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Synthesis and evaluation of novel water-soluble copolymers based on acrylamide and modular β-cyclodextrin

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ABSTRACT

Mono-6-(allyl amino)-β-cyclodextrin (*N*-β-CD) and mono-2-*O*-(allyl oxygen radicals-2-hydroxyl propyl)-β-cyclodextrin (*O*-β-CD) were copolymerized with acrylamide (AM), acrylic acid (AA), and 1-llyl-3-oil acyloxyimidazole-1-ammonion bramide (AOAB) initiated by redox initiation system in an aqueous medium. The AM/AA/AOAB/*N*-β-CD and AM/AA/AOAB/*O*-β-CD were prepared by adjusting the reactive conditions, such as initiator concentration, pH, temperature, and monomer ratios. The obtained copolymers were characterized by means of infrared (IR) spectroscopy, ^{1}H NMR spectroscopy, scanning electron microscope (SEM), rotational rheometer, intrinsic viscosity, salt resistance, core flood test, etc. The temperature-tolerance, shear-tolerance, salt-resistance and thickening function of these copolymers are improved remarkably compared with partially hydrolyzed polyacrylamide (HPAM). About 18.3% and 12.5% oil recovery could be enhanced by 2000 mg/L AM/AA/AOAB/*N*-β-CD and AM/AA/AOAB/*O*-β-CD comparing with water-flooding. In addition, the result of X-ray diffractometry (XRD) test showed that the solutions of obtained copolymers could remarkably reduce the crystalline interspace of sodium montmorillonite (from 18.9 Å to 15.3 Å).

1. Introduction

The challenge to increase oil recovery from reservoir is a motive force behind the fact that the easily recoverable oil is running out and that much original oil remains in the reservoir after primary and secondary recovery processes. Water-soluble polymer flooding has been used as enhanced oil recovery chemical technology in recent years (Lake, 1989; Li, Zhai, Xu, Shen, & Mao, 2000). Among the applied water-soluble polymers, polyacrylamide (PAM) and partially hydrolyzed polyacrylamide (HPAM) are utilized mostly carrying out some good results. However, given the harsh conditions present in most oil reservoir, new problems and limitations emerge with the applied of water-soluble polymers. For instance, HPAM is not appropriate for high-temperature reservoir and HPAM could not withstand high salt concentration (Abhijit, Achinta, Keka, & Ajay, 2010; Li et al., 2000; Thomas, 2008).

In recent decades, many researches indicated that acrylamide (AM) copolymerized with a suitable functional monomer can offer a more satisfied polymer owning higher thickening capability, better temperature-, shear-, and salt-resistance (Khune et al., 1985; Liu, Jiang, Gou, Ye, & Luo, 2012; Liu, Jiang, Gou, Ye, & Xie, 2012; Taylor, & Nasr, 1998; Wever, Picchionia, & Broekhuisa, 2011). Numerous water-soluble polymers based on this mechanism for EOR have been published, for instance, associative copolymers of acrylamide with *N*-alkylacrylamides, terpolymers of acrylamide, *N*-decylacrylamide, sodium-2-acrylamido-2-methylpropane sulfonate (NaAMPS), sodium acrylate (NaA), sodium-3-acrylamido-3-methylbutanoate (NaAMB), [2-(acrylamido)-2-methylpropyl] trimethylammonium chloride (AMPTAC), dimethyldodecyl(2-acry1amidoethyl)ammonium bromide (DAMAB), 3-[(2-acrylamido-2-methylpropyl)dimethylammonio]-l-propan-esulfonate (AMPDAPS), N-phenyl acrylamide, 2-acrylamido-2-methylpropanedimethylammonium chloride, 3-methacrylamido-3-methylbutanoate or 3-(2-acrylamido-2-methyl propanedimethyl-ammonio)-1-propanesulphonate have been shown to possess the required rheologic behavior to be suitable for enhanced oil-recovery processes. (Abu-Sharkh, Yahaya, Ali, Hamad, & Abu-Reesh, 2003; Anupom, Arun, & Inamul, 2003; Chang & McCormick, 1993; Erich, Kathmann, Davis, & McCormick, 1994; Kathmann & McCormick, 1997; Kathmann, Davis, & McCormick, 1994; McCormick & Blackmon, 1986a,b; McCormick & Elliott, 1986; McCormick, Elliot, & Blackmon, 1986; McCormick, Middleton, & Cummins, 1992; McCormick & Salazar, 1992a; McCormick, & Salazar, 1992b; Wever et al., 2011).

