


Preparation, solution characteristics and displacement performances of a novel acrylamide copolymer for enhanced oil recovery (EOR)

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Received: 4 August 2016 / Revised: 26 April 2017 / Accepted: 24 May 2017
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Abstract The radical polymerization of acrylamide, acryloylmorpholine, acrylate or 2-acrylamide-2-methyl propane-sulfonate in water initiated with ammonium persulfate or 2,2'-azobis(2-methylpropanamide)dihydrochloride was carried out to produce copolymer for enhanced oil recovery (EOR). The structure of the acrylamide copolymer was determined by infrared (IR) and ¹H-NMR. Influence of synthesis condition on viscosities of products was studied. As a kind of potential displacement agent the salt tolerance temperature resistance and displacement performance of copolymer were also investigated in this paper. The introduction of ACMO and AMPS improves the thermostability of copolymer. The ability of the AM/AANA/ACMO/AMPS copolymer to reduce permeability is higher than HPAM. The tertiary recovery of the former is also higher than that of the latter whether in homogeneous or heterogeneous condition.

Keywords Acrylamide copolymer · Enhanced oil recovery (EOR) · Temperature tolerance · Salt resistance · Displacement performance

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Introduction

Partially hydrolyzed polyacrylamide (HPAM) has been the most widely used polymer for EOR applications at the moment [1]. However, in the condition of high temperature and high salinity, irreversible chain scission may occur, which may cause the decrease in viscosity.

So, some scholars have begun to turn their attention to develop ultrahigh molecular weight HPAM (UMW-HPAM). Although the breakage of macromolecule chain is unavoidable, the chain length after breakage of UMW-HPAM is greater than that of ordinary HPAM. Unfortunately, there is no way to improve the molecular weight of HPAM without limitation. At present the molecular weight of most UMW-HPAM is $3.0\text{--}3.5 \times 10^7$ [2]. This seems to be an extreme value. The molecular weight depends on far too many variables including the initiator concentration, temperature, the kind of solvent, monomer purity, initiation system, chain-transfer agent, and so on. It is not easy to further increase the molecular weight of HPAM using the traditional polymerization method.

Besides UMW-HPAM, hydrophobically associating polyacrylamide (HAPAM) is also attracting increasing attention because of its unique viscosifying ability. HAPAM is derived from polyacrylamide by incorporating a small fraction of hydrophobic groups. In aqueous solution, the hydrophobic groups tend to associate together leading to the formation of network structure which increases the solution viscosity greatly. However, the introduction of hydrophobic groups decreases the solubility of HAPAM, which severely handicaps its application.

In addition, some suitable modified monomers are copolymerized with acrylamide to yield product which would be thermally stable for a certain period of time [3]. The modified monomers include strong sulfonate electrolytes (2-acrylamide-2-methyl propane-sulfonate (AMPS) [4], sodium vinyl sulfonate [5], sodium-*p*-styrenesulfonate [6, 7]) and ring structure monomers (vinylpyrrolidone (NVP) [8–12], allyl- β -cyclodextrin [13, 14], chitosan [15] and so on). Compared with carboxyl group, sulfonate group would offer stronger hydrogen bonding to provide higher stability in solution. In addition, the latter has stronger hydrophilicity to improve the water-solubility of copolymer [16]. The ring structure group such as VP may decrease the thermal hydrolysis of amide group [1]. In addition, the ring monomer might provide robust steric hindrance to resist chain degradation in high temperature [15].

Enlightened by this, in this paper, we choose a ring structure acryloylmorpholine as modified monomer to prepare a novel acrylamide copolymer for EOR. The structure of copolymer was analyzed by means of FT-IR and $^1\text{H-NMR}$. The salt tolerance and temperature resistance of copolymer were investigated in this paper. The displacement performance of copolymer as a potential displacement agent was also studied.

Experimental

Materials and polymerization

Acryloylmorpholine (ACMO) is an industrial chemical product. Acrylic acid sodium salt is prepared by equimolar neutral reaction of acrylic acid and NaOH solution. Ammonium persulfate (APS), 2,2'-azobis(2-methylpropanamide)dihydrochloride (AIBA), acrylamide (AM), and 2-acrylamide-2-methyl propane-sulfonate (AMPS) are analytical reagent or chemical grade and are used without further purification. Distilled water was used throughout. A certain mass of AM, AANa, ACMO, AMPS and distilled water were added into the two-necked flask equipped with a nitrogen inlet tube. Then, the high purity nitrogen was injected into the mixture solution for 30 min to remove dissolved oxygen. Next, the prepared initiator aqueous solution was injected into the two-necked flask and the temperature was increased to 70 °C for 6 h. The obtained gel was cut up and dried at 80 °C until a constant weight was attained. At last, the dried gel was shattered by shredding machine. As a reference, HPAM was synthesized under identical conditions.

