

Water-Soluble Allyl and Diallyl Camphor Sulfonamides-Based Polyacrylamide Copolymers for Enhanced Oil Recovery

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ABSTRACT: The monomers *N*-allyl camphor sulfonamide (CSAP) and *N,N*-diallyl camphor sulfonamide (CSDAP) were copolymerized with acrylamide (AM), acrylic acid (AA) for EOR, respectively. The effect of the synthesis conditions on apparent viscosity was investigated, and the copolymers were characterized by Fourier transform infrared spectroscopy (FTIR), ¹H nuclear magnetic resonance (¹H NMR), environmental scanning electron microscope (ESEM), and thermogravimetric analysis (TGA). Increasing mass ratio of diallyl CSDAP could lead to the water-insoluble of copolymer, and competition of free radicals could make polymerization of AM/AA/CSDAP more difficult than AM/AA/CSAP. The thickening function and temperature resistance of two copolymers were remarkably improved in comparison with similar molecular weight partially hydrolyzed polyacrylamide (HPAM). In addition, the pronounced temperature resistance of the copolymers has been also demonstrated by temperature resistance test. It has also found that copolymers AM/AA/CSAP and AM/AA/CSDAP brine solutions could obtain significant enhanced oil recovery at 70°C suggesting their potential being applied in chemical enhanced oil recovery. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41238.

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INTRODUCTION

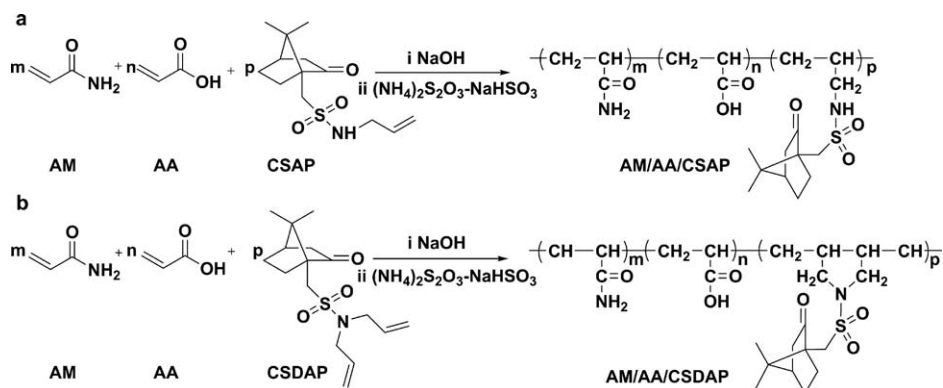
Chemical enhanced oil recovery has been proven to be effective methods in recovering the remaining oil from reservoirs. Currently, the most crucial methods for chemical flooding are polymer flooding, and the commonly used chemicals in this technique are partially hydrolyzed polyacrylamide (HPAM).^{1,2} The main limitations with HPAM are temperature dependency, shear thinning, and salt sensitivity under harsh conditions present in most oil reservoirs, which could result in a reduction of oil recovery rate due to the decreasing viscosity of HPAM solution.³

In the last few decades, a large number of chemical modification methods to HPAM have been studied which could be classified in three categories: the introduction of functionalization monomers,^{4,5} the investigation of branched polyacrylamides,⁶ and the research of the cross-linked polymer.^{7,8} One of the vital aspects is introducing functionalization structure in the backbone of the polymers, such as cyclic structure,^{9,10} zwitterion structure,^{11,12} and long chain hydrophobic groups.^{13,14} It is believed that the rigid monomers like, aromatic nucleus,⁹ naphthalene nucleus,¹⁵ and piperazine ring¹⁰ could improve the

temperature resistance, salt tolerance, and shear resistance of polymer. In our previous works, cyclic monomer *N*-allylbenzamide,¹⁶ β -cyclodextrin,^{17,18} and *N,N*-diallyl nicotinamide¹⁹ were introduced in polyacrylamide chains, respectively, and the viscosity retention rate about 60% from 30 to 100°C was obtained by β -cyclodextrin-based copolymer.¹⁸ Although the different chemical modification polymers with improved properties for EOR have been studied, researching and investing new polymers for EOR still constitutes a challenging field.

Because of the rigidity of the camphor ring and the hydrogen bonds of sulfonamide structure, camphor sulfonic acid and its derivatives have attracted considerable interests. Throughout organic chemistry, they are considered to be a catalyst, medical intermediate, and separation reagent.^{20,21} Also, the self-organization of camphor sulfonic acid-doped polyaniline chains could increase conductivity.²² Nevertheless, there are few literatures reported about polymers containing camphor structure for EOR applications.

In this study, two polymerizable monomer *N*-allyl camphor sulfonamide (CSAP) and *N,N*-diallyl camphor sulfonamide (CSDAP) were prepared to copolymerize them with HPAM,



Scheme 1. Synthesis routes of copolymers (a) AM/AA/CSAP; (b) AM/AA/CSDAP.

respectively, aiming to obtain the polymer with improved performance due to the rigid structure of the camphor sulfonic acid derivatives linked to HPAM and hydrogen bonds of sulfonamide structure in the polymer molecular chains.

EXPERIMENTAL

Materials

Acrylamide (AM), acrylic acid (AA), D-camphor-10-sulfonic acid, thionyl chloride (SOCl_2), allylamine, diallylamine, nonaphenol polyethyleneoxy (10) ether (OP-10), dichloromethane (CH_2Cl_2), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$), sodium bisulfite (NaHSO_3), partially hydrolyzed polyacrylamide (HPAM, with viscosity-average molecular weight 5 and 9 million, respectively), NaCl, KCl, CaCl_2 , MgCl_2 , etc. were all chemically pure and obtained from Chengdu Kelong Chemical Reagent Factory, Sichuan. CH_2Cl_2 was dried prior to use, and others were used as commercial without further purification. The water used was deionized water, and N_2 has the purity of 99.99%. The viscosity-average molecular weight of HPAM used in this study was 5×10^6 except to point out that.