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β-Cyclodextrin and its derivatives have been reported widely through many applied fields such as environmental protection, food, medicine, cosmetics and dye industry. Chitosan C6-substituted cyclodextrin (CTS-en-CD) showed superior thermal stability which could withstand 500 °C with high mass retaining ratio of 42% (Chen, Ye, Wang, Guo, & Tan, 2012). β-CD used as additive in dyeing baths, enhanced thermal stability with mass retaining ratio of 90% at 270 °C (Santagapitaa et al., 2011). Copolymers with modular β-CD showed satisfactory salt resistance which pointed out salt seems to favor the association of polymers, strengthening hydrophobic associations (Gosselet, Naranjo, Renard, Amiel, & Sebille, 2002). All these researches have indicated that copolymer with β-CD branched chain structure could exhibit remarkable thermal and salt resistance. Nevertheless, little literatures about polymers containing β-CD have been reported focusing on enhanced oil recovery (Zou, Zhao, Ge, Lei, & Luo, 2012).

Recent studies have demonstrated that β-CD can perform "site-selective complexation" on a specific segment of the copolymer due to steric fitting, hydrophobic (or van der Waals) interaction, and/or other interactions between the cavity of β-CD and the polymer, which can generate and/or enhance amphiphilicity of the copolymers (Parlati et al., 2007; Peeters, Neeskens, Tollenaere, Van Remoortere, & Brewster, 2002; Tomáš, Miloš, & Jiří, 2001; Tsai et al., 2010; Vélaz, Isasi, Sánchez, Uzqueda, & Ponchel, 2007; Wang et al., 2007; Zhao, Zhao, Zhu, Huang, & Hu, 2009). The hydrophobic interactions of β-CD derivatives which could act as surfactant playing an important role to decrease oil/water interfacial tension (IFT) and wettability modification are so important for oilfield chemical additives. Based on this feature, polymer synthesized with β-CD derivatives could be used as flood chemicals to achieve the hydrophilic-hydrophobic property.

Keeping in mind all above points, we designed mono-6-(allyl amino)-β-cyclodextrin (*N*-β-CD) or mono-2-*O*-(allyl oxygen radicals-2-hydroxyl propyl)-β-cyclodextrin (*O*-β-CD) to linked them into the HPAM, aiming to improve the displacing efficiency by recognizing oil molecule ability of β-CD cavity, enhance the solubility of copolymers owing to the hydroxyl groups on β-CD, and obtain satisfying temperature and salt resistance. In addition, to avoid the negative effect on clay in the reservoir, cationic monomer 1-llyl-3-oil acyloxyimidazole-1-ammonion bramide (AOAB) was chose to copolymerize. Hence, novel water-soluble quaternary copolymers (AM/AA/AOAB/*N*-β-CD and AM/AA/AOAB/*O*-β-CD) were prepared with acrylamide (AM), acrylic acid (AA), *N*-β-CD and/or *O*-β-CD and AOAB.

2. Experimental

2.1. Material

1-Allyloxy-2,3-epoxy propane (AGE, CP) was purchased from Nanjing Forward Chemical (Nanjing/China). β-CD (AR), 4-toluene sulfonyl chloride (TsCl, AR), allylamine (CP), acetonitrile (AR), *N,N*-dimethyl formamide (DMF, AR, dried over calