polymer molecular chain, and the other included the preparation of cross-linked polymer systems.<sup>23,24</sup> Despite the achievements made in this field of ultrahigh molecular weight PAM and HPAM or these chemical modification polymers, it is still necessary to develop new types of EOR chemicals and to probe how the EOR chemicals work for the temperature resistance, salt tolerance, and shear stability.

In our previous works, the different attempts were made to alter the chemical structure of PAM and HPAM to obtain some novel copolymers with improved properties.<sup>25–32</sup> We reported that poly(AM-AMS-AA-DANA) including cyclic monomer *N,N*-diallyl nicotinamide (DANA) exhibited good salt tolerance, but when the temperature raised from 30 to 120°C, the apparent viscosity retention rate was barely 39.8%.<sup>31</sup> In such cases,



**Scheme 1.** Synthesis route of poly(AM-AA-DMDAAC-TCAP).

*N*-allyl-4-methylbenzenesulfonamide (TCAP) containing an aromatic ring and a sulfonamide group was prepared as a functional monomer using paratoluensulfonyl chloride (TsCl) and allyl amine (AP). A number of researches have indicated that the copolymer with aromatic ring structure could exhibit remarkable thermal stability, and some literatures have introduced sulfonamide group in polymer chain,<sup>13,14</sup> but have not mentioned that the hydrogen bonding of O=S=O or  $-(\text{SO}_2)-\text{NH}-$  in the intramolecular or intermolecular<sup>33</sup> could improve the performance of the polymer in EOR. Furthermore, we also introduced cationic monomer diallyl dimethyl ammonium chloride (DMDAAC)<sup>34</sup> to improve the inhibition hydration swelling ability of sodium montmorillonite (Na-MMT). Hence, we aimed to use TCAP, cationic monomer DMDAAC, acrylamide (AM), and acrylic acid (AA) to obtain poly(AM-AA-DMDAAC-TCAP).

## EXPERIMENTAL

### Materials

AM, AA, TsCl, AP, triethylamine ( $\text{Et}_3\text{N}$ ), DMDAAC, poly(oxyethylene octylphenol ether) (OP-10), sodium hydrogen sulfite ( $\text{NaHSO}_3$ ), ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ), ethanol, sodium chloride (NaCl), magnesium chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), calcium chloride anhydrous ( $\text{CaCl}_2$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_3$ ) and HPAM et al. were chemically pure or above and supplied by Chengdu Kelong Chemical Reagent Factory, Sichuan. Na-MMT was provided by Xinjiang Xiazijie Bentonite Company, Xinjiang. The viscosity-average molecular weight of HPAM was  $5 \times 10^6$  g/mol.  $\text{CH}_2\text{Cl}_2$  was dried using anhydrous sodium sulfate, and others were used as commercial without further purification.

### Synthesis of Copolymer

The indicated TCAP, OP-10, and deionized water were added in a 250 mL three-neck flask with a magnetic stir bar. Then DMDAAC, AM, and AA solution were used by 1.0 mol/L NaOH solution to adjust the pH to a certain value and then the solution were added into the flask. After 15 min under  $\text{N}_2$  atmosphere, the initiator  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and  $\text{NaHSO}_3$  (molar ratio 1 : 1) were added in the flask at a certain temperature for 8 h. The reaction product was washed by ethanol repeatedly and dried to obtain the white granular poly(AM-AA-DMDAAC-TCAP). The synthesis route is shown in Scheme 1.

### Characterizations

The various concentrations of polymer solutions were prepared by dissolving a given quality of polymer particles in deionized water under mechanical agitation. The apparent viscosities of

polymer solution were measured with a Brook field D-III + Pro viscometer (Brook Field). FTIR spectra were measured in the optical range of  $400\text{--}4000\text{ cm}^{-1}$  by averaging 32 scans at a resolution of  $4\text{ cm}^{-1}$  with KBr pellets using WQF-520 Fourier transform infrared spectrometer (Beijing Rayleigh Analytical Instrument Corporation, China).  $^1\text{H-NMR}$  of copolymer was recorded by a Bruker AV III-400 NMR spectrometer (Bruker, Switzerland) in  $\text{D}_2\text{O}$ . The intrinsic viscosity of copolymer solution was measured by Ubbelohde capillary viscometer (Shanghai Sikeda Scientific Instruments Incorporation, China) at  $(30 \pm 0.1)^\circ\text{C}$ . The conversion rate of AM and AA was determined by high performance liquid chromatography technology (Shimadzu Company, Japan) using ODS column at UV detector (210 nm),  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  90/10 (v/v). Scanning electron microscopy (SEM) analysis of copolymer solutions was obtained with FEI Quanta 450 (FEI).

### Performance Evaluation

Rheological measurement was conducted on a HAAKE RS 600 Rotational Rheometer (HAAKE, Germany) equipped with cone/plate geometry (diameter = 60 mm, angle =  $1^\circ$ , plate-to-plate gap = 0.104 mm). The temperature dependence of the copolymer was obtained at the rate of  $3^\circ\text{C}/\text{min}$  from 30 to  $130^\circ\text{C}$  and the shear rate of  $170\text{ s}^{-1}$ . The shear resistance test was performed varying with different shear rates at  $30^\circ\text{C}$  and the shear stress was recorded. Thermo gravimetric analysis (TG) of the samples used a STA449 F3 synchronous thermal analyzer (Netzsch, Germany) from 40 to  $700^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  under air atmosphere. Small-angle XRD was taken by X-ray diffractometer (X'Pert PRO MPD PANalytical B. V., The Netherlands). The total organic carbon (TOC) of the polymer solution was measured by TOC—V CPH detector (SHIMADZU, Japanese) at nitrogen atmosphere.

### Core Flooding Test

The core assembly was a stainless steel cylinder packed with sand and the size distribution of sand was 80–100 items. The sand was washed with 18% hydrochloric acid and then washing it with distilled water until the pH was 7. The simulation crude oil was collected from Shengli Oil Field (China) and the apparent viscosity is 65.5 mPa s at  $65^\circ\text{C}$ . The device of core flooding test system is constituted with the ISCO pump, thermostat, pressure sensor, cylinder, and back-pressure valve. The maximum work pressure of the ISCO pump is 50 MPa, and its maximum and minimum displacement rates are 50.000 and 0.001 mL/min, respectively. The pressure drop was recorded by a pressure sensor. Figure 1 shows the setup of the core flooding tests.