Table I. Effect of m (AM): m (AA): m (CSAP) on Viscosity

Entry ^a	m (AM):m (AA):m (CSAP)	AV/mPa s ^{-1b}
1	7 : 3 : 0.01	252.1
2	7 : 3 : 0.02	213.8
3	7 : 3 : 0.03	266.4
4	7 : 3 : 0.04	282.4
5	7 : 3 : 0.05	231.2
7	5 : 5 : 0.04	285.4
8	6 : 4 : 0.04	311.1
9	8 : 2 : 0.04	161.6
10	9 : 1 : 0.04	20.2

^aOP-10 0.4 wt %, initiator 0.3 wt %, 45°C, and pH = 7.

^bApparent viscosity was tested at 30°C and the concentration of copolymer solution was 1000 mg L⁻¹.

Preparation of Monomers

The monomers *N*-allyl camphor sulfonamide (CSAP) and *N*,*N*-diallyl camphor sulfonamide (CSDAP) were prepared by utilizing camphorsulfonic acid, thionyl chloride, allyl amine, and diallyl amine based on reported method.²³ Obtained CSAP was white solid. Yield: 92.8%, m. p. 192–195°C, and CSDAP was light brown liquid. Yield: 90.3%. Both CSAP and CSDAP were water-insoluble. CSAP: ¹H NMR (400 MHz, CDCl_3): δ = 5.87–5.96 (m, 1H, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 5.30–5.37 (m, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 3.82–3.84 (m, 2H, $-\text{SO}_2-\text{NH}-\text{CH}_2-$), 3.42, 3.46; 2.99, 2.95, (d, 2H, $-\text{CH}_2-\text{SO}_2-\text{NH}-$), 2.39–2.41; 2.43–2.45 (m, 1H); 2.14–2.16 (m, 1H), 2.21–2.28. 1.43–1.50 (m, 2H), 1.93–2.10 (m, 3H), (7H assigned to camphor ring) 1.05 and 0.93 (s, 6H, $\text{CH}_3-\text{C}-\text{CH}_3$), ppm. CSDAP: ¹H NMR (400 MHz, CDCl_3): δ = 5.75–5.94 (m, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 5.18–5.27 (m, 4H, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 3.78–3.93 (m, 4H,

Table II. Effects of Initiator, pH, and Temperature on Viscosity of AM/AA/CSAP

Entry ^a	Initiator/wt %	T/°C	pH	AV/mPa s ⁻¹
1	0.08	45	7	309.5
2	0.1	45	7	368.5
3	0.2	45	7	349.4
4	0.4	45	7	266.4
5	0.5	45	7	247.3
6	0.1	45	3	25.5
7	0.1	45	5	241.5
8	0.1	45	6	355.8
9	0.1	45	8	-
10	0.1	45	9	-
11	0.1	30	7	199.2
12	0.1	35	7	244.1
13	0.1	40	7	281.4
14	0.1	50	7	320.9

^aOP-10 0.4 wt % and m (AM): m (AA): m (CSAP) = 6 : 4 : 0.04. wt based on the mass of total monomers, and - represented the copolymerization could not occur.

Table III. Effect of m (AM): m (AA): m (CSDAP) on Viscosity

Entry	m (AM): m (AA): m (CSDAP) ^a	AV/mPa s ⁻¹
1	7 : 3 : 0.008	244.1
2	7 : 3 : 0.01	266.4
3	7 : 3 : 0.02	247.3
4	7 : 3 : 0.03	199.4
5	7 : 3 : 0.05	100.5
7	5 : 5 : 0.01	140.4
8	6 : 4 : 0.01	250.5
9	8 : 2 : 0.01	236.1
10	9 : 1 : 0.01	44.7

^aOP-10 0.2 wt %, initiator 0.3 wt %, 40°C, and pH = 7.

—SO₂—N—(CH₂)₂—, 3.40, 3.36; 2.83, 2.79, (d, 2H, —CH₂—SO₂—N—), 2.50–2.55(m, 2H), 2.37–2.39; 2.32–2.34 (m, 1H), 1.88–2.09 (m, 3H), 1.37–1.47(m, 1H), (7H assigned to camphor ring) 1.12 and 0.86 (s, 6H, CH₃—C—CH₃), ppm.

Preparation of Copolymers

The appropriate amounts of AM, AA, CSAP (or CSDAP) and emulsifier OP-10 were dissolved in deionized water, and the pH was adjusted to the indicated value using 1 mol L⁻¹ NaOH solution at constant temperature under N₂ atmosphere. Then (NH₄)₂S₂O₈ and NaHSO₃ aqueous solutions were added, respectively (n (NH₄)₂S₂O₈)/n (NaHSO₃) = 1/1). The polymerization was carried out at constant temperature under N₂ atmosphere for 10 h. The resulting products AM/AA/CSAP and AM/AA/CSDAP were precipitated by repeatedly washing with ethanol, followed drying at 40°C *in vacuo* for 12 h. The synthesis routes of copolymers are shown in Scheme 1.

Table IV. Effects of Initiator, pH, and Temperature on Viscosity of AM/AA/CSDAP

Entry ^a	Initiator/wt %	T/°C	pH	AV/mPa s ⁻¹
1	0.08	45	7	63.9
2	0.1	45	7	311.1
3	0.2	45	7	295.1
4	0.4	45	7	272.8
5	0.5	45	7	170.7
6	0.1	40	3	19.1
7	0.1	40	5	175.5
8	0.1	40	6	277.6
9	0.1	40	8	-
10	0.1	40	9	-
11	0.1	30	7	293.6
12	0.1	35	7	296.7
13	0.1	45	7	290.4
14	0.1	50	7	284.0

^aOP-10 0.2 wt % and m (AM) : m (AA) : m (CSDAP) = 7 : 3 : 0.01.

Characterization

The apparent viscosity of polymer solution was measured using Brook field DV-III + Pro viscometer (Brook field, USA) with viscometer rotors 0# (6.0 rpm) and 62# (18.8 rpm). The polymer solutions were prepared by dissolving a certain quality of polymer in distilled water or different brines with mechanical agitation. FTIR spectra of samples were recorded with KBr pellets in the range of 4500–500 cm⁻¹ using WQF-520 Fourier transform infrared spectrometer (Beijing Rayleigh Analytical Instrument Corporation, China) by the averaging of 32 scans at a resolution of 4 cm⁻¹. ¹H NMR of the samples were carried out by Bruker AV III - 400 NMR spectrometer (Bruker, Switzerland) in CDCl₃ and D₂O. The intrinsic viscosity of copolymers diluted by the 1.0 mol L⁻¹ NaCl aqueous solution at certain concentration (0.2500, 0.3333, 0.5000, 0.6667, 1.0000 g L⁻¹) were measured by Ubbelohde viscometer (Shanghai Sikeda Scientific Instruments Incorporation, China) at 30°C. The conversion rates of monomers were determined by high performance liquid chromatography technology (Shimadzu Company, Japan) using ODS column with UV detector (210 nm), flow rate (1.000 mL min⁻¹), sample size (5 μL) and H₂O/CH₃OH 90/10 (v/v) at 40°C. Environmental scanning electron microscopy (ESEM) analysis of polymer solutions was obtained with FEI Quanta 450 (FEI, USA). Nearly 2000 mg L⁻¹ polymer solutions were cryogenically fractured using liquid nitrogen and vacuumized to make the moisture sublimation, then observed with the ESEM operating at an accelerating voltage of 20 kV.

Rheological Measurement

Rheological property was measured using a HAAKE RS 600 Rotational Rheometer (HAAKE, Germany). Temperature resistance of polymers solutions was measured at a constant shear rate of 170 s⁻¹ during temperature going from 30 to 130°C at a heating rate of 3°C min⁻¹, and the shear resistance test of polymers was carried out varying with different shear rates from 10 to 500 s⁻¹ at 30°C meanwhile the shear stress being recorded.

Thermogravimetry and Differential Scanning Calorimetry

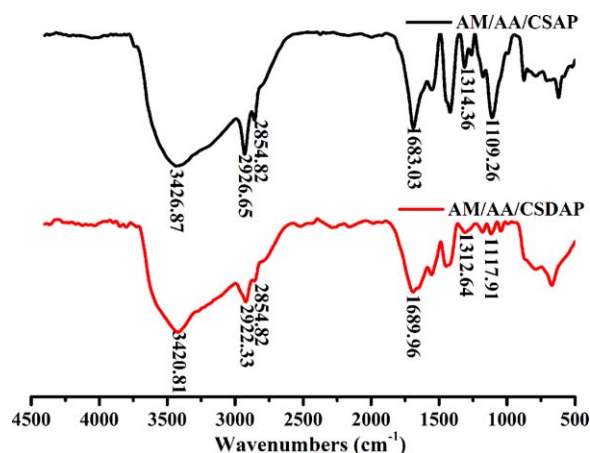
Thermogravimetry and differential scanning calorimetry (TG-DSC) of the copolymers employed a STA449 F3 synchronous thermal analyser (Netzsch, Germany) from 40 to 700°C at a heating rate of 10°C min⁻¹ in an air flow using standard alumina crucibles with samples mass of about 2.5 mg.

Sandpack Flooding Test

The cores used in tests was stainless steel packed with sand (~2.55 cm × 30.0 cm), and the size distribution of sand were 80–100 items. The apparent viscosity of simulated crude oil was 63.7 mPa·s at 70°C, which was prepared by crude oil and kerosene. Injecting the reservoir brine in core until steady pressure to obtain the porosities of core by gravimetry, and permeability (K) was obtained by injecting reservoir brine at a constant rate of 9.99 mL min⁻¹ measuring the pressure drop using Darcy's law.²⁴ Simulated crude oil was poured into the sand, which had been saturated at 0.1 mL min⁻¹ at 70°C for 96 h, then calculate oil saturation. The reservoir brine was prepared with 3092 mg L⁻¹ Na⁺ and K⁺, 276 mg L⁻¹ Ca²⁺, 14 mg L⁻¹ CO₃²⁻,

Table V. Composition of Copolymers

Entry	Copolymers	Feed ratio/wt %			Final composition/wt %		
		AM	AA	Functional monomer	AM	AA	Functional monomer
1	AM/AA/CSAP	59.76	39.84	0.40	60.23	39.41	0.36
2	AM/AA/CSDAP	69.93	29.97	0.10	70.46	29.45	0.09

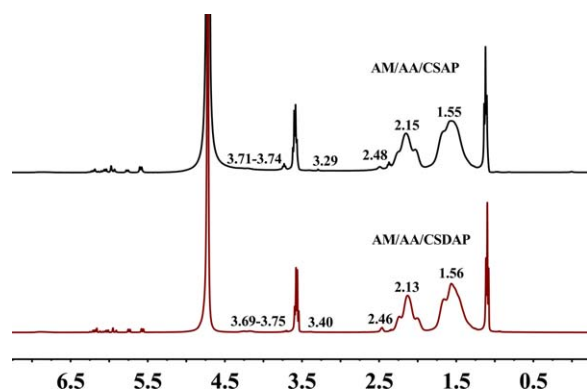
**Figure 1.** FTIR spectra of copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

311 mg L⁻¹ HCO₃⁻, 85 mg L⁻¹ SO₄²⁻, 5436.34 mg L⁻¹ Cl⁻, and the total dissolved solids (TDS) was 9374 mg L⁻¹.

