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ARTICLE

Anti-biodegradable hydrophobic sulfonate-based acrylamide copolymer containing 2,4-dichlorophenoxy for enhanced oil recovery

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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We report here a novel anti-biodegradable hydrophobic acrylamide copolymer that was prepared from acrylamide, acrylic acid, sodium 3-(allyloxy)-2-hydroxypropane-1-sulfonate and *N*-allyl-2-(2,4-dichlorophenoxy) acetamide using 2,2'-azobis(2-methylpropionamide) dihydrochloride initiation system. Subsequently, the copolymer was characterized by FT-IR, ¹H NMR, TG-DTG and water-solubility. And the biodegradability test indicated that the copolymer was not deemed to be readily biodegradable *via* closed bottle test established by the Organization for Economic Co-operation and Development (OECD 301 D). Meanwhile the copolymer could significantly enhance the aqueous solution viscosity in comparison with partially hydrolyzed polyacrylamide. The viscosity retention of 51.9% indicated the result of dramatic improvement of temperature tolerance. And then the excellent salt resistance, shear resistance, viscoelasticity, long-term stability of the copolymer could be obtained, which provides a good theoretical foundation for the application in enhanced oil recovery. In addition, this copolymer exerted stronger mobility control ability with resistance factor of 22.1 and residual resistance factor of 5.0, and superior ability for enhanced oil recovery of 12.9%. Hence, the copolymer has potential application for enhanced oil recovery in high-temperature and high-salinity reservoirs.

Introduction

As an important global energy, petroleum holds a significant position in the development of national economy.¹ Many countries around the world, such as America, Russia, and Arab countries, are rich in oil. However, many oil fields in China have entered the development phase of high water cut. Thereby, a set of perfect enhanced oil recovery (EOR) technologies have been formed due to the enormous petroleum consumption.^{2, 3} Among these, the application of polymer flooding has achieved approving results.⁴⁻⁷ For polymer flooding, the viscosity and long-term stability of displacing fluid are not only two of the important indexes but also two key factors of polymer flooding effectiveness, because polymer flooding technology is mainly to enhance oil recovery by increasing the swept volume and oil displacement efficiency of displacing fluid.⁸⁻¹¹ However, the commonly used EOR chemicals, partially

hydrolyzed polyacrylamide (HPAM) and xanthan gum, are difficult to completely meet the factor under high-temperature and high-salinity conditions due to the hydrolysis, biodegradation, poor ability of increasing viscosity, and others.^{12, 13} Therefore, the development of some new HPAM substitutes has played an important role in the research of the polymer flooding.^{4, 14}

Considerable researches have focused on the ways to improve the resistance of the polymers to the harsh conditions, such as increasing the rigidity of the polymer, and strengthening intermolecular forces.¹⁵⁻¹⁹ McCormick and Bock *et al.* synthesized hydrophobically associating polyacrylamides and examined the effect of temperature and salt on the viscosity of the polymers.^{20, 21} Additionally, the polymers containing hydrophobic and rigid ring groups exhibit obvious thickening ability, and temperature-thickening property.^{22, 23} Therefore, a number of hydrophobically associating polymers are studied as a candidate in enhanced oil recovery. However, the poor dissolubility has become the limit for their wide application in oil exploration. As we know, strong hydrate groups, such as sulfonic and hydroxyl groups, can significantly improve the water-solubility of the polymers.^{24, 25} In this paper, sodium 3-(allyloxy)-2-hydroxypropane-1-sulfonate (APS) as functional monomer was introduced into the polymer chain to enhance water solubility.

In addition, because a great of bacteria survive in the formation water, commonly used acrylamide copolymers and xanthan gum are vulnerable to be degraded by natural microorganisms. The excellent result for EOR is hard to be obtained when using ordinary polymers. Bao *et al.* found that the HPAM removal efficiency of

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† Electronic Supplementary Information (ESI) available: Optimum of copolymerization conditions; Intrinsic viscosity of copolymer. See DOI: 10.1039/x0xx00000x

36.3% was obtained within the 7-d period when HPAM served as the sole nitrogen source.²⁶ It was reported that chlorobenzene derivatives were relatively difficult to be degraded by general microorganisms and they can be degraded by only a handful of microorganisms, such as *Pseudomonas* sp. and *Flavobacterium*. Wang *et al.* reported that an average degradation of 5.5% of 1,3-dichlorobenzene by adapted bacterium PF-11 was monitored every day.²⁷⁻³⁰ And the introduction of chlorobenzene groups into copolymer could improve its thermal stability and enhance the rigidity of the copolymer.³¹⁻³⁴ In this work, *N*-allyl-2-(2,4-dichlorophenoxy) acetamide (DCAP) as a functionalized hydrophobic monomer was copolymerized with sodium 3-(allyloxy)-2-hydroxypropane-1-sulfonate (APS), acrylamide (AM) and acrylic acid (AA). This water-soluble hydrophobic copolymer was investigated systematically on several aspects such as water solubility, biodegradability, thickening property, salt resistance, rheological property, and EOR ability, which provides a theoretical basis for its potential application as a new EOR chemical.

Experimental

Materials

The chemicals, acrylamide (AM), acrylic acid (AA), 2,2'-azobis(2-methylpropionamide) dihydrochloride (V-50), alkylphenol ethoxylates (OP-10), 2-(2,4-dichlorophenoxy) acetic acid, triethylamine, thionyl chloride, CH₂Cl₂, NaOH, NaCl, MgCl₂·6H₂O, CaCl₂, NaSO₃, were analytical pure and purchased from Chengdu Kelong Chemical Reagent Factory Co. (Sichuan, China). Allylamine was purchased from Nanjing Forward Chemical Reagent Factory Co. (Nanjing, China). 1-allyloxy-2,3-epoxy propane was supplied by Qufu Huarong New Chemical Materials Co., Ltd. (Shandong, China). HPAM ($M_n=6.5 \times 10^6$) was obtained from Daqing Refining and Chemical Company. Other chemicals were commercially available and used directly without further purification.