Characterization

¹H-NMR spectra were measured on a VarianGemini-500 NMR spectrometer with D₂O as the solvent. A Bruker IFS 66 v/s IR spectrometer was used for FTIR spectroscopy analysis.

Displacement tests

The displacement tests were conducted using sandpack models of 30 cm in length and 2.5 cm in diameter. Sand of 80–120 mesh was wet-packed in the sandpack. The injection water was first injected into the sandpack at a constant rate of 1 mL/min until pressure reached a stable value (ΔP_B). After that, a certain amount of copolymer solution (1500 ppm) was injected at the same flow rate until pressure reached a stable value (ΔP_p). Next, subsequent injection water was injected until pressure reached a plateau (ΔP_F) again. The resistance factor (F_R) and residual resistance factor (F_{RR}) can be calculated by Eqs. (1) and (2).

$$F_R = \frac{\Delta P_p}{\Delta P_B} \quad (1)$$

$$F_{RR} = \frac{\Delta P_F}{\Delta P_B} \quad (2)$$

The laboratory oil displacement experiment was carried out as follows. The wet-packed sandpack was flooded with the oil sample until water production ceased. Thereafter, brine flooding continued until the water cut was greater than 98%. After that, 0.3 Pore Volume (PV) of microsphere solution slug was injected (1500 mg/L),

followed by water flood until the water cut of the efflux reached 98% again. The above experiments were all carried out at 80 °C.

Results and discussion

Characterization of the copolymers

The structure schematic of the monomers and polymerization are shown in Fig. 1. The IR spectrum of HPAM and AM/AANa/ACMO copolymer is reported in Fig. 2. The peak at 1700 cm^{-1} is characteristic peak of C=O stretching from the amide group and carboxylate ions. But for AM/AANa/ACMO copolymer, there is a characteristic peak at 1640 cm^{-1} due to C=O stretching from ACMO (Fig. 2b).

The synthesized HPAM, AM/AANa/ACMO copolymer and AM/AANa/ACMO/AMPS copolymer are characterized by $^1\text{H-NMR}$ spectroscopy (Fig. 3). For HPAM, the signal at $\delta = 1.86\text{--}2.33\text{ ppm}$ is the characteristic peak of methine protons from main chains. The signal at $\delta = 0.91\text{--}1.78\text{ ppm}$ is assigned to methylene protons from chain backbone. For AM/AANa/ACMO copolymer, the newly appeared signal at $\delta = 3.16\text{--}3.70\text{ ppm}$ is associated with methylene protons from morpholine ring. For AM/AANa/ACMO/AMPS copolymer, the newly appeared signal at $\delta = 1.06\text{ ppm}$ is assigned to methyl from AMPS.

Influence of synthesis condition on viscosity

Figure 4 shows the influence of the mass ratio of AM and ACMO on viscosity of AM/AANa/ACMO copolymer and AM/AANa/ACMO/AMPS copolymer solution. The apparent viscosity first increases and then decreases with increasing ACMO proportion. For AM/AANa/ACMO copolymer, when the ratio is beyond 6:4, the viscosity will decrease slowly from 35.52 to 33.60 mPa s. The apparent viscosity first increases and then decreases with increasing ACMO proportion. The supreme value appears when the optimum mass ratio of AM and ACMO is 7:3. For AM/AANa/ACMO/AMPS copolymer, there is also an optimum mass ratio of AM and ACMO (6:4) with a maximum of viscosity. The proposed interpretation for the phenomena is as follows. Due to the steric effect of bulky side group, the morpholine of ring structure can enhance the expansion extent of polymer chains