RESULTS AND DISCUSSION

Effect of Synthesis Conditions on Viscosity

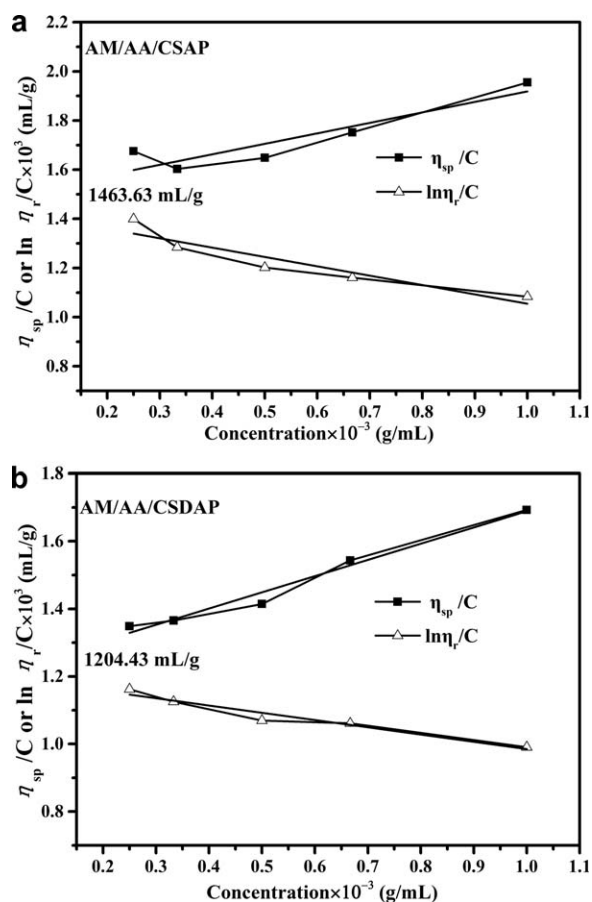
The effect of the synthesis conditions, such as mass concentration of monomers and initiator, pH, and temperature on apparent viscosity of copolymer solutions was studied using single factor analysis. The results are listed in Tables (I–V). Among these conditions, the optimal apparent viscosity of AM/AA/CSAP is 368.5 mPa s⁻¹ at 1000 mg L⁻¹ (Table II, Entry 2), while AM/AA/CSDAP is 311.1 mPa s⁻¹ (Table IV, Entry 2). It is worth raising that with the mass ratio of CSDAP increasing (Table III, Entry 2–5), the copolymer solutions show lower

**Figure 2.** ¹H NMR spectra of copolymers in D₂O. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

viscosity than AM/AA/CSAP at the same conditions (Table I, Entry 1–5 and Table III, Entry 1–5), which could be ascribed to the cyclic copolymerization of non-conjugated diallyl CSDAP leading to mutual competition of three free radicals during copolymerization. And as well poor solubility is observed with the increasing CSDAP might be due to the cyclic annular structure in main polymer chains.^{25–27}

FTIR and ¹H NMR of Copolymers

FTIR and ¹H NMR spectra of both AM/AA/CSAP and AM/AA/CSDAP are shown in Figures 1 and 2. In FTIR spectra, the peaks at 3426.87 and 3420.81 cm⁻¹ are attributed to the stretching vibrations of the —NH— bond of —CONH₂ group of AM/AA/CSAP and AM/AA/CSDAP, respectively. And a sharp absorption peak at 1683.03 and 1689.96 m⁻¹ are the stretching vibrations of the C=O bond in —CONH₂ group of two copolymers. The stretching vibration absorption peak of S=O bond in