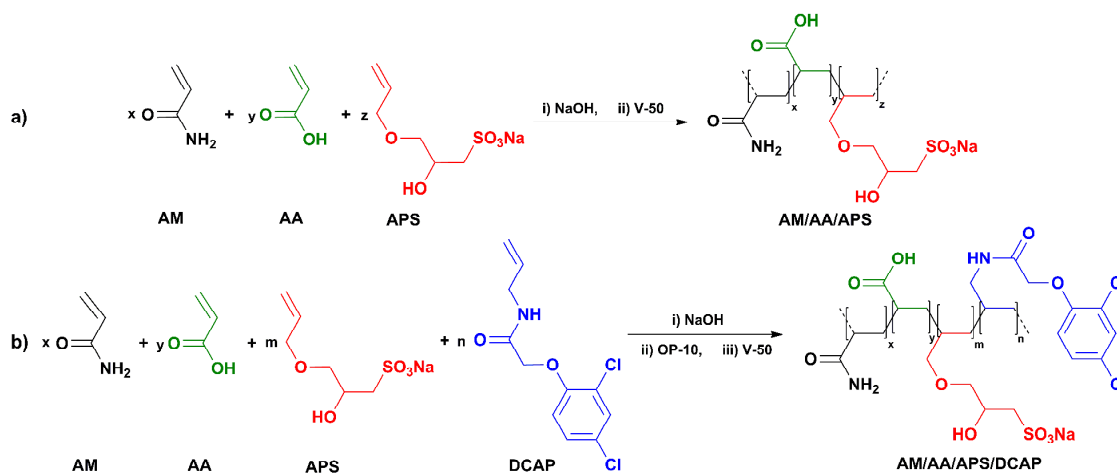
Synthesis of APS and DCAP

Sodium 3-(allyloxy)-2-hydroxypropane-1-sulfonate (APS) was synthesized according to the method reported by literature, and

the synthesis route was shown in Scheme S1a (see ESI[†]).³⁵ *N*-allyl-2-(2,4-dichlorophenoxy) acetamide (DCAP) was obtained using 2-(2,4-dichlorophenoxy) acetic acid, thionyl chloride and allylamine as raw materials, as shown in Scheme S1b (see ESI[†]). 2-(2,4-dichlorophenoxy) acetic acid (2a) (0.10 mol) was completely dissolved with 30 mL CH₂Cl₂ in a 250 mL round bottom flask, and then thionyl chloride (0.12 mol) was slowly added within 30 min. The reaction carried out under reflux at 55 °C for 4 h. Then the mixture was cooled to room temperature. The solvent and excessive thionyl chloride was removed by rotary evaporating. 2-(2,4-dichlorophenoxy) acetyl chloride (2b) was obtained. All of 1c was dissolved in 50 mL round bottom flask with 15 mL CH₂Cl₂. In an ice bath, allylamine (0.11 mol) and triethylamine (0.15 mol) dissolved in 10 mL CH₂Cl₂ was slowly added with intensely stirring for 5 h. Then the mixture were successively washed by deionized water, dilute hydrochloric acid, and saturated salt solution, dried using anhydrous sodium sulfate, evaporated. Then light yellow solid *N*-allyl-2-(2,4-dichlorophenoxy)acetamide (DCAP, 83.4% yield) was obtained. The ¹H NMR and ¹³C NMR spectra of DCAP were displayed in Fig. S1 (see ESI[†]). DCAP: ¹H NMR (400 MHz, CDCl₃, δ, ppm): 4.0 (s, 2H, -CH₂-NH-), 4.5 (s, 2H, -C(O)-CH₂-O-), 5.2-5.3 (dd, $J_1 = 17.3$ Hz, $J_2 = 10.4$ Hz, 2H, CH₂-HC=CH₂), 5.9 (m, 1H, H₂C=CH-CH₂-), 6.9 (t, $J_1 = 4.9$ Hz, $J_2 = 2.8$ Hz, 2H, Ar-5'-H, Ar-6'-H), 7.2 (dd, $J_1 = 2.8$ Hz, $J_2 = 4.0$ Hz, 1H, Ar-3'-H), 7.4 (s, 1H, N-H); ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 41.3, 68.4, 114.7, 116.6, 123.8, 127.5, 128.0, 130.2, 133.5, 151.6, 166.9.

Synthesis of AM/AA/APS and AM/AA/APS/DCAP

AM/AA/APS and AM/AA/APS/DCAP were prepared by AM, AA, APS and DCAP using V-50 initiator system (for details, see ESI[†]), as shown in Scheme 1. Briefly, all the monomers with appropriate composition were dissolved in deionized water. Additionally, for AM/AA/APS/DCAP, OP-10 was added as solubilizing agent. The pH of the reaction system was adjusted by NaOH solution. The initiator V-50 was added into reaction system under nitrogen atmosphere at indicated temperature. After reacted for 8 h, the copolymer gels were washed with ethanol, and then dried at 40 °C in a vacuum for 24 h to obtain the corresponding copolymers, AM/AA/APS and AM/AA/APS/DCAP.



Scheme 1 (a) The synthesis route of AM/AA/APS, (b) the synthesis route of AM/AA/APS/DCAP.

Characterization

Gel permeation chromatography (GPC). The molecular weights of AM/AA/APS and AM/AA/APS/DCAP with the concentration of 100 mg·L⁻¹ were measured using a Waters E2695 Gel Permeation Chromatography (Waters, America) at 30 °C using NaNO₃ aqueous solution (1.0 M) as eluent. The flow rate was 1.0 mL·min⁻¹.

Elemental analysis. The elemental analysis of AM/AA/APS and AM/AA/APS/DCAP was carried out by Vario EL-III elemental analyzer (Elementar, Germany).

Fourier transform infrared (FT-IR) spectroscopy. The FT-IR spectra of AM/AA/APS and AM/AA/APS/DCAP were obtained using a WQF-520A Fourier Transform Infrared spectrophotometer (Beijing Beifen-Ruilu Analytical Instrument Co., Ltd., China) with KBr pellets by averaging 32 scans at room temperature.

¹H nuclear magnetic resonance (¹H NMR) spectroscopy. The ¹H NMR spectra of AM/AA/APS and AM/AA/APS/DCAP were recorded on a Bruker AVANCE III 400 MHz NMR spectrometer (Bruker, Switzerland) in D₂O.

Intrinsic viscosity measurement. The flux time of different concentrations copolymers solution with 1 mol·L⁻¹ NaCl were measured with Ubbelohde viscometer at 30 °C. The specific viscosity (η_{sp}) and intrinsic viscosity [η] was calculated using the following eqn (1), and (2).³⁶

$$\eta_{sp} = \frac{t - t_0}{t_0} \quad (1)$$

$$[\eta] = \lim_{C \rightarrow 0} \eta_{sp} / C \quad (2)$$

in which η_{sp} is the specific viscosity of copolymer; t_0 is flux time of 1 mol·L⁻¹ NaCl solution, s ; and t is flux time of copolymer brine solution, s .

As shown in Fig. S4 (see ESI[†]), the results revealed that the [η] of AM/AA/APS and AM/AA/APS/DCAP were 1326 mL·g⁻¹ and 1317 mL·g⁻¹, respectively.

Thermogravimetry and derivative thermogravimetry (TG-DTG). In a nitrogen atmosphere (flow rate: 50 mL/min), 7.0305 mg AM/AA/APS and 7.1900 mg AM/AA/APS/DCAP were tested by TGA/SDTA851e Thermogravimetric and Differential Thermal Analyzer (METTLER TOLEDO Co., Switzerland) from 25 to 800 °C at 10 °C·min⁻¹, and then the TG and DTG curves were obtained to analyze the thermal stability of the copolymers.

Water solubility

Copolymer particles (40 - 45 meshes, 2000 mg) were dissolved in 1000 mL deionized water, recording solution conductivity. The solution conductivity was measured by using a DDS-11A conductivity meter (Shanghai Rex Xinjing Instrument Co., Ltd.,

China). Dissolution time is defined as the time from adding the copolymer to solution conductivity stabilizing.³⁷

Biodegradability test

Biodegradability of AM/AA/APS, AM/AA/APS/DCAP, HPAM and xanthan gum was obtained from biochemical oxygen demand (BOD) and chemical oxygen demand (COD) using the closed bottle test (OECD 301 D).³⁸⁻⁴⁰ Briefly, the mixture of the copolymer (3.0 mg·L⁻¹), as the sole carbon source, and the secondary effluent was respectively added into the same BOD bottles. All the bottles were maintained in full and then incubated in dark at 20 °C for 28 days. The dissolved oxygen of each BOD bottles was measured by a DO-200 dissolved oxygen analyzer (Nanjing Zhuoma electromechanical Co. Ltd., China), and then the remaining BOD bottles continued to be cultured at the same condition. The COD was determined by the potassium dichromate reflux method. The degradation rate (D_t) is obtained at frequent intervals over a 28-d period by the following eqn (3).

$$D_t(\%) = \frac{BOD(O_2 \text{ mg} / \text{test substance mg})}{COD(O_2 \text{ mg} / \text{test substance mg})} \times 100 \quad (3)$$

Tackifying and salt tolerance

Tackifying of copolymers was investigated by measuring the apparent viscosity of different concentration of the copolymer solutions. Salt tolerance of 2000 mg·L⁻¹ copolymer solutions was investigated under different concentration of small molecule electrolyte, such as NaCl, MgCl₂, and CaCl₂. The apparent viscosities of the copolymer solutions were determined using a Brookfield DV-III Programmable Rheometer (Brookfield Co., America) with a 00[#] (6 rpm) or 62[#] (18.8 rpm) rotor.

Rheological measurement

Temperature resistance of the copolymers solution with 2000 mg·L⁻¹ was measured using a HAAKE MARS III rheometer (HAAKE, Germany) from 20 to 120 °C at 7.34 s⁻¹.

Shear thinning behavior of the copolymers solution with 2000 mg·L⁻¹ was investigated on a HAAKE MARS III rheometer (HAAKE, Germany) from 7.34 to 1000 s⁻¹ at 25 °C.

Shear resistance of the copolymers solution with 2000 mg·L⁻¹ was studied on a HAAKE MARS III rheometer (HAAKE, Germany) at 25 °C. The copolymer solution was measured at 7.34 s⁻¹, 1000 s⁻¹, and 7.34 s⁻¹ for 30 min, respectively.

Viscoelasticity of the copolymers solution with 2000 mg·L⁻¹ was obtained by measuring the elastic modulus and viscous modulus of the copolymers solution in the frequency scanning range, 0.01 - 10 Hz.

Long-term stability

Long-term stability of the 2000 mg copolymers dissolved in 1.0 L

Table 1 Composition and content of the total dissolved solid in the simulated formation water

Inorganic ions	Na ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻	TDS
Content (mg·L ⁻¹)	6588	348	435	10883	1004	126	205	19589

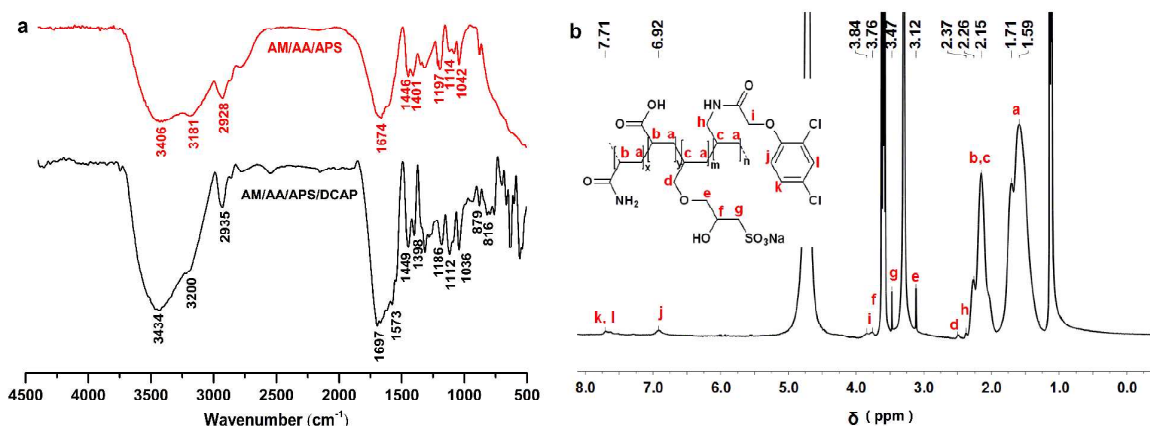


Fig. 1 (a) IR spectra of AM/AA/APS and AM/AA/APS/DCAP, (b) ^1H NMR spectra of AM/AA/APS and AM/AA/APS/DCAP.

simulated formation water was investigated by measuring the apparent viscosity of the solution at different times at 80 °C for 60 days a Brookfield DV-III Programmable Rheometer (Brookfield Co., America) with a 00# (6 rpm) or 62# (18.8 rpm) rotor. And the content and composition of the total dissolved solid (TDS) in simulated formation water were listed in Table 1.

Mobility control analysis

Mobility control ability of the copolymer solutions with 2000 $\text{mg}\cdot\text{L}^{-1}$ was characterized by the resistance factor (RF) and the residual resistance factor (RRF).^{41,42} The core barrel with length of 250 mm and internal diameter of 25 mm was packed with quartz sand which was washed by hydrochloric acid and distilled water for several times. The copolymers were dissolved in simulated formation water (Table 1). Core flow experiments were carried out at 80 °C in an incubator. The injection pressure was recorded by a pressure sensor. The infection rate of water saturation, copolymer solution and water flooding was 2.0 $\text{mL}\cdot\text{min}^{-1}$ with the ISCO 260D syringe pump. The RF and RRF were calculated by the following eqn (4) and (5).

$$RF = \frac{P_p / Q_p}{P_{ws} / Q_{ws}} \quad (4)$$

$$RRF = \frac{P_{wf} / Q_{wf}}{P_{ws} / Q_{ws}} \quad (5)$$

in which P_p is stable pressure when injecting copolymer solution, MPa; Q_p is injecting rate when injecting copolymer solution, $\text{mL}\cdot\text{min}^{-1}$; P_{ws} is stable pressure when saturating water, MPa; and Q_{ws} is injecting rate when saturating water, $\text{mL}\cdot\text{min}^{-1}$; P_{wf} is stable

pressure when water flooding, MPa; and Q_{wf} is injecting rate when water flooding, $\text{mL}\cdot\text{min}^{-1}$.

Enhanced oil recovery analysis

EOR ability of the copolymer solutions with 2000 $\text{mg}\cdot\text{L}^{-1}$ was investigated via core flooding experiments at 80 °C. The core was saturated and aged with crude oil for 2 days. The core was flooded with simulated formation water at 0.2 $\text{mL}\cdot\text{min}^{-1}$ until the water cut was up to 95%, the copolymer solution of 0.3 times pore volume (PV) at, and simulated formation water at 0.2 $\text{mL}\cdot\text{min}^{-1}$ until the water cut was up to 95%, respectively. EOR value was obtained by the following eqn (6).

$$EOR = H_t - H_w \quad (6)$$

in which EOR is enhanced oil recovery, %; H_t is the oil recovery of the whole displacement process, %; and H_w is the oil recovery of water flooding, %.

Results and discussion

Synthesis of AM/AA/APS and AM/AA/APS/DCAP copolymers

The copolymers AM/AA/APS and AM/AA/APS/DCAP were synthesized through copolymerization of AM, AA, APS and DCAP. The compositions for copolymers AM/AA/APS were obtained by elemental analysis. And the composition of AM/AA/APS/DCAP was determined by ^1H NMR and elemental analysis (see ESI[†]). The molecular weights of AM/AA/APS and AM/AA/APS/DCAP were measured by GPC. The results are listed in Table 2.

Table 2 Compositions and molecular weights of AM/AA/APS and AM/AA/APS/DCAP copolymers

Copolymer	Molar ratio of reactants (%)				Elements mass ratio (%)			Molar composition of copolymer (%)				$M_w(\times 10^5)$	M_w/M_n
	AM	AA	APS	DCAP	C	N	S	AM	AA	APS	DCAP		
AM/AA/APS/DCAP	82.55	15.46	1.70	0.29	47.26	14.59	0.65	80.93	17.25	1.57	0.25	6.51	2.12
AM/AA/APS	82.79	15.50	1.71	-	47.21	15.00	0.69	83.06	15.26	1.68	-	6.69	2.03

Fig. 1a shows the FT-IR spectra of AM/AA/APS and AM/AA/APS/DCAP copolymers. For AM/AA/APS, the peaks at 3406 cm^{-1} and 3181 cm^{-1} were the stretching vibration peaks of N-H. The stretching vibration peak of C-H was at 2928 cm^{-1} . The peak at 1674 cm^{-1} was assigned to the characteristic peak of C=O. The peaks at 1197 cm^{-1} and 1042 cm^{-1} were the characteristic absorption peaks of $-\text{SO}_3\text{Na}$. The stretching vibration of C-O-C was the peak at 1114 cm^{-1} . The result indicated that AM, AA, and APS were copolymerized to the chain of the copolymer. For the FT-IR spectra of AM/AA/APS/DCAP, the characteristic absorption peaks of N-H, C-H, C=O, C-O-C, and $-\text{SO}_3\text{Na}$ groups existed in the corresponding location that were similar to the FT-IR spectra of AM/AA/APS. Additionally, two weak absorption peaks at 879 cm^{-1} and 816 cm^{-1} could be observed, which was attributed to the characteristic peaks of 1,2,4-trisubstituted benzene groups. It has been found the successful copolymerization of AM, AA, APS, and DCAP.

The ^1H NMR spectrum of AM/AA/APS/DCAP was shown in Fig. 1b. It was obvious that the protons of the aliphatic $-\text{CH}_2-$ group of main copolymer chain appeared at 1.59-1.71 ppm. The chemical shift value at 2.15-2.26 ppm was related to the protons of $-\text{CH}-$ in the main copolymer chain. The signal of protons at 2.37 ppm showed the existence of $-\text{CH}_2-\text{NH}-\text{CO}-$ groups. The signal of protons at 2.50 ppm was due to $-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}(\text{OH})-$ groups. The characteristic peak at 3.12 ppm was assigned to the protons of $[-\text{O}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-]$ groups. The signal of protons was observed at 3.47 ppm due

And the signal of protons at 6.92 ppm and 7.71 ppm exhibited the presence of the protons in the benzene ring.

Water solubility

The introduction of hydrophobic monomer can significantly affect water solubility of the copolymer. Therefore, the dissolution time of AM/AA/APS, AM/AA/APS/DCAP and HPAM was determined to investigate the water solubility of the copolymers, as shown in Fig. 2a. It was found that the dissolubility curves of three copolymers displayed similar trend. The results indicated that the complete dissolution of AM/AA/APS/DCAP just needed an extra 15 min compared with HPAM (84 min). The dissolubility of hydrophobic copolymer was significantly improved by introducing strong hydrate groups, sulfonic and hydroxyl groups, which could be found from the result of the dissolubility of AM/AA/APS with short dissolution time of 73 min. The hydrophobic copolymer AM/AA/APS/DCAP had excellent water solubility as expected.

Biodegradability

Biodegradability of AM/AA/APS/DCAP, AM/AA/APS, HPAM and xanthan gum was analysed *via* degradation rate (D_t), as displayed in Fig. 2b. From the comparative degradation study, it has been observed that xanthan gum, AM/AA/APS and HPAM showed exhibited rapid degradatin within the 16-d period, and then reached a plateau. It was obvious that xanthan gum, AM/AA/APS and HPAM exhibited accelerated rate of degradation than AM/AA/APS/DCAP. Refer to the standard 301 established by the Organization for Economic Co-operation and Development (OECD), the degradation which reaches the pass level of 60% is considered to be as "ready biodegradability". As shown in Fig. 2b, the degradation of xanthan gum, AM/AA/APS and HPAM had been reached 60% within the 28-d period of the test. The degradation rate of AM/AA/APS/DCAP was far less than 60%, which indicated that the degradation could be minimized by incorporation of 2,4-dichlorophenoxy and AM/AA/APS/DCAP was less susceptible to biodegradability.

Effect of concentration on the apparent viscosity

Tackifying, as one of the most important copolymer properties, was investigated by measuring the apparent viscosity of AM/AA/APS, AM/AA/APS/DCAP, and HPAM solution under the concentration, $100 - 3000\text{ mg}\cdot\text{L}^{-1}$. It was clear from Fig. 3 that the apparent viscosity of AM/AA/APS and HPAM solution displayed a linear growth with the increase of the copolymer concentration. Unlike AM/AA/APS and HPAM, a slow increase in apparent viscosity under the concentration from 100 to $800\text{ mg}\cdot\text{L}^{-1}$ was observed for AM/AA/APS/DCAP, which might be explained by the coil of the polymer chain as the result of intramolecular association of 2,4-dichlorophenoxy groups under low copolymer concentration. However, AM/AA/APS/DCAP displayed a rapid growth in apparent viscosity above $800\text{ mg}\cdot\text{L}^{-1}$ copolymer solution. With the increase of the solution concentration, the formed three-dimensional network due to hydrophobic association among the polymer chain can contribute to the rapid increase in apparent viscosity.⁴³ Therefore, from 800 to $900\text{ mg}\cdot\text{L}^{-1}$, AM/AA/APS/DCAP exhibited a sharp

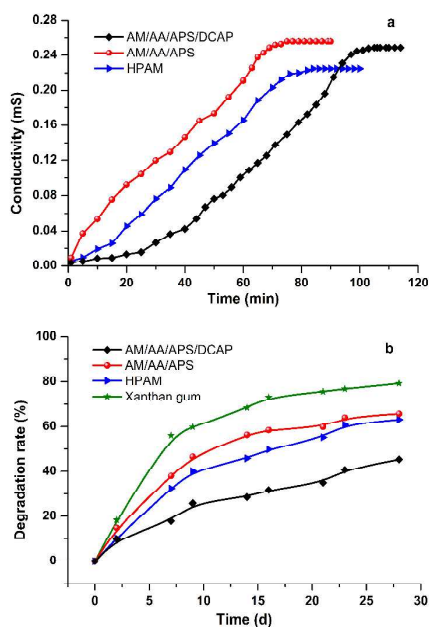


Fig. 2 (a) Dissolution time curves of HPAM, AM/AA/APS and AM/AA/APS/DCAP, (b) biodegradability of HPAM, AM/AA/APS, AM/AA/APS/DCAP and xanthan gum.

to the $-\text{CH}_2-$ of $[-\text{CH}(\text{OH})-\text{CH}_2-\text{SO}_3\text{Na}]$ groups. The signal of protons of $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-$ appeared at 3.76 ppm. The chemical shift at 3.84 ppm was assigned to the protons of $-\text{NH}-\text{CO}-\text{CH}_2-\text{O}-$ groups.

increase in apparent viscosity of copolymer solution. As shown in Fig. 3, AM/AA/APS/DCAP exhibited higher apparent viscosity of 410.5 mPa·s than that of AM/AA/APS (386.7 mPa·s) and HPAM (349.4 mPa·s) under the concentration of 2000 mg·L⁻¹, which revealed that AM/AA/APS/DCAP possessed better thickening ability.

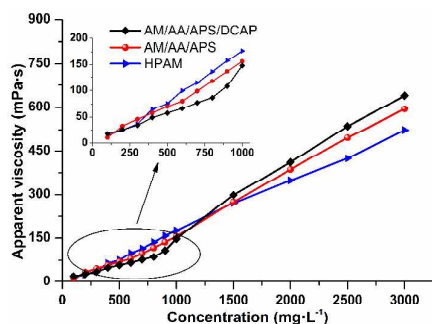


Fig. 3 Tackfying of HPAM, AM/AA/APS and AM/AA/APS/DCAP.

Effect of salt on the apparent viscosity

Salt tolerance, as another important performance, was investigated because of the existence of various inorganic ions in the formation water. The apparent viscosity as a function of NaCl, CaCl₂, and MgCl₂ was usually studied to obtain salt tolerance of the copolymer.⁴⁴ The results are shown in Fig. 4. For three copolymers, a first decrease, and then a stationary trend in apparent viscosity were observed when adding NaCl, CaCl₂, and MgCl₂ into the copolymer solution. In deionized water, an extended state of polymer chain contributes to the high apparent viscosity due to the electrostatic repulsion of -COO⁻. Adding small molecule electrolyte can lead to the coil of polymer chain because of the electrostatic shielding, which showed relatively low apparent viscosity. However,

in comparison with HPAM solution, the stable viscosity of AM/AA/APS was higher than HPAM because of the introduction of strong hydrate group, sulfonate group. In addition, AM/AA/APS/DCAP had higher value of apparent viscosity than AM/AA/APS and HPAM, which was ascribed to hydrophobic 2,4-dichlorophenoxy and sulfonate groups.⁴⁵ It has also found that the effect of divalent cation on apparent viscosity of the copolymer solution was greater than that of monovalent cation.