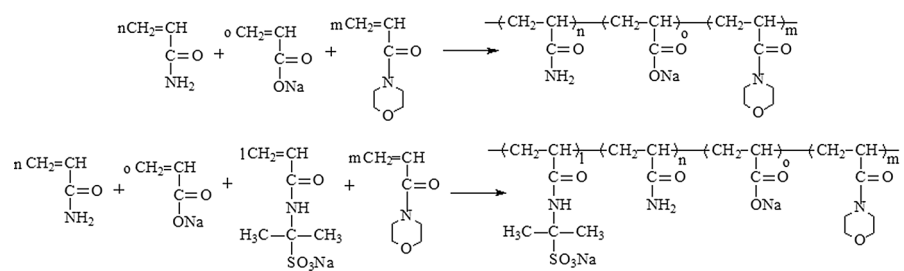


Fig. 1 The structure schematic of the monomers and polymerization

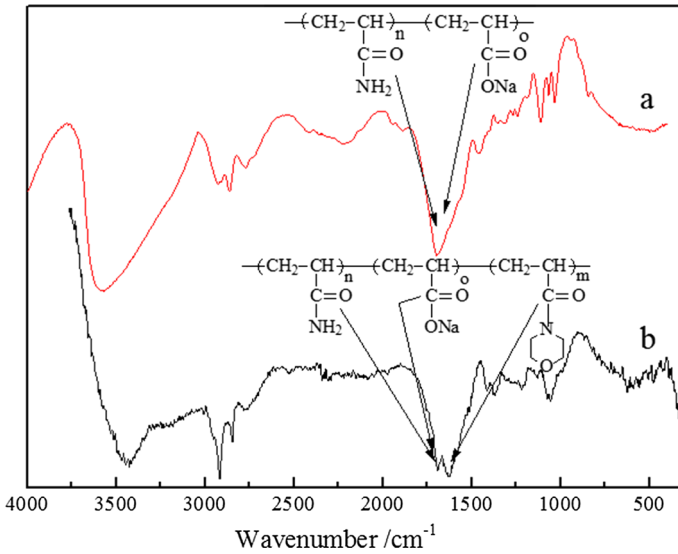


Fig. 2 FTIR spectrum of HPAM (a) and AM/AANa/ACMO copolymer (b)

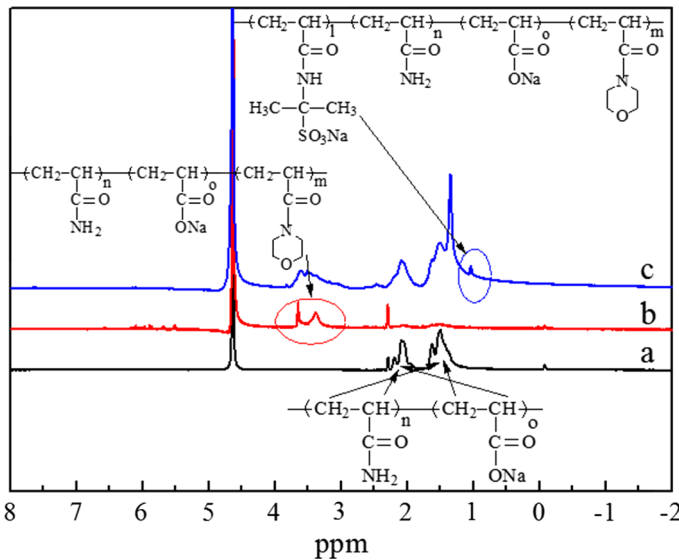


Fig. 3 Expansions of the 500-MHz ¹H-NMR spectra of HPAM (a), AM/AANa/ACMO copolymer (b) and AM/AANa/ACMO/AMPS copolymer (c)

which increases the viscosity of copolymer solution. At the same time the steric effect of morpholine can also decrease the molecular weight of copolymer. Before the mass ratio of ACMO and AM is less than 3:7 for AM/AANa/ACMO copolymer, the effect of chain expansion in polymer is stronger than the effect of reducing the molecular weight leading to the increase of viscosity. With the further increase of

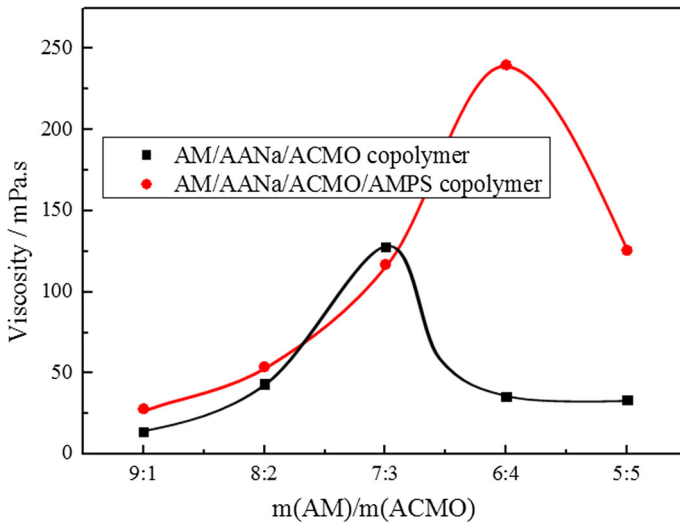


Fig. 4 The influence of the mass ratio of AM and ACMO on viscosity of AM/AANa/ACMO copolymer and AM/AANa/ACMO/AMPS copolymer solution (rotor: S62; rotation speed: 100 RPM)