## RESULTS AND DISCUSSION

### Effect of the Synthesis Conditions

The effect of synthesis conditions on apparent viscosity of copolymer solutions was investigated by the single variable method in Figure 2. The apparent viscosity was measured at  $30^\circ\text{C}$  and  $7.34\text{ s}^{-1}$ , and the concentration of copolymer solution was 1000 mg/L. The results reveal that the maximum apparent viscosity of copolymer solution is 429.2 mPa s at 1000 mg/L. And the corresponding optimal synthesis conditions are established: the optimal concentrations of TCAP and DMDAAC are 0.19 wt % and 3.8 wt %, respectively; the ratio of AM and AA

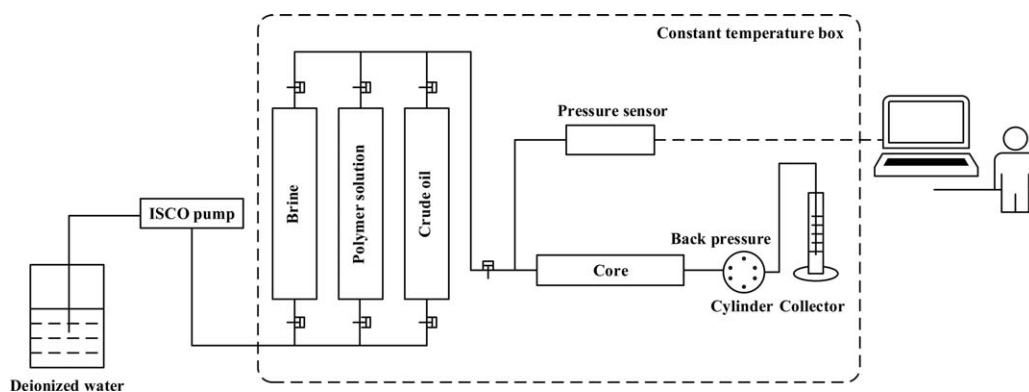


Figure 1. Setup of the core flooding test.

on weight is 5 : 5; the initiator concentration is 0.1 wt %; the solution pH is 7 and the temperature is 50°C.

### FTIR and $^1\text{H-NMR}$ Spectra Analysis

The FTIR and  $^1\text{H-NMR}$  spectra of the obtained copolymer are shown in Figure 3(a,b). From the FTIR spectra, the peak at  $3451.09\text{ cm}^{-1}$  is due to the stretching vibrations of the  $-\text{NH}-$  bond in the  $-\text{CONH}_2$  group, and a sharp absorption peak at  $1699.13\text{ cm}^{-1}$  is assigned to the stretching vibrations of the  $\text{C}=\text{O}$  bond. The peaks at  $2930.57$  and  $2857.85\text{ cm}^{-1}$  are attributable to the  $-\text{CH}-$  bond in copolymer chain. At  $1313.10$  and

$1108.69\text{ cm}^{-1}$ , the stretching vibration absorption peaks of  $\text{S}=\text{O}$  bond in sulfonamide are monitored. In the  $^1\text{H-NMR}$  spectrum of copolymer, the chemical shift value at 7.84 and 7.57 ppm is assigned to the protons of the aromatic ring. The chemical shift value at 2.51 ppm is due to the protons of the  $-\text{CH}_3$  connected to aromatic ring. The protons of the aliphatic  $-\text{CH}_2-$  of polymeric chain appear at 1.52–1.67 ppm, and the protons of the aliphatic  $-\text{CH}-$  of polymeric chain appear around 2.13 ppm. The distinct peaks at 2.97 ppm, 3.08–3.17 ppm are  $-\text{CH}_3$  and  $-\text{CH}_2-$  of  $-\text{CH}_2-\text{N}^+-\text{CH}_3$ , respectively.

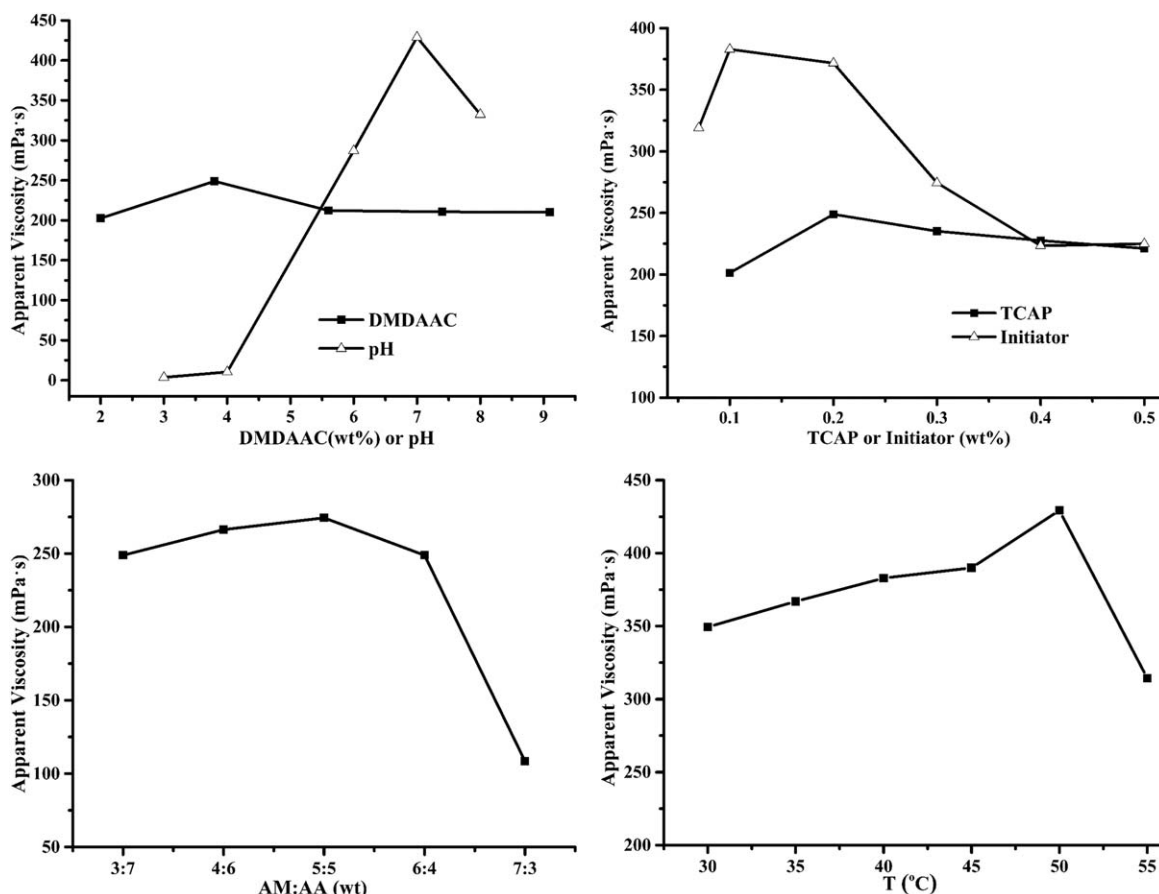


Figure 2. Effect of synthesis conditions on copolymerization.