As shown in Fig. 4a, the viscosity rate of AM/AA/APS/DCAP, AM/AA/APS, and HPAM solution with 20000 mg·L⁻¹ NaCl was 17.6%, 11.8%, and 3.2%, respectively. And the copolymers with 2000 mg·L⁻¹ CaCl₂ exhibited slightly low viscosity retention rate (AM/AA/APS/DCAP: 16.7%, AM/AA/APS: 10.1%, and HPAM: 4.1%) as shown in Fig. 4b. A similar change tendency of the apparent viscosity of the copolymers with 2000 mg·L⁻¹ MgCl₂ was observed in Fig. 4c, which showed that the viscosity retention rate of AM/AA/APS/DCAP, AM/AA/APS, and HPAM were 15.2%, 9.3% and 3.1%, respectively.

Thermal stability

The thermal stability of the copolymers, AM/AA/APS and AM/AA/APS/DCAP, was investigated as shown in Fig. 5. It was found that the TG curve of AM/AA/APS displayed three stages in Fig. 5a. The copolymer lost 8.18% of its mass in the range of 25 - 176 °C, which was due to the loss of free water and bound water present in the copolymer sample. The second process occurred in the range of 176 - 431 °C, with a mass loss of 50.64%. Meanwhile, there were three peaks of the weight loss rate appearing at 205, 225 and 323 °C in the DTG curve. At this stage, the reduction of the copolymer's mass was mainly due to breaking up of the polar bonds (C-O, C-H and C-N bonds) and decomposition of sulfonate groups in the side chains. The third step took place beyond 431 °C with the mass loss of 33.53%, which was believed to be associated with the breakage of the C-C bonds in the AM/AA/APS chain.^{46, 47}

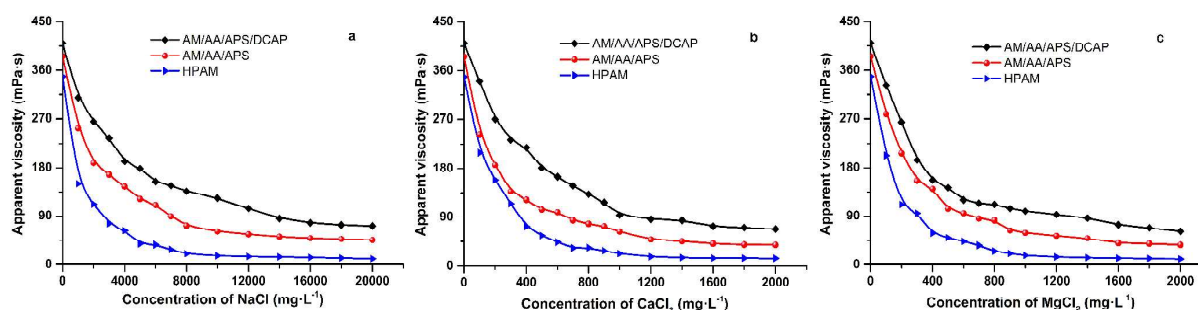


Fig. 4 NaCl, CaCl₂ and MgCl₂ tolerance of AM/AA/APS, AM/AA/APS/DCAP and HPAM solution.

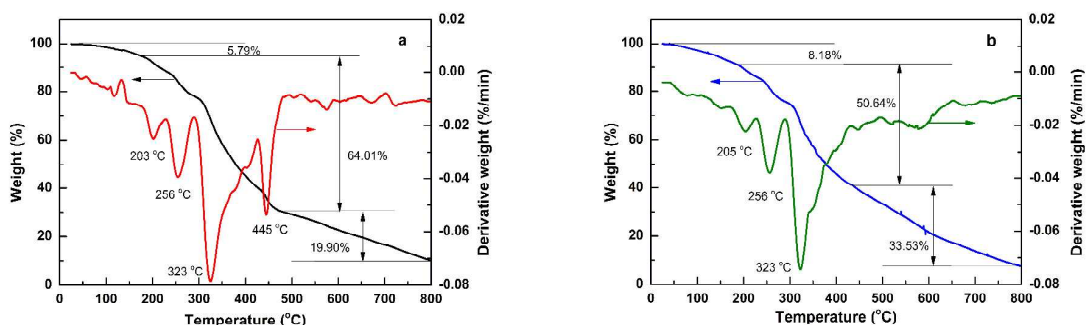


Fig. 5 TG-DTG curves of (a) AM/AA/APS/DCAP and (b) AM/AA/APS.

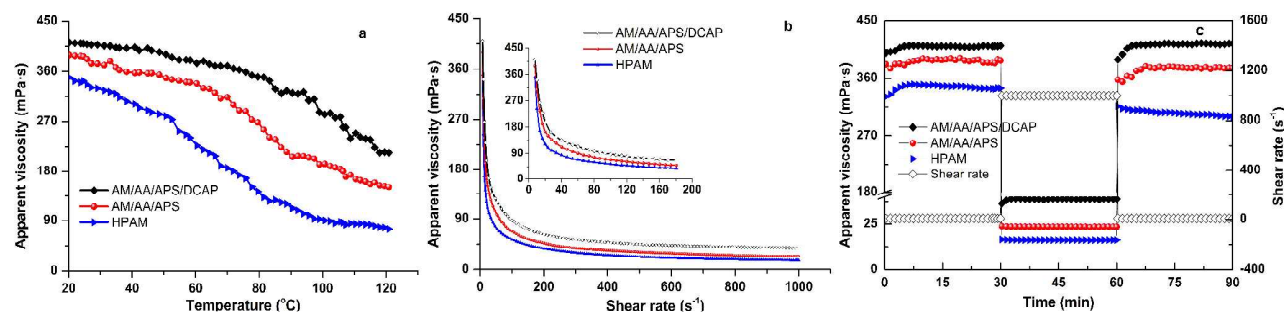


Fig. 6 (a) Temperature resistance of the copolymers, (b) shear thinning behavior of the copolymers, (c) shear recovery of the copolymers.