ACMO, the effect of the latter gradually became predominant compared to that of the former resulting in the decrease of viscosity.

Figure 5 shows the influence of the initiator on viscosity of copolymer solution. The apparent viscosity decreases with the increase of initiator concentration. The viscosity of product initiated by APS is higher than that of AIBA when the initiator concentration is below 0.3 wt%. The polymerization is initiated by the free radicals

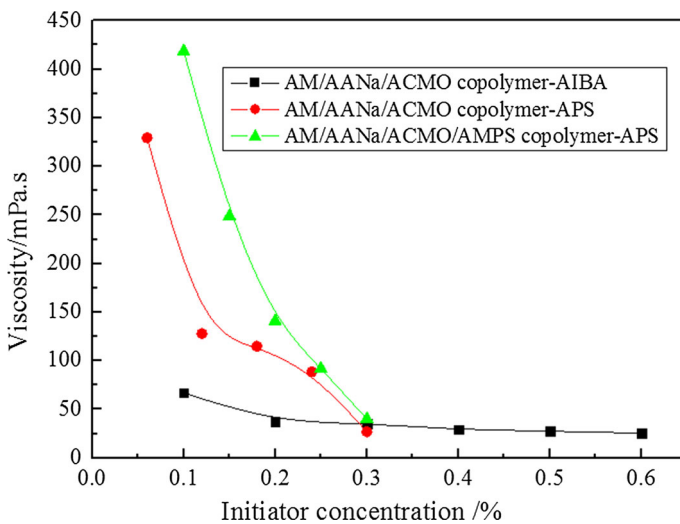


Fig. 5 The influence of the initiator on viscosity of AM/AANa/ACMO copolymer and AM/AANa/ACMO/AMPS copolymer solution (rotor: S62; rotation speed: 30RPM)

produced by decomposition of initiator. The more the dosage of initiator used, the higher the concentration of free radicals gets. The excessive free radicals will create many polymeric chains with shorter chain length. This means that high initiator concentrations tend to lead to low molecular weight, hence the drop in solution viscosity.

Temperature tolerance and salt resistance of copolymers

For the samples used in temperature tolerance, salt resistance and displacement tests, the compositions of the reagents for producing the AM/AANa/ACMO copolymer are 15% of ACMO, 10% of AANa and 75% of AM in weight percent. The compositions of the reagents for producing the AM/AANa/ACMO/AMPS copolymer are 30% of ACMO, 15% of AANa, 10% of AMPS and 45% of AM in weight percent. The influence of electrolytes concentration on viscosity of copolymer and HPAM solution is shown in Fig. 6. With increase of electrolytes concentration, the viscosity of copolymer solution reduces gradually. The bivalent salts have greater impact on viscosity than the monovalent salt. This behavior is similar to influence of salt concentration on viscosity of HPAM solution. It is due to the compression of the diffuse double electric layer of the carboxylate ions by electrolyte ions which decreases electrostatic repulsive force [17]. Thus, the conformation of the polymer chains are coiled but not extended, which leads to the decrease of viscosity.

Figure 7 shows the variation of viscosity with aging time without the addition of salt at 80 °C. As the increase of aging time, viscosities of three kinds of polymer reduce in different levels. After aging for 8 days, the viscosity of AM/AANa/