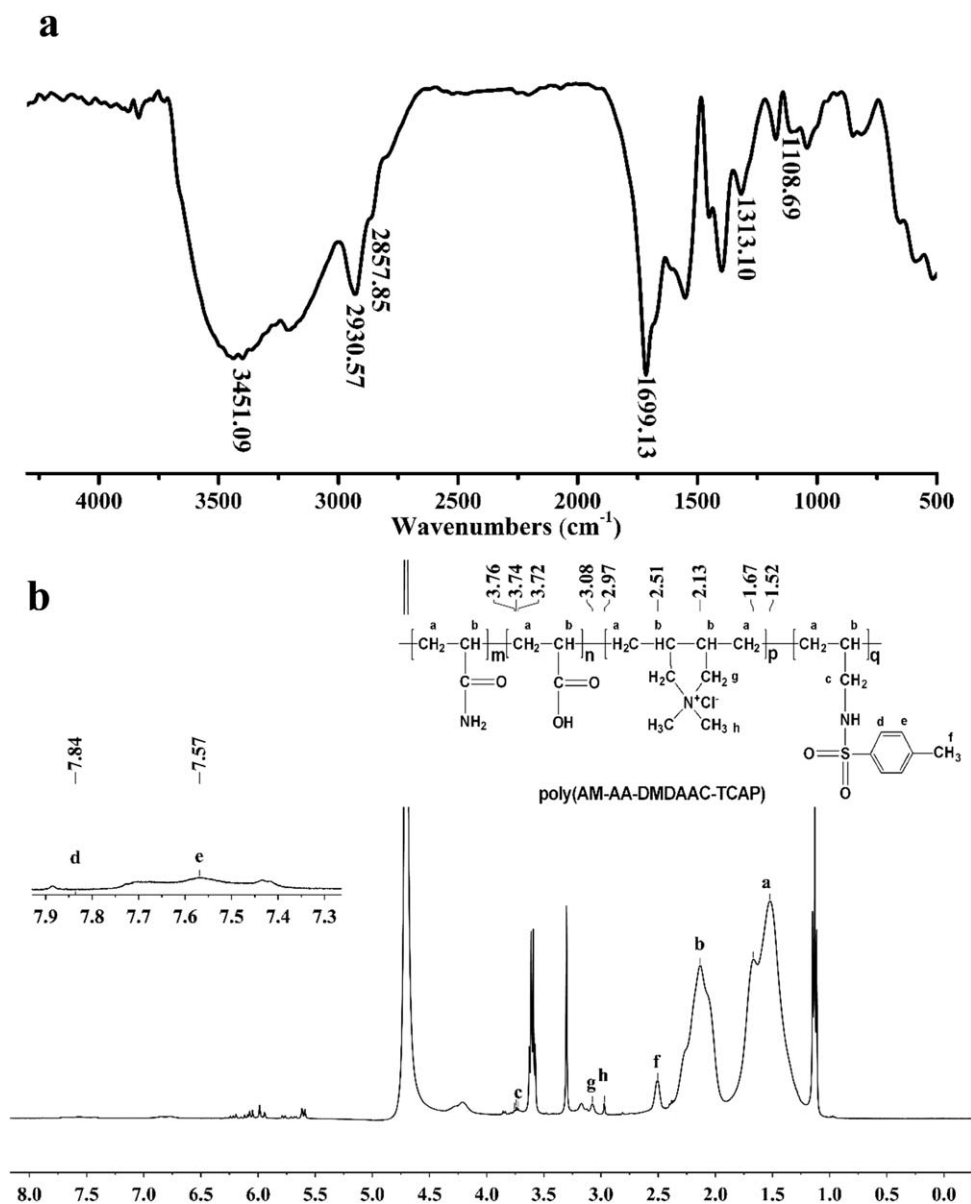


Figure 3. (a) FTIR spectra of copolymer and (b)  $^1\text{H-NMR}$  spectra of copolymer in  $\text{D}_2\text{O}$ .

### Electron Microscope Scanning Analysis

The electron microscope scanning (SEM) of 2000 mg/L HPAM and poly(AM-AA-DMDAAC-TCAP) is shown in Figure 4. Among these images, Figure 4(a,b) are HPAM solution at different scan sizes (2000 $\times$  and 5000 $\times$ , respectively), and Figure 4(c,d) (2000 $\times$  and 5000 $\times$ , respectively) are images of poly(AM-AA-DMDAAC-TCAP). It could be clearly observed that microcosmic nets of poly(AM-AA-DMDAAC-TCAP) are more compact than that of HPAM due to the interaction of the polymer chains, which may be a cause of higher thickening function of poly(AM-AA-DMDAAC-TCAP).

### Conversion Rate of Monomers

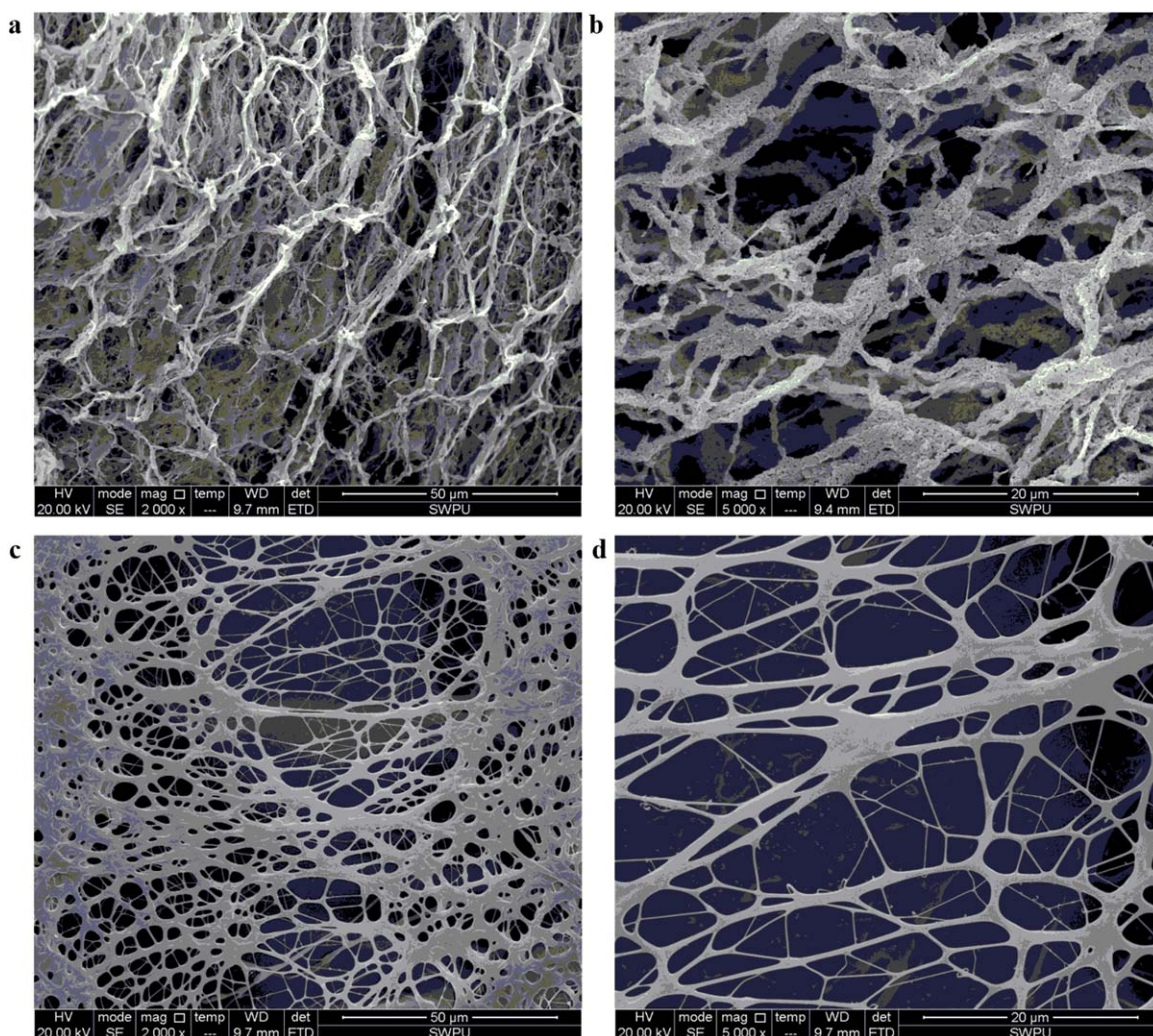
The linearity was investigated for standard sample concentrations range and the calibration curve was derived by plotting the peak-area ratios of the analyte and the internal standard