**Figure 3.** The intrinsic viscosity of (a) AM/AA/CSAP; (b) AM/AA/CSDAP.

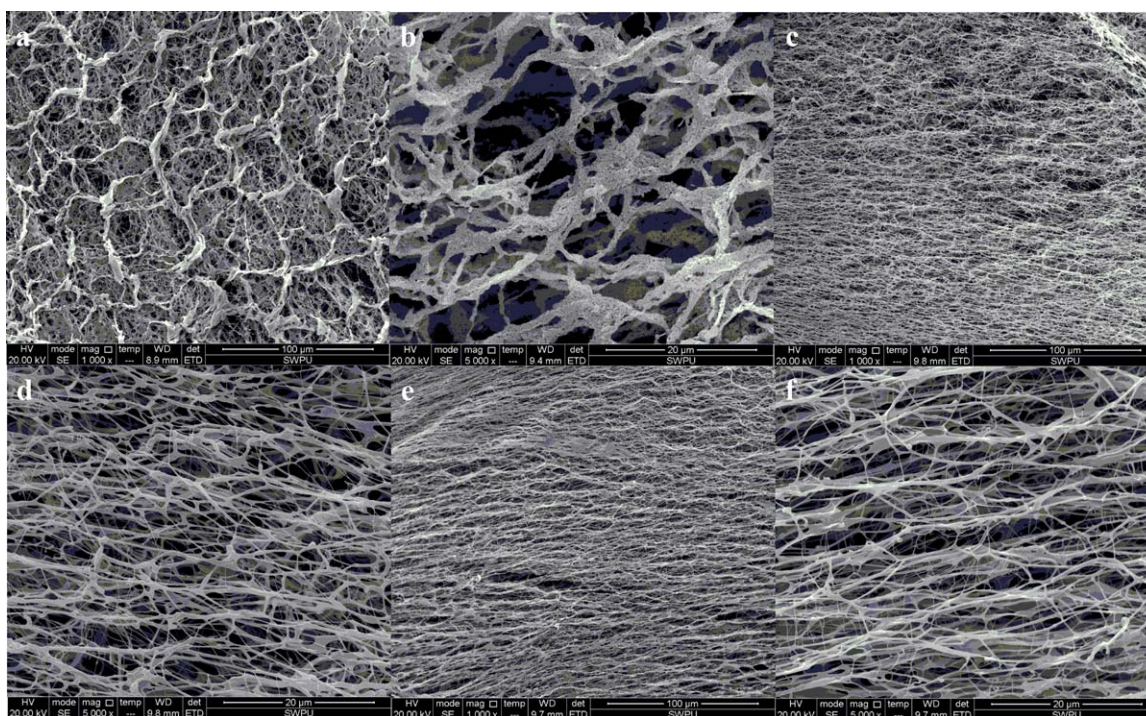


Figure 4. ESEM images of polymers (a) HPAM, $\times 1000$, scale bar $100\ \mu\text{m}$; (b) HPAM, $\times 5000$, scale bar $20\ \mu\text{m}$; (c) AM/AA/CSAP, $\times 1000$, scale bar $100\ \mu\text{m}$; (d) AM/AA/CSAP, $\times 5000$, scale bar $20\ \mu\text{m}$; (e) AM/AA/CSDAP, $\times 1000$, scale bar $100\ \mu\text{m}$; (f) AM/AA/CSDAP, $\times 5000$, scale bar $20\ \mu\text{m}$.

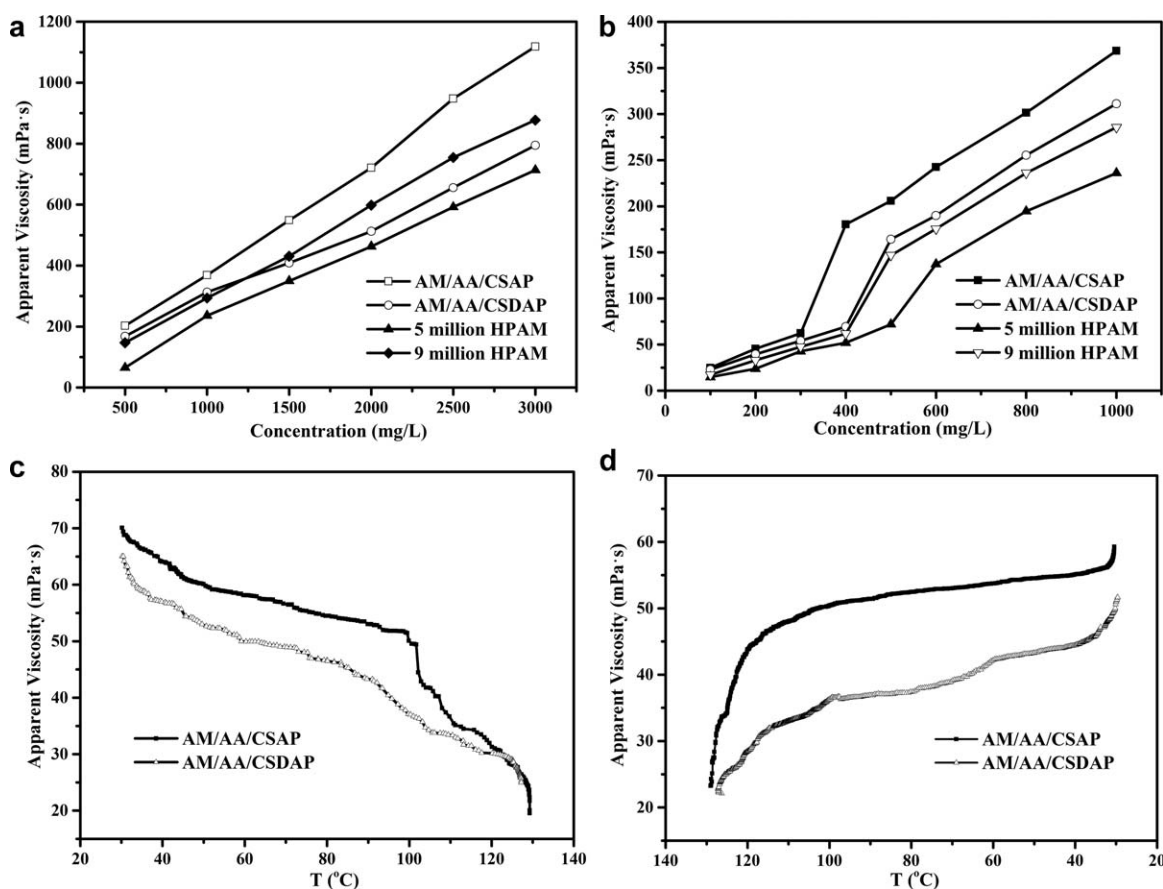


Figure 5. (a) Effect of concentration on viscosity; (b) Overlap concentration of polymers; (c) Effect of increasing temperature on viscosity; (d) Effect of cooling temperature on viscosity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