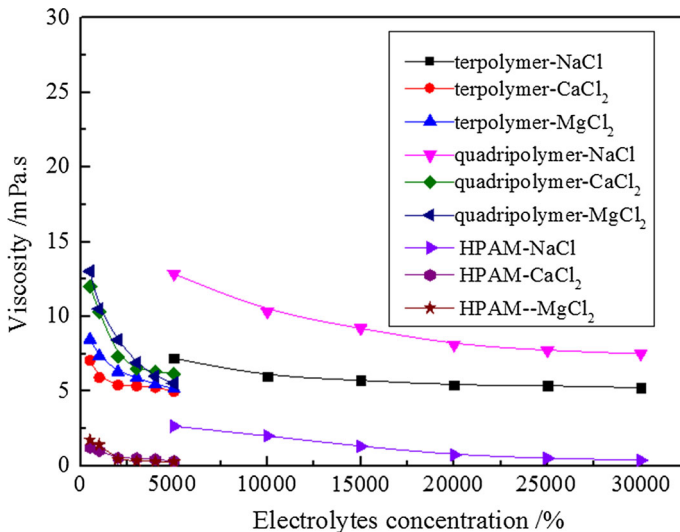


Fig. 6 Influence of electrolytes concentration on viscosity of copolymer and HPAM solution (rotor: S61; rotation speed: 200RPM)

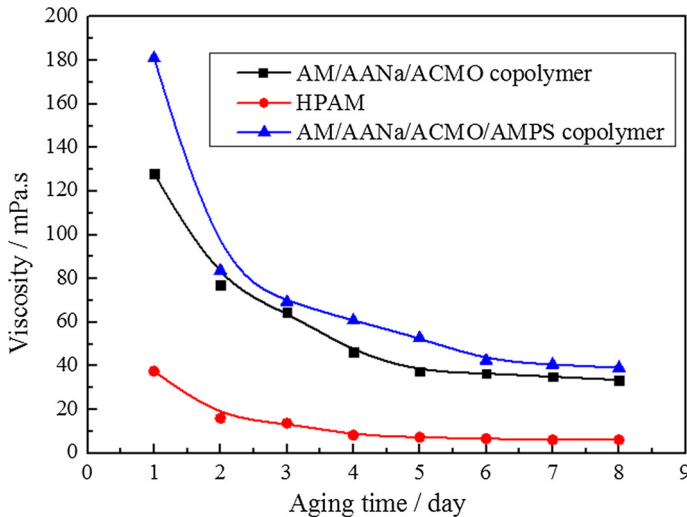


Fig. 7 Relationship of the aging time to the viscosity of copolymer solution at 80 °C (rotor: S62; rotation speed: 30RPM)

ACMO/AMPS copolymer is highest, followed by AM/AANa/ACMO copolymer, and the viscosity of HPAM is lowest. The results show that the introduction of ACMO and AMPS improves the thermostability of copolymer. On the one hand, the sulfo group contained in AMPS can not only increase the stability of the main chain, but also control the degradation of AM [18]. On the other hand, large steric hindrance of ACMO may enhance the backbone rigidity, because some monomers containing ring structure such as NVP [19] and chitosan [15] might provide robust steric hindrance to resist chain degradation in high temperature. Compared with HPAM, there is bulky morpholine with ring structure in AM/AANa/ACMO copolymer. The steric effect of bulky side group enhances the expansion extent of polymer chains which increases the viscosity of copolymer solution. For AM/AANa/ACMO/AMPS copolymer, sulfonate group would offer strong hydrogen bonding to provide higher stability in solution. In addition, sulfonate is strong electrolyte group, so electrostatic repulsion in the polymer chain segment is the strongest in three polymers. The electrostatic repulsion interaction makes the chain segment stretch and form uncoiled chains leading to the increase of viscosity.

Displacement performance

The research mentioned above mainly focused on the viscosity of copolymer in solution. Actually, the displacement behavior of copolymer solution in porous media is more significance for a potential polymer flooding agent. The sandpacks are injected with different polymer solution, and the variation of injection pressures with injection volume at the similar permeability ($0.5 \mu\text{m}^2$) is shown in Fig. 8. The injection pressure of AM/AANa/ACMO/AMPS copolymer is much higher than that of HPAM. In addition, the injection pressure of the subsequent water flooding of