against the concentration of monomers using linear regression analysis. The calibration curves of monomers are shown in Figure 5(a,b):  $A_{\text{AM}} = 106708.78678 + 1.26617 \times 10^9 \times C$ ,  $A_{\text{AA}} = -39184.15794 + 1.08022 \times 10^9 \times C$ .

The conversion of AM and AA was calculated with the following equation:

$$W\% = \frac{m - C \times V \times M}{m} \times 100\% \quad (1)$$

where  $W\%$  is the conversion of AM or AA,  $m$  is the total weight of samples in the reaction, g,  $C$  is the concentration of samples, mol/L,  $A$  is the chromatographic peak area of the unreacted AM or AA,  $M$  is the molar mass samples, g/mol, and  $V$  is the solution volume of ethanol in which the copolymer was isolated by precipitation, L.



**Figure 4.** SEM images of polymer: (a) HPAM solution at  $\times 2000$  magnification, (b) HPAM solution at  $\times 5000$  magnification, (c) poly(AM-AA-DMDAAC-TCAP) solution at  $\times 2000$  magnification, and (d) poly(AM-AA-DMDAAC-TCAP) at  $\times 5000$  magnification. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The conversion of AM and AA is 95.21% and 96.36%, respectively, which shows that high conversion rate of AM and AA could be obtained at optimal synthesis conditions.

#### Intrinsic Viscosity of Copolymer

The copolymer was diluted in the 1.0 mol/L NaCl solution at five different concentrations (1.0, 0.67, 0.50, 0.33, and 0.25 g/L), and  $\eta_{sp}/C$  and  $\ln \eta_r/C$  of each concentration were determined by following equations. The viscosity average molecular weight of copolymer could be generally calculated by employing the Mark–Houwink equation. The values  $K$  and  $\alpha$  are constants for a given polymer/solvent system at a given temperature which could refer to the reported studies.<sup>35–38</sup>

$$\eta_{sp} = \frac{(t - t_0)}{t_0} \quad (2)$$

$$\frac{\eta_{sp}}{C} = [\eta] + K_H [\eta]^2 C \quad (3)$$

$$\frac{\ln \eta_r}{C} = [\eta] + K_K [\eta]^2 C \quad (4)$$

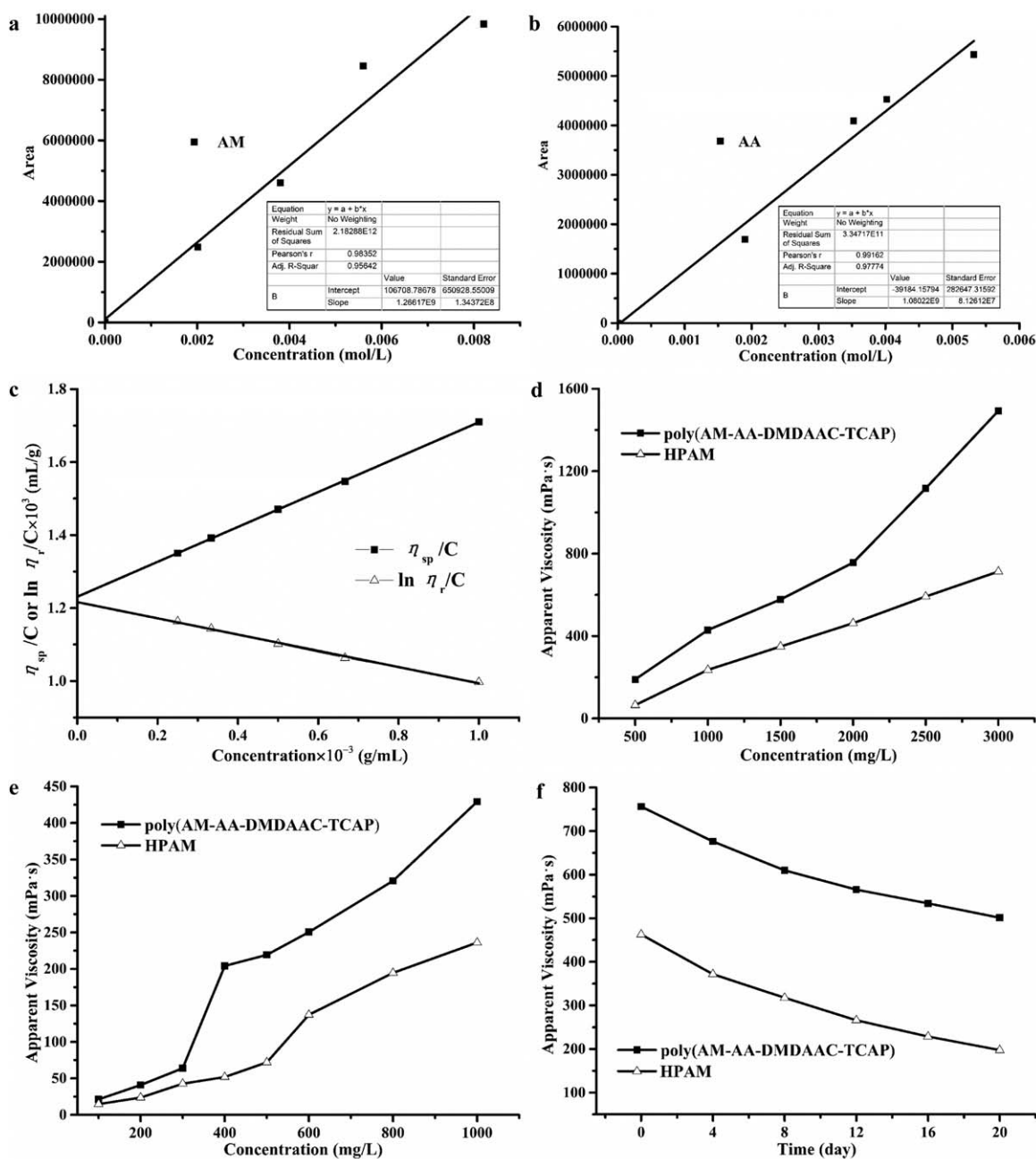
$$[\eta] = \lim_{C \rightarrow 0} \eta_{sp}/C = \lim_{C \rightarrow 0} \ln \eta_r/C \quad (5)$$