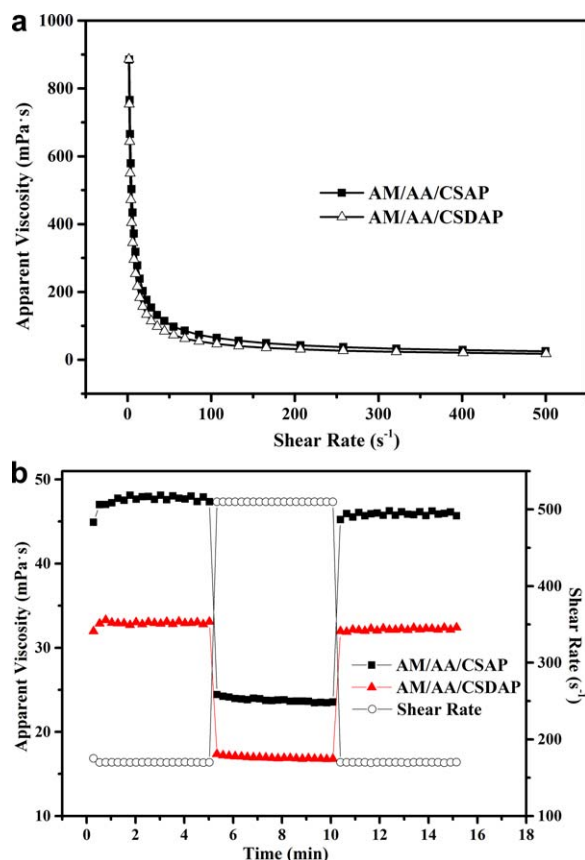


Figure 6. (a) Effect of increasing shear rate on viscosity; (b) Effect of rapid shear rate variation on viscosity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sulfonamide are observed at 1314.36 and 1109.26 cm⁻¹ in AM/AA/CSAP, and 1312.64 and 1117.91 cm⁻¹ in AM/AA/CSDAP.²⁸

As shown in ¹H NMR spectrum of AM/AA/CSAP, the chemical shift value at 3.71–3.74 ppm assign to the protons of –SO₂–NH–CH₂–, and in AM/AA/CSDAP the protons of –SO₂–N–(CH₂)₂– the chemical shift value is at 3.69–3.75 ppm. The chemical shift value about 3.29 and 3.40 ppm are due to the protons of the –CH₂–SO₂–N– in AM/AA/CSAP and AM/AA/CSDAP, respectively. The protons of the –CH₂– and –CH– of polymeric chain appear around 2.15 and 1.55 ppm, and these chemical shift value are similar to the protons in polymeric chain of AM/AA/CSDAP. The protons of camphor ring could be observed in spectrum but other peaks of camphor ring are covered by the protons in polymeric chain.

Composition of Copolymers

It is generally known that ¹H NMR is difficult to quantitatively determine the compositions of copolymers because of the complex molecular structures and the ambiguous integrals in the spectra.²⁹ Thereupon high performance liquid chromatography technology was employed to accurate the conversion rate of AM and AA weighing the final product and determine the copolymer compositions. Both feed ratio and calculated final monomer mass percentages of copolymers were listed in Table V.

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

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

where C% is the conversion of AM or AA, *m* is the total weight of samples in the reaction, g, *C* is the concentration of samples, g L⁻¹, and *V* is the solution volume of ethanol in which the copolymer was isolated by precipitation, L.

The calibration curves of monomers are $A_{AM} = 335339.3634 + 1.84187 \times 10^9 \times C$, $A_{AA} = 39184.15794 + 1.08022 \times 10^9 \times C$, respectively. *A* is the chromatographic peak area of the unreacted AM or AA. The conversion of AM and AA (93.20 and 91.47%, respectively) are obtained by AM/AA/CSAP, and 90.99 and 88.98% for AM and AA, respectively were obtained by AM/AA/CSDAP.

Intrinsic Viscosity of Copolymers

The intrinsic viscosity and viscosity-molecular weight of two copolymers were also calculated based on the measurement methods of HPAM that have been reported.^{30–33} The results are shown in Figure 3. The intrinsic viscosity of AM/AA/CSAP, 1463.63 mL g⁻¹, is higher than that of AM/AA/CSDAP, 1204.43 mL g⁻¹. And as well AM/AA/CSAP possesses higher viscosity-molecular weight (7.26×10^6) than AM/AA/CSDAP (5.69×10^6).

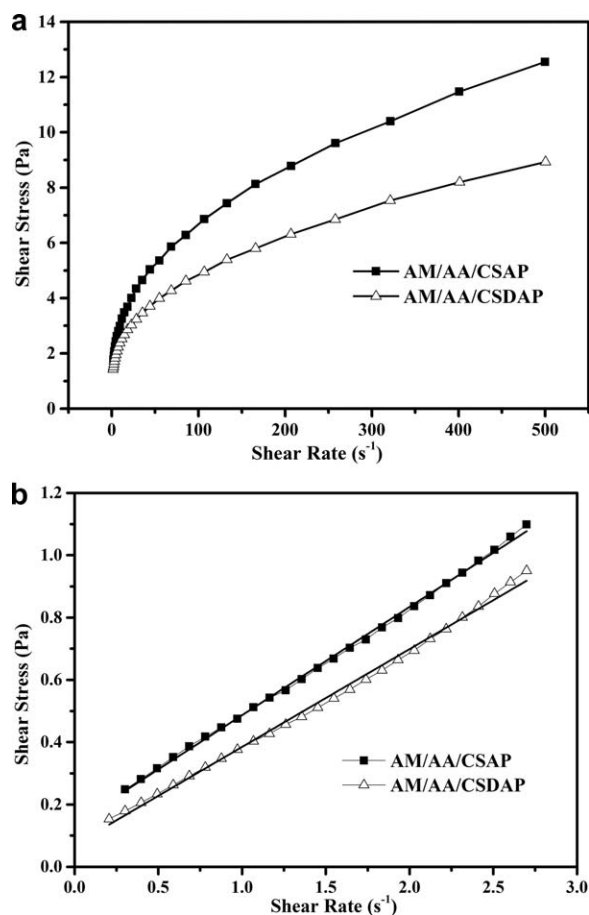


Figure 7. (a) Effect of shear rate on shear stress; (b) Effect of shear rate on shear stress (in log–log).

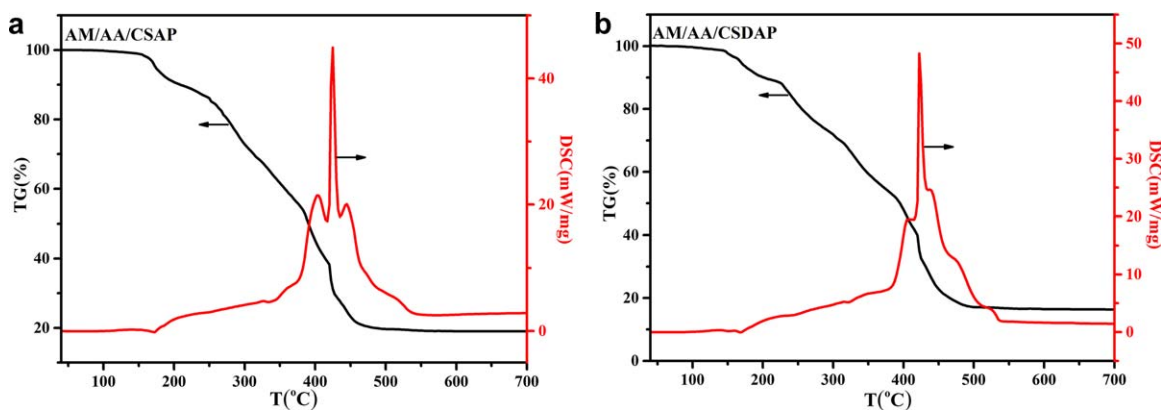


Figure 8. TG and DSC of (a) AM/AA/CSAP; (b) AM/AA/CSDAP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ESEM

The ESEM images of HPAM, AM/AA/CSAP and AM/AA/CSDAP solutions are shown in Figure 4. The junctions of the network structures formed by AM/AA/CSAP and AM/AA/CSDAP solutions are clearly visible in Figure 4(c–f), while structures of HPAM are incompact and irregular. It can be observed that the microscopic nets of AM/AA/CSAP and AM/AA/CSDAP show observably smaller pores and thinner filaments compared to HPAM by observing at 1000 and 5000 \times magnification attributed to the interaction among copolymer chains resulting from hydrogen bonds of sulfonamide structure and amide group and hydrophobic interaction of hydrophobic structure.

Effect of Concentration on Viscosity

The effect of concentration on viscosity of AM/AA/CSAP and AM/AA/CSDAP was investigated during the concentration from 500 to 3000 mg L⁻¹. A 5 and 9 million HPAM were performed to compared with two kinds of copolymers. The data are shown in Figure 5(a). The apparent viscosity of AM/AA/CSAP reaches at 1118.0 mPa s⁻¹ under concentration of 3000 mg L⁻¹ showing excellent thickening ability, by contrast, under the same concentration the apparent viscosity 9 million HPAM is 877.5 mPa s⁻¹. Though only 794.5 mPa s⁻¹ at 3000 mg L⁻¹ could have been obtained by AM/AA/CSDAP solutions, in comparison with similar molecular weight 5 million HPAM, the fine viscoelasticity could be observed due to the interaction among polymer molecular chains.³⁴

Overlap Concentration

The viscosity versus concentration from 100 to 1000 mg L⁻¹ is shown in Figure 5(b). A strong hydrophobic interaction occurring in the AM/AA/CSAP and AM/AA/CSDAP concentration is above 300 and 400 mg L⁻¹, respectively. The results depict the interaction among polymer chain of AM/AA/CSAP and AM/AA/CSDAP are stronger than 5 million HPAM, and the association concentration of AM/AA/CSAP is lower than that of AM/AA/CSDAP. Also the association concentration of AM/AA/CSDAP and 9 million HPAM are approximately the same.

Effect of Temperature and Shear Rate on Viscosity

The effect of temperature on the apparent viscosity of the 2000 mg L⁻¹ copolymer solutions at a shear rate of 170 s⁻¹ is shown in Figure 5(c,d). The viscosity of two copolymers decreased gradually with temperature raising from 30 to 130°C. The viscosity retention rate (using 30°C at same shear rate as a reference) of AM/AA/CSAP was up to 69.5% (100°C) and 43.4% (120°C), respectively, while the viscosity retention rate of AM/AA/CSDAP was up to 56.9% (100°C) and 46.4% (120°C), respectively. Compared with HPAM (retention rate 3.7%, 120°C),¹⁹ two copolymers showed excellent temperature resistance due to the rigid structure of copolymer chains. It is interesting that at 120°C AM/AA/CSDAP exhibit a little higher viscosity retention rate than AM/AA/CSAP which might be attribute to the cyclization of annular conjugated diene in main chain. In addition, when the temperature began to decrease from 130 to 30°C, the apparent viscosity retention rate of the

Table VI. Results of Sandpack Flooding Test of Polymer Flooding

Entry	Polymer	Porosity/%	K/mD	Oil saturation/%	E_1	E_2	EOR
1	HPAM	32.85	451.07	70.31	43.09	53.43	10.34
2	AM/AA/CSAP	32.11	449.23	70.56	42.82	57.35	14.53
3	AM/AA/CSDAP	33.42	450.61	71.56	43.27	56.53	13.26
4	AM/AA/CSAP	34.93	1009.86	85.19	46.77	65.56	18.79
5	AM/AA/CSDAP	34.71	1018.76	85.96	46.89	62.15	15.26

copolymers increased to 84.6% for AM/AA/CSAP and 80.0% for AM/AA/CSDAP suggesting that the viscosity of copolymer solutions have better recovering ability for temperature.

Aging Test

The viscosity retention of the polymer solution at different times in weeks to months at a certain temperature is also important for polymer EOR. This test was demonstrated by ageing 2000 mg L⁻¹ HPAM (462.7 mPa s⁻¹), AM/AA/CSAP (721.1 mPa s⁻¹), and AM/AA/CSDAP (512.7 mPa s⁻¹) solutions filled with N₂ and kept tightly sealed at 90°C for 20 days. After 20 days, the apparent viscosity value of HPAM, AM/AA/CSAP, and AM/AA/CSDAP were 25.7, 144.6, and 77.8 mPa s⁻¹ after 20 days, and the retention rate were 5.6, 20.1, and 15.2%, respectively. The apparent viscosity of the polymers solution reduced continuously, but two novel copolymers exert higher retention rate compared with HPAM due to the rigid monomers in the polymer chains and the interaction among copolymer chains resulting from hydrogen bonds and hydrophobic interaction suggesting they could be well applied in polymer EOR.

Effect of Shear Rate on Viscosity

The anti-shearing of copolymers is shown in Figure 6(a). It was found that the apparent viscosity had a very obvious drop at high shear rate (about 170 s⁻¹). The shear thinning behavior is desirable for polymer injection. To further research the recovering ability for shear rate, copolymers solution were maintained shearing at 170 s⁻¹ for 5 min, next keeping shearing at 500 s⁻¹ for 5 min, then went on shearing at 170 s⁻¹ for 5 min. The results are shown in Figure 6(b). When shear rate sudden changed from 170 to 500 s⁻¹, the viscosity of two copolymers dropped sharply, whereas there is a better recovering ability to both of copolymers at high shear rate when shear rate decreased from 500 to 170 s⁻¹.

Effect of Shear Rate on Shear Stress

Most polymer solution are pseudoplastic fluid, which show decreasing flow resistance when shear rate increase. The effect of shear rate on shear stress could refer to non-Newtonian liquid, the formula as following:

$$\tau = k\gamma^n \quad (2)$$

where τ is shear stress, Pa; γ is shear rate, s⁻¹, k is consistency coefficient, Pa s⁻ⁿ; and n is power law exponent.

The 2000 mg L⁻¹ copolymer solutions were tested by shear stress scanning, and the flow curves of two copolymers were shown in Figure 7(a). Through logarithm on both sides of the eq. (2), consistency coefficient and power law exponent were obtained by linear fitting [Figure 7(b)]. The consistency coefficient and power law exponent were 1.37 Pa s^{-0.35} and 0.35 for AM/AA/CSAP and 1.17 Pa s^{-0.31} and 0.31 for AM/AA/CSDAP suggesting that the functional monomer linked to polymer chain have a significant effect on the viscoelasticity of copolymer solution due to the interaction among polymer chains which have been contribution to the structural viscosity.

TG and DSC of Copolymers

TG and DSC were used to study the thermal stability of polymers, thus providing a means of polymer candidates. The curves were shown in Figure 8(a,b). Around 171.1 and 167.4°C the weak endothermic peaks were observed in the DSC curve of

AM/AA/CSAP and AM/AA/CSDAP, respectively due to the decomposition temperature of the moisture of intramolecular and intermolecular combined with oxygen, sulfur atom of copolymers through stronger hydrogen bonds. According to TG curves a little preferable thermal stability could have been observed in AM/AA/CSAP compared with AM/AA/CSDAP due to the more amount of CSAP.

Sandpack Flooding Test

The oil recovery was carried out by the following: the water flooding was conducted with brine solution at 0.3 mL min⁻¹ until the water cut exceeded 95%. Subsequently about 0.5 PV polymers brine solution were injected at 0.3 mL min⁻¹. Afterward the extrapolated water flooding was conducted with brine at 0.3 mL min⁻¹ to the water cut of 95%. All core flood processes were run at 70°C. The parameters of cores and the results of core flooding tests were shown in Table VI.

The oil recovery of 2000 mg L⁻¹ HPAM with brine solution could reach 10.34% enhance oil recovery at permeability about 450 mD. The EOR of 2000 mg L⁻¹ AM/AA/CSAP with brine could reach a value of 18.79 and 14.53% at 70°C, when the permeability of core are 450 and 1000 mD, respectively, and in the same conditions the EOR of 2000 mg L⁻¹ AM/AA/CSDAP could respectively reach to 15.26 and 13.26%. The results suggest that the EOR of the copolymers are improved remarkably even under harsh condition compared with HPAM, especially AM/AA/CSAP, which might be due to relatively higher viscosity of the copolymers than HPAM to decrease the water/oil mobility ratio.

CONCLUSIONS

The anion allyl and diallyl camphor sulfonamides-based polyacrylamide copolymers AM/AA/CSAP and AM/AA/CSDAP and the rheological property have been experimentally studied. AM/AA/CSAP could increase the production of oilfields in exploitation about 14.53% during an EOR process under harsh conditions due to the advantages of its appropriate viscosity at high temperature being complemented by aging test for 20 days. Increasing the mass ratio of CSDAP, the viscosity and water-solubility of AM/AA/CSDAP was increasingly not well leading to the poor performance in comparison with AM/AA/CSAP. The results show cyclic copolymerization of non-conjugated monomer could lead to mutual competition of three free radicals during copolymerization, and the cyclic annular structure in main polymer chains could improve the performance of copolymers which in turn lead to poor water-solubility.

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