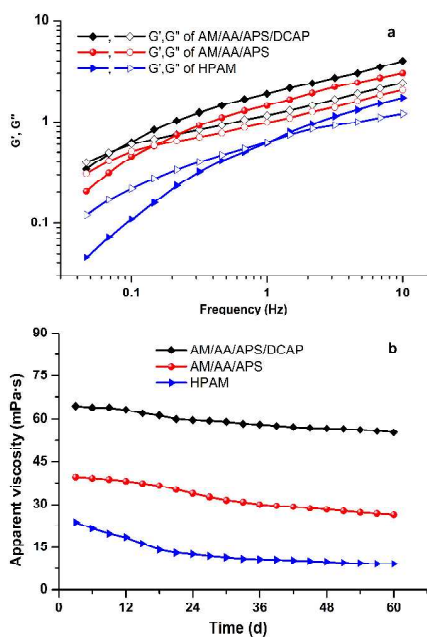


Fig. 7 (a) Viscoelastic behavior of the copolymers, (b) long-term stability of the copolymers.

As shown in Fig. 5b, the TG curve of AM/AA/APS/DCAP exhibited three similar stages with AM/AA/APS of a mass loss of 5.79% at 25 - 176 °C, a mass loss of 64.01% in the range of 176 - 482 °C and a mass loss of 19.90% beyond 482 °C. What's more, the position and

strength of the weight loss rate peaks in DTG curve of AM/AA/APS/DCAP at the second stage was essentially identical with AM/AA/APS. A additional peak at 445 °C was observed in the DTG curve of AM/AA/APS/DCAP, which might be the extraction of 2,4-dichlorophenoxy groups. The residual mass of AM/AA/APS/DCAP (10.30%) at 800 °C was more than that of AM/AA/APS (7.65%). The result indicated that the AM/AA/APS/DCAP copolymer had excellent thermal stability.

Effect of temperature on the apparent viscosity

The thermal stability of AM/AA/APS AM/AA/APS/DCAP, and HPAM solution were investigated by measuring the change of the apparent viscosity from 20 °C to 120 °C. The changed trend was displayed in Fig. 6a. A significant decline in apparent viscosity exhibited as the temperature increased, and the viscosity retention rate of 21.5% at 120 °C was relatively low by compared with 25 °C for HPAM solution. The apparent viscosity of AM/AA/APS/DCAP and AM/AA/APS showed a slight variety under low temperature and then a large reduction under high temperature. However, the apparent viscosity of AM/AA/APS/DCAP decreased significantly from 85 °C, and the initiatory temperature of decline apparent viscosity was distinctly higher than that of AM/AA/APS. The obtained high viscosity retention, 51.9%, indicated the extraordinary temperature resistance at 120 °C, which was ascribed to the strong hydration ability of sulfonate groups and the strong interaction among hydrophobic groups within the temperature range.^{48,49}

Effect of shear on the apparent viscosity

Shear thinning behavior. The effect of shear rate on the apparent viscosity of the copolymers was studied, as illustrated in Fig. 6b. It was found that AM/AA/APS/DCAP, AM/AA/APS and HPAM solutions revealed non-Newtonian shear-thinning behavior. As the shear rate increased from 7.34 to 100 s⁻¹, the viscosity of copolymer solutions dropped obviously, and then the viscosity maintained a small decreasing trend within the shear rate range. However, because of the introduction of rigid groups, 2,4-dichlorophenoxy, the higher viscosity retention value of AM/AA/APS/DCAP, 9.4%, could be obtained as the shear rate changed from 7.34 to 1000 s⁻¹ in comparison with AM/AA/APS (6.0%) and HPAM (4.7%).

Shear recovery behavior. The shear recovery behavior was investigated because a long time interaction of high shear is easy to destroy the molecular structure of the polymer when displacing fluid was injected into the formation. As exhibited in Fig. 6c, it was evident that the apparent viscosity of AM/AA/APS/DCAP returned to the initial value after 30 min shear at 1000 s⁻¹. For AM/AA/APS, a low viscosity loss, 3.0%, was observed under 1000 s⁻¹. However, the apparent viscosity of HPAM decreased obviously after 30 min shear at 1000 s⁻¹, and exhibited a loss of 12.9%. The results indicated that AM/AA/APS/DCAP possessed fantastic shear resistance due to the introduction of rigid groups.

Viscoelasticity

The viscoelasticity of AM/AA/APS/DCAP, AM/AA/APS, and HPAM solutions was researched by obtained viscous modulus (G'') and elastic modulus (G'), as shown in Fig. 7a. It could be seen from Fig. 7a that both G'' and G' increased gradually within the oscillation frequency range. Both G'' and G' of AM/AA/APS/DCAP and AM/AA/APS were significantly higher than that of HPAM. As shown in Fig. 7a, G' of HPAM surpassed its G'' at high frequency (>1.0 Hz), which indicated that HPAM exerted the elastic property. The elasticity of AM/AA/APS was greater than viscosity at low frequency of 0.2 Hz. While AM/AA/APS/DCAP showed distinct elastic behavior within the scan frequency range, which was mainly due to enhanced rigidity of the copolymer.⁵⁰ The excellent viscoelasticity, especially elasticity, might contribute to improving the swept area of displacing fluid to enhance oil recovery in a porous medium.⁵¹

Long-term stability

The long-term stability is significant important for displacing fluid that flows in formation for a long time. As shown in Fig. 7b, the apparent viscosity as a function of the time was investigated under the condition of seal. All the copolymers exhibited a slight reduction in apparent viscosity, and the loss in apparent viscosity of HPAM, 38.2%, was larger than that of AM/AA/APS/DCAP and AM/AA/APS. Little viscosity loss was observed for AM/AA/APS/DCAP after sealed 60 days at 80 °C. The results showed that AM/AA/APS/DCAP possessed remarkable long-term stability.