$$[\eta] = KM \eta^\alpha \quad (6)$$

where  $t$  is the flow time of copolymer solution,  $s$ ,  $t_0$  is the flow time for 1.0 mol/L NaCl solution,  $s$ ,  $C$  is the concentration of copolymer, g/mL,  $\eta_{sp}$  is the specific viscosity,  $K_H$  is the Huggins constant,  $K_K$  is the Kraemer coefficient and theoretically,  $K_H - K_K = 1/2$ , and  $[\eta]$  is the intrinsic viscosity of copolymer, mL/g. Figure 5(c) shows that the intrinsic viscosity of poly(AM-AA-DMDAAC-TCAP) is 1223.60 mL/g, and the viscosity-average molecular weight is  $5.8 \times 10^6$  g/mol.

#### Effect of Copolymer Concentration on Apparent Viscosity

The effect of copolymer concentration on apparent viscosity of poly(AM-AA-DMDAAC-TCAP) is shown in Figure 5(d). The apparent viscosity increases gradually with the increase of copolymer concentration from 500 to 3000 mg/L, although at these concentrations poly(AM-AA-DMDAAC-TCAP) shows excellent water solubility. Apart from that, it could be observed



**Figure 5.** (a) The calibration curve of AM; (b) the calibration curve of AA; (c) intrinsic viscosity of copolymer; (d) effect of polymer concentration on apparent viscosity; (e) overlap concentration of polymers; (f) aging test of polymers.

that poly(AM-AA-DMDAAC-TCAP) exhibits higher thickening ability than that of HPAM due to the hydrophobic chain interaction and hydrogen bonding of  $O=S=O$  or  $-(SO_2)-NH-$  in the intramolecular or intermolecular.

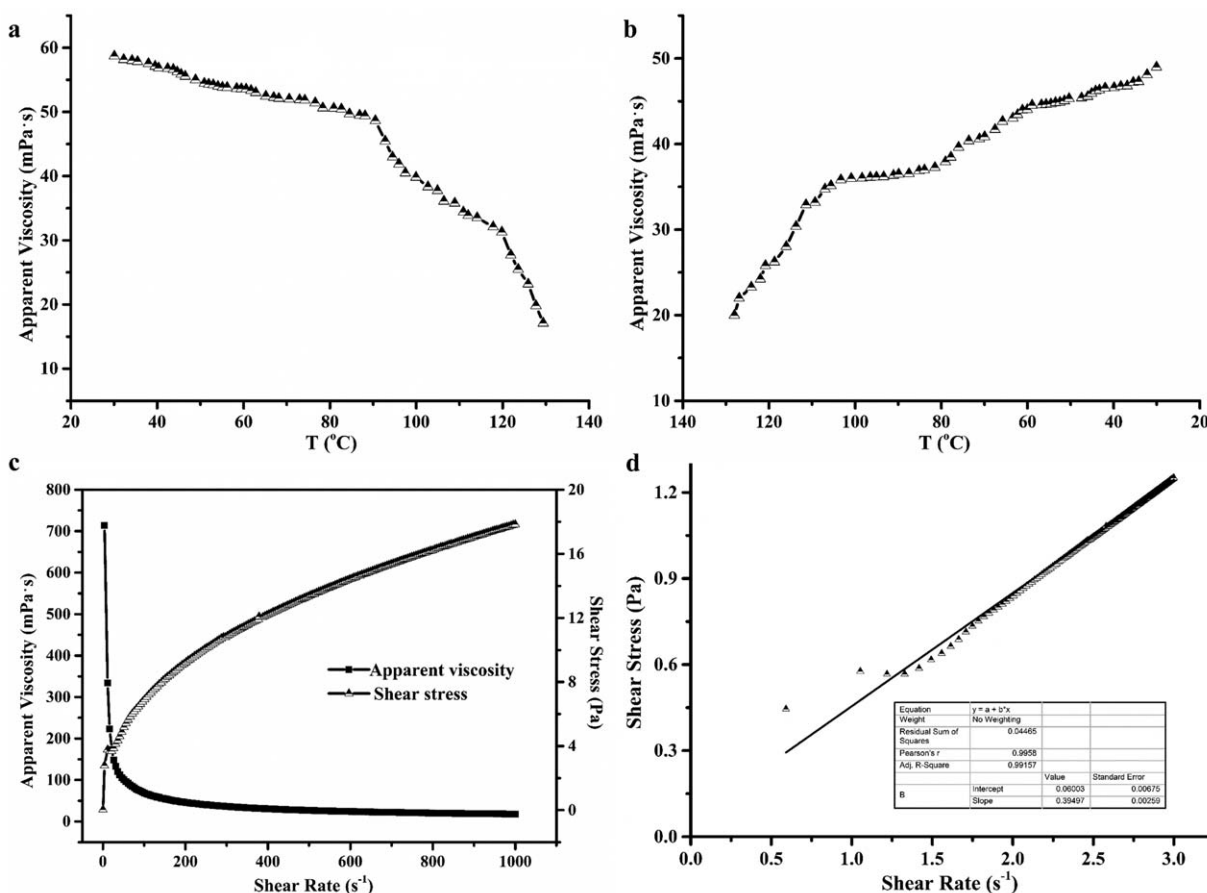
#### Overlap Concentration

The overlap concentration of polymer was determined by a strong increase in viscosity with the copolymer concentration changing from 100 to 1000 mg/L in deionized water. The viscosity versus concentration is shown in Figure 5(e). When the concentration of HPAM is above 500 mg/L, there is a strong increase in viscosity. For poly(AM-AA-DMDAAC-TCAP) an

obvious increase in viscosity is occurring at the concentration of 300 mg/L. The results indicate that the overlap concentration of poly(AM-AA-DMDAAC-TCAP) is lower than that of HPAM due to the interaction of poly(AM-AA-DMDAAC-TCAP) chains.

#### Aging Test

The viscosity variation with the aging time was tested at a certain temperature. This test is important for polymer candidates in EOR application at high temperatures (above  $70^\circ\text{C}$ ). Two thousand milligrams per liter HAPM and poly(AM-AA-DMDAAC-TCAP) solutions were sealed at  $70^\circ\text{C}$  for 20 days,



**Figure 6.** (a) Effect of increasing temperature on apparent viscosity; (b) effect of a ramp down temperature on apparent viscosity; (c) effect of shear rate on apparent viscosity and shear stress; (d) effect of shear rate on shear stress in log–log scale.

and the viscosity was recorded every 4 days at  $7.34^{-1}$ . The results are shown in Figure 5(f). The viscosity of poly(AM-AA-DMDAAC-TCAP) solutions could reach at 66.3% retention rate compared with that at 30°C, while 42.7% viscosity retention rate has been obtained by HPAM. The results show that poly(AM-AA-DMDAAC-TCAP) exhibiting significant thermal stability in comparison with HPAM could be expected to better application in EOR.

#### Effect of Temperature and Shear Rate on Apparent Viscosity

The effect of temperature on the apparent viscosity of the 2000 g/mL copolymer solution at a shear rate of  $170 \text{ s}^{-1}$  is shown in Figure 6(a,b). With the temperature rising, the apparent viscosity reduces gradually. The viscosity of ploy(AM-AA-DMDAAC-TCAP) is up to 67.8% retention rate at 100°C and 53.3% at 120°C compared with that at 30°C, respectively. Compared with HPAM (viscosity retention rate 3.7%, 120°C), the copolymer shows excellent high temperature resistance which could be due to the interaction of copolymer chains. With the temperature falling, the apparent viscosity begins to restore, and the viscosity reaches at 83.4% retention rate compared with initial viscosity at 30°C. It is worth to mention that poly(AM-AA-DMDAAC-TCAP) having positive and negative charges in separate building blocks makes the viscosity of the copolymer solution less sensitive to the external tempera-

ture. In Figure 6(c), it is found that a very obvious drop to apparent viscosity by changing the shear rate from 10 to  $170 \text{ s}^{-1}$ , and viscosity gradually flatten at the high shear rate is desirable for polymer injection and transportation in oil displacement.

#### Effect of Shear Rate on Shear Stress

The effect of shear rate on shear stress and the data in log–log scale are shown in Figure 6(c,d). The consistency coefficient ( $k$ ) and power law exponent ( $n$ ) were obtained by the equation of non-Newtonian liquid.

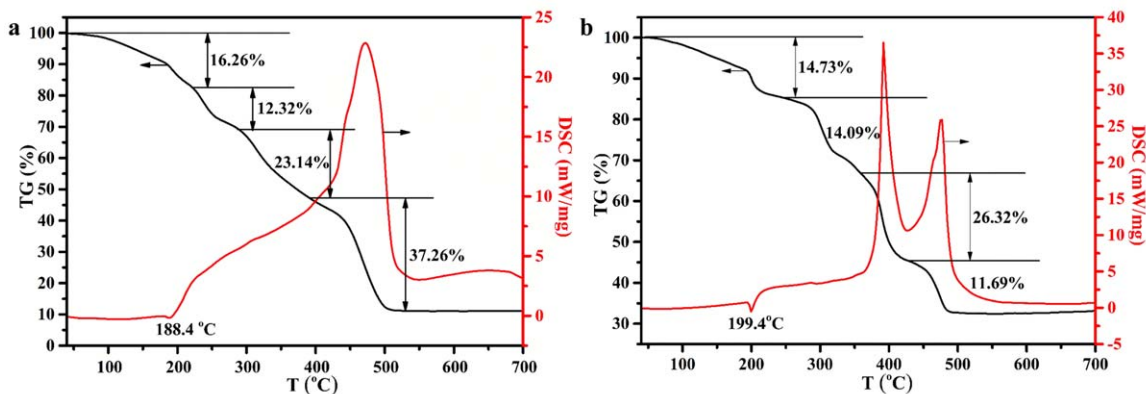
$$\tau = k\gamma^n \quad (7)$$

where  $\tau$  is shear stress, Pa;  $\gamma$  is shear rate,  $\text{s}^{-1}$ ,  $k$  is consistency coefficient,  $\text{Pa s}^n$ ; and  $n$  is power law exponent.

It is clear that HPAM and poly(AM-AA-DMDAAC-TCAP) are both the pseudoplastic fluid which could often be used as chemical flooding agents.  $n$  and  $k$  of poly(AM-AA-DMDAAC-TCAP) are 0.39 and  $1.15 \text{ Pa s}^{0.39}$ , respectively, but for HPAM,  $n$  and  $k$  are 0.63 and  $2.32 \text{ Pa s}^{0.63}$ , respectively.

#### TG Analysis

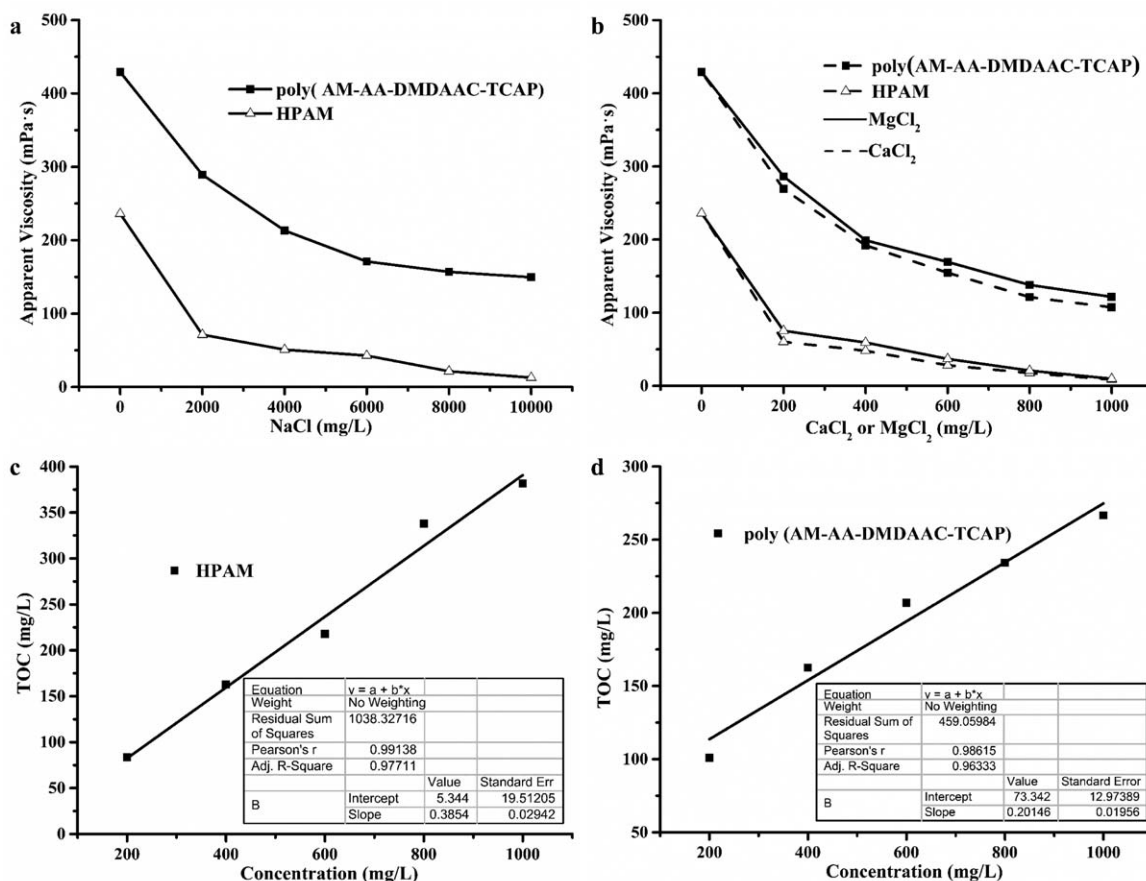
TG analysis of polymers is shown in Figure 7(a,b). The TG diagram of poly(AM-AA-DMDAAC-TCAP) shows four stages for the weight loss. The first stage loses mass of 14.73 wt % in 30–246°C, which is ascribed to the evaporation of intermolecular