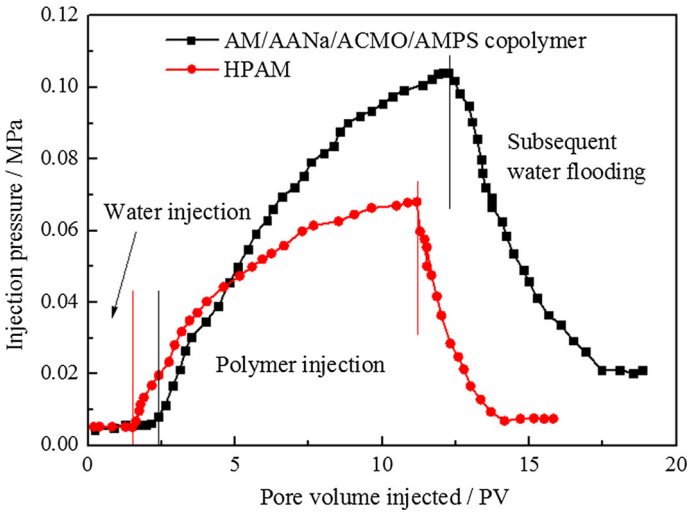


Fig. 8 Variation of injection pressures during the injection of the two 1500 mg/L polymer solutions

AM/AANa/ACMO/AMPS copolymer is higher than that of HPAM. The injection parameters of the two polymers are shown in Table 1. The F_R and F_{RR} values of AM/AANa/ACMO/AMPS copolymer are higher than those of HPAM under the condition of approximate permeability, which indicates that the ability to reduce permeability of the former is higher than that of the latter.

A series of oil displacement experiments were carried out in homogeneous sandpack models of approximate permeability ($0.5 \mu\text{m}^2$) and heterogeneous model of approximate permeability ratio (3.6–3.9) at $85 \text{ }^\circ\text{C}$ (Table 2). The tertiary recovery of polymer flooding and the final oil recovery of each flood test are shown in Table 2. It can be seen that the tertiary recovery of the AM/AANa/ACMO/AMPS copolymer (15.43 and 10.81%) is higher than that of HPAM (7.41 and 5.37%)

Table 1 The injection parameters of the two polymers

Polymer	Permeability (μm^2)	Pressure of water (MPa)	Pressure of polymer flooding (MPa)	Pressure of subsequent water flooding (MPa)	F_R	F_{RR}
HPAM	0.523	0.0052	0.068	0.0075	13.08	1.44
	1.518	0.0046	0.036	0.0065	7.83	1.41
	2.491	0.0019	0.014	0.0026	7.37	1.37
AM/AANa/ACMO/AMPS copolymer	0.539	0.0058	0.104	0.021	17.93	3.62
	1.497	0.0049	0.085	0.010	17.35	2.04
	2.518	0.0016	0.019	0.0031	11.88	1.94

Permeability measured with gas

Table 2 Summary of polymer flooding tests in sandpack model (1500 mg/L)

Condition	Polymer	Permeability (μm^2)	Permeability ratio	Recovery of water flood (%)	Final oil recovery (%)	Tertiary recovery (%)
Homogeneous	HPAM	0.583	–	47.31	54.72	7.41
	copolymer ^a	0.536	–	45.91	61.34	15.43
Heterogeneous	HPAM	1.284/0.329	3.90	30.41	35.78	5.37
	copolymer ^a	1.128/0.313	3.60	28.39	39.20	10.81

^a AM/AANa/ACMO/AMPS copolymer

whether in homogeneous or heterogeneous condition. In addition, the copolymer synthesized would be more suitable for homogeneous formation.

Conclusions

AM/AANa/ACMO copolymer and AM/AANa/ACMO/AMPS copolymer were prepared by free radical polymerization. The structure of copolymer was characterized by IR and ¹H-NMR. The apparent viscosity of AM/AANa/ACMO copolymer and AM/AANa/ACMO/AMPS copolymer first increases and then decreases with increasing ACMO proportion. The viscosity of AM/AANa/ACMO copolymer initiated by APS is higher than that of AIBA when the initiator concentration is below 0.3 wt%. With the increase of electrolytes concentration, the viscosity of copolymer solution reduces gradually. After aging 8 days at 80 °C, the viscosity of AM/AANa/ACMO/AMPS copolymer is highest, second AM/AANa/ACMO copolymer, and the viscosity of HPAM is lowest. The F_R and F_{RR} values of AM/AANa/ACMO/AMPS copolymer are higher than that of HPAM under different permeabilities (0.5–2.5 μm^2). The tertiary recovery of the AM/AANa/ACMO/AMPS copolymer (15.43 and 10.81%) is higher than that of HPAM (7.41 and 5.37%) whether in homogeneous or heterogeneous condition.

Acknowledgements Financial support from Research Foundation of Chongqing University of Science & Technology (CK2016B07), Scientific and Technological Research Program of Chongqing Municipal Education Commission (KJ1501327, KJ1401308, KJ1401324) and National Natural Science Foundation of China (51504050, 21302237).

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