Mobility control ability

The flow characteristic behavior of AM/AA/APS/DCAP, AM/AA/APS, and HPAM solutions in porous media were studied *via* core flooding experiments. As seen in Fig. 8a, three evident stages for three copolymers were visible in the injection pressure curves. It was

clear that the injection pressure of water saturation was gradual stable until injecting 2.4 PV simulated formation water. Then the injection pressure rose to a large extent along with the increase of injection volume of the copolymer solutions. And a platform indicated obtained stable pressure was observed in every pressure curve within the injection volume range, about 5.0 to 8.0 PV. However, the stable pressure of injecting different polymers solution varied enormously on account of various polymers possessing hydrodynamic volume. It could be observed that AM/AA/APS/DCAP exhibited the greatest injection pressure, 0.2427 MPa, in comparison with AM/AA/APS and HPAM. The introduction of hydrophobic 2,4-dichlorophenoxy and sulfonate groups led to the increase of hydrodynamic volume, which made potentially detrimental flow of the copolymers in porous media. Thereby, the greater pressure and larger volume might be needed to promote the steady flow for the polymers with big hydrodynamic volume. In the process of sequent water, the polymer content in the core became less and less with the more formation water injecting into the core. It was recognized that the pressure declined sharply when injecting sequent water.

As listed in Table 3, all the injection pressure was recorded and the resistance factor (RF) and the residual resistance factor (RRF) were obtained by eqn (4) and (5). It was found the AM/AA/APS/DCAP solution could establish much higher RF of 22.1 and RRF of 5.0 than that of AM/AA/APS (RF: 11.5, RRF: 2.5) and HPAM (RF: 8.9, RRF: 1.3) under the same conditions, which indicated that AM/AA/APS/DCAP solution had stronger mobility control ability that was favourable to enhance oil recovery.

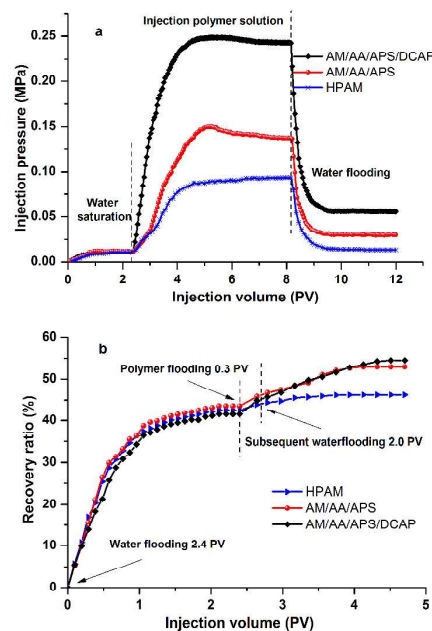


Fig. 8 (a) Mobility control ability of AM/AA/APS/DCAP, AM/AA/APS and HPAM, (b) enhanced oil recovery ability of AM/AA/APS/DCAP, AM/AA/APS and HPAM.



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Table 3 RF and RRF of AM/AA/APS/DCAP, AM/AA/APS and HPAM

Polymer	Water saturation pressure (10 ⁻³ MPa)	Polymer solution pressure (10 ⁻³ MPa)	Water flooding pressure (10 ⁻³ MPa)	RF	RRF
AM/AA/APS/DCAP	11.0	242.7	55.4	22.1	5.0
AM/AA/APS	11.9	137.4	30.0	11.5	2.5
HPAM	10.5	93.5	13.6	8.9	1.3

Enhanced oil recovery

EOR ability of AM/AA/APS/DCAP, AM/AA/APS and HPAM was investigated on the basis of water flooding, as displayed in Fig. 8b. The polymer solution of 0.3 PV was injected into the core to achieve high recovery ratio after gaining steady recovery, 42.5%, under the condition of water flooding of 2.4 PV. It was found that AM/AA/APS solution could enhance additional recovery of 9.3% compared with HPAM (3.7%). However, the extra recovery ratio of 12.9% could be obtained when flooding with AM/AA/APS/DCAP solution. The core flooding experiments results showed that AM/AA/APS/DCAP had superior ability to enhance oil recovery, which was supported by the excellent performance in the previous researches.

Conclusions

In conclusion, the hydrophobic acrylamide copolymer was prepared successfully by acrylamide, acrylic acid, sodium 3-(allyloxy)-2-hydroxypropane-1-sulfonate and *N*-allyl-2-(2,4-dichlorophenoxy)acetamide using 2,2'-azobis(2-methyl propionamide) dihydrochloride system for enhanced oil recovery. The copolymer exhibited excellent performances on water solubility, resistance to biodegradability, and tackifying. It has also found that the copolymer possessed remarkable salt resistance with viscosity retention rate of 17.6% under the condition of 20000 mg·L⁻¹ NaCl, 16.7% under the condition of 2000 mg·L⁻¹ CaCl₂, and 15.2% under the condition of 2000 mg·L⁻¹ MgCl₂. And the better temperature tolerance, shear resistance, viscoelasticity, and long-term stability could be obtained compared with partially hydrolyzed polyacrylamide. It was also shown that the copolymer displacing solution had stronger mobility control ability with the RF of 22.1 and the RRF of 5.0, and superior ability to enhance oil recovery of 12.9%. And the further research on the microstructure structure of the copolymer solution, displacement efficiency under various conditions, and applications of other similar copolymers for EOR chemical is in progress.

Acknowledgements

This work was supported by the Scientific Research Starting Project of Southwest Petroleum University (contract grant number 2014PYZ008), the Key Programs of Educational Commission of Sichuan Province of China (Natural Science, contract grant number 15ZA0051), the Foundation of Youth Science and Technology Innovation Team of Sichuan Province (contract grant number 2015TD0007).

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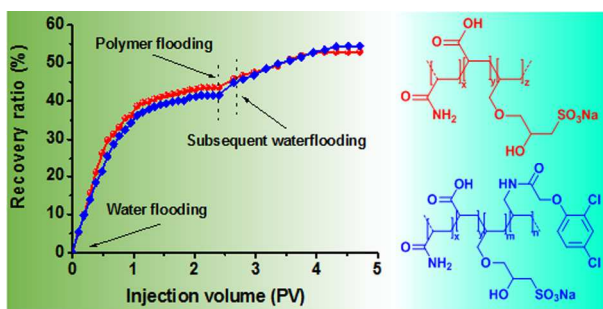
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Graphical abstract

Anti-biodegradable hydrophobic sulfonate-based acrylamide copolymer containing 2,4-dichlorophenoxy for enhanced oil recovery

Shaohua Gou, Yang He, Lihua Zhou, Peng Zhao, Qin Zhang, Shiwei Li and Qipeng Guo



We report the synthesis of a novel hydrophobic sulfonate-based acrylamide copolymer which exhibits remarkable water solubility, excellent resistance to biodegradability, and superior ability to enhance oil recovery.