**Figure 7.** TG analysis of (a) HPAM; (b) poly(AM-AA-DMDAAC-TCAP). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and intermolecular moisture combined by strong hydrophilic groups. The second one takes place in the range of 246–328°C with mass loss of 14.09 wt %, and the third one loss mass of 26.32 wt % occurring in 328–436°C, which could be attributed to the decompositions of amide groups, quaternary ammonium salt, and benzenesulfonamide groups. The last stage occurs beyond 436°C with the mass loss of 11.69 wt % which could be attributed to the carbonization.

Similarly, the TG diagram of HPAM displays four stages of weight loss. The first step takes place in the range of 30–215°C with a mass loss of 16.26 wt % corresponding to the evaporation of intra and intermolecular moisture. The second one occurs in the 215–270°C with a mass loss of 12.32 wt %, and the third one occurs in 270–384°C with a mass loss of 23.14 wt %, which could be ascribed to the amide groups and the decompositions of amide groups. The fourth stage occurs



**Figure 8.** (a) Effect of NaCl on apparent viscosity of polymers; (b) effect of CaCl<sub>2</sub> or MgCl<sub>2</sub> on apparent viscosity of polymers; (c) standard curve of HPAM; (d) standard curve of poly(AM-AA-DMDAAC-TCAP).



**Table I.** Effect of Copolymer Solutions on the *d*-Spacing of Na-MMT

Entry	Samples	<i>d</i> -Spacing (Å) <sup>a</sup>
1	Na-MMT	12.1066
2	Na-MMT + water	18.9430
3	Na-MMT + NaCl 10 wt %	15.8745
4	Na-MMT + KCl 10 wt %	15.4582
5	Na-MMT + CaCl <sub>2</sub> 10 wt %	18.1523
7	Na-MMT + copolymer 0.2 wt %	18.6103
8	Na-MMT + copolymer 0.3 wt %	18.6168
9	Na-MMT + copolymer 0.4 wt %	17.9063
10	Na-MMT + copolymer 0.5 wt %	17.8683
12	Na-MMT + copolymer 0.3 wt % + NaCl 10 wt %	15.6951
14	Na-MMT + copolymer 0.3 wt % + KCl 10 wt %	14.8624
16	Na-MMT + copolymer 0.3 wt % + CaCl <sub>2</sub> 10 wt %	18.3642

<sup>a</sup>*d*-Spacing: the samples were kept wet and tested by X-ray diffraction in small angle scattering.

beyond 384°C with the mass loss of 37.26 wt %, which could be attributed to the carbonization. In addition, observation from the DSC curves, a peak of heat absorption at 199.4°C is provided by poly(AM-AA-DMDAAC-TCAP) and this temperature is higher than 186.5°C obtained by HPAM, which is due to the evaporation of moisture combined by stronger hydrophilic groups of poly(AM-AA-DMDAAC-TCAP).

#### Salt Tolerance

The salt tolerance of copolymer was tested with increasing salt concentration at 30°C and 7.34 s<sup>-1</sup>, and the results are shown in Figure 8(a,b). The concentration of the polymer was 1000 mg/L. The viscosity retention rate of poly(AM-AA-DMDAAC-TCAP) could reach up to 34.9% (10,000 mg/L NaCl), 27.4% (1000 mg/L CaCl<sub>2</sub>), and 28.3% (1000 mg/L MgCl<sub>2</sub>). It could be observed that poly(AM-AA-DMDAAC-TCAP) has better salt tolerance to Na<sup>+</sup> than Ca<sup>2+</sup> or Mg<sup>2+</sup> in the same conditions. Compared with 5.4% (10,000 mg/L NaCl), 3.6% (1000 mg/L CaCl<sub>2</sub>), and 4.1% (1000 mg/L MgCl<sub>2</sub>) obtained by HPAM, poly(AM-AA-DMDAAC-TCAP) shows better brine compatibility.

#### Adsorption Test

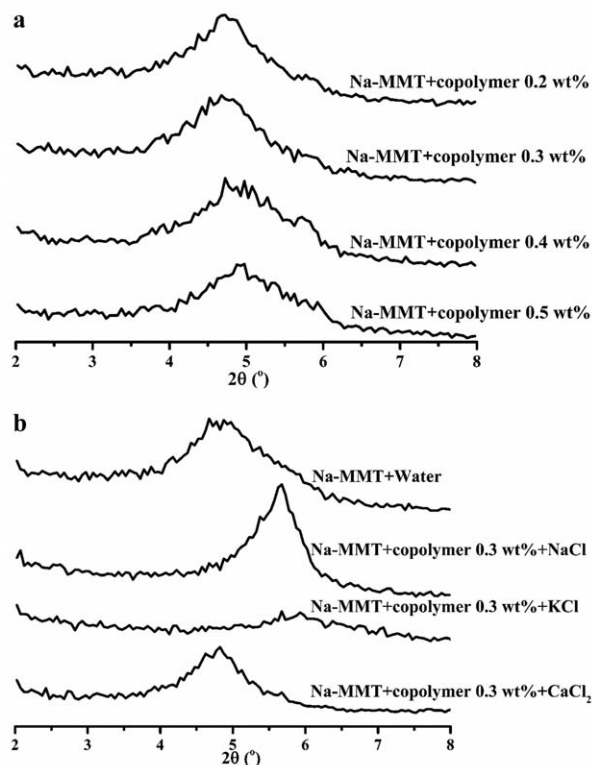
The various concentrations (200, 400, 600, 800, 1000 mg/L) of the polymer solutions were prepared by dissolving in deionized water to obtain the standard curve of polymer concentrations and total organic carbon (TOC)<sup>39</sup> and the standard curves of polymers are shown in Figure 8(c,d). Two thousand milligrams per liter polymer solution was mixed with the same sand used in core flooding test (with a mass ratio of 5 : 1) and placed in the water bath oscillator at a certain temperature for 24 h. Then, the samples were centrifuged at 3500 r/min for 30 min and the supernatant was diluted to a concentration of 600 mg/L to obtain the final concentration according to standard curve. The adsorption quantity was calculated according to the following equation:

$$\Gamma = \frac{(C_1 - C_2)V}{m} \quad (8)$$

where  $\Gamma$  is the adsorption quantity of polymer on sand,  $\mu\text{g/g}$ ;  $C_1$  is the initial concentration of polymer, mg/L;  $C_2$  is the con-

centration of polymer after adsorption, mg/L;  $V$  is the volume of the solution (mL);  $m$  is the quality of the sand, g.

With the temperature changing from 30 to 70°C, the adsorption quantity of HPAM slightly increased from 164.8 to 264.6  $\mu\text{g/g}$ , while the adsorption quantity of poly(AM-AA-DMDAAC-TCAP) decreased from 529.3 to 285.8  $\mu\text{g/g}$ . It is because that high temperature is beneficial for hydrophobic effect of



**Figure 9.** (a) Effect of copolymer concentration on *d*-spacing of Na-MMT, (b) effect of copolymer combined with NaCl, KCl, and CaCl<sub>2</sub> solutions on *d*-spacing of Na-MMT.

**Table II.** The Parameters of Cores

Polymer	Cores	Length (cm)	Diameter (cm)	Porosity (%)	Permeability (mD)	$S_{wi}$ (%)
HPAM	1#	30.02	2.57	33.56%	450.32	20.28
Poly(AM-AA-DMDAAC-TCAP)	2#	30.00	2.58	33.81%	451.75	20.13

copolymers and disadvantage for adsorption on sand.<sup>40</sup> The results further illuminate the association interaction of copolymer chains which were accorded with experimental results reported in literatures.<sup>41</sup>

#### Effect of Copolymer Solutions on the *d*-Spacing of Na-MMT

Effect of copolymer solutions on the *d*-spacing of Na-MMT is shown in Table I and Figure 9(a,b). The obtained copolymer could not stabilize Na-MMT remarkably. It is found that poly(AM-AA-DMDAAC-TCAP) has slightly improved of anti-swelling with copolymer concentration increasing from 2000 to 5000 mg/L. The results obviously show that copolymer combined with the brine (NaCl and KCl) could exhibit excellent clay stabilization of Na-MMT. The solutions of 3000 mg/L poly(AM-AA-DMDAAC-TCAP) combined with 10 wt % KCl could remarkably reduce the *d*-spacing of Na-MMT from 18.94 to 14.86 Å, while 10 wt % KCl solution could reduce the *d*-spacing from 18.94 to 15.46 Å. However, the copolymer combined with CaCl<sub>2</sub> could not exhibit better results compared with the previous researches.<sup>28</sup> In this setting, copolymer helps stabilize the clay by coating them with a protective layer by hydrogen bond and cation adsorption.<sup>42</sup>

#### Core Flood Test

The chemical composition of the brine are 3092 mg/L Na<sup>+</sup> and K<sup>+</sup>, 276 mg/L Ca<sup>2+</sup>, 14 mg/L CO<sub>3</sub><sup>2-</sup>, 311 mg/L HCO<sub>3</sub><sup>-</sup>, 85 mg/L SO<sub>4</sub><sup>2-</sup>, 5436.34 mg/L Cl<sup>-</sup>, and the total dissolved solids (TDS) was 9374 mg/L. The polymer (2000 mg/L) solutions were prepared with brine. The core was placed into Hassler core holder with 1.0 MPa backpressure and 3.0 MPa confining pressure. The sand pack was saturated with brine and flooded with crude oil at 0.1 mL/min injection rate until irreducible water saturation ( $S_{wi}$ ) was established. Then 96 h aging was performed

at 65°C. The parameters of cores are shown in Table II. The oil recovery was determined as the following equation:

$$EOR = E_1 - E_2 \quad (9)$$

where  $E_1$  is the oil recovery of copolymer flooding,  $E_2$  is the oil recovery of water flooding.

First, the water flooding was conducted with the brine until water cut reached at 95%, and then it was flooded with polymer solutions. Finally, the extrapolated water flooding was conducted with the brine to obtain water cut 95% once more. The injection rate was 0.3 mL/min. From Figure 10 we found an oil recovery of the brine system was about 41.9%. The values about 16.6% and 10.5% for EOR are revealed by poly(AM-AA-DMDAAC-TCAP) and HPAM at 65°C, respectively, which indicate the oil recovery rate of the copolymer solution is higher compared to that of HPAM exhibiting its potential application in enhance oil recovery.

## CONCLUSIONS

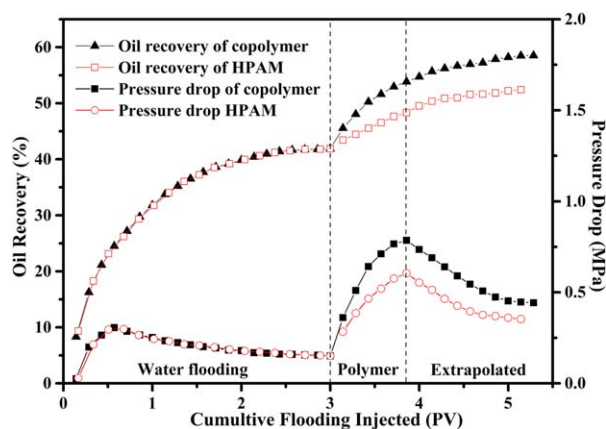
A water-soluble poly(AM-AA-DMDAAC-TCAP) was successfully synthesized by redox free-radical polymerization and characterized by FTIR, <sup>1</sup>H-NMR, SEM, TG, and XRD. Compared with HPAM, poly(AN-AA-DMDAAC-TCAP) exhibited superior thickening capability which could be up to 429.2 mPa s at 1000 mg/L. The apparent viscosity retention rate of poly(AN-AA-DMDAAC-TCAP) was as high as 53.3% at 120°C. The solutions of poly(AM-AA-DMDAAC-TCAP) (3000 mg/L) with KCl (10 wt %) could remarkably reduce the *d*-spacing of Na-MMT from 18.94 to 14.86 Å. In addition, the results of EOR signified that 16.6% oil recovery rate could be obtained by poly(AM-AA-DMDAAC-TCAP) brine solution for potential application in enhance oil recovery.

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**Figure 10.** EOR results of polymers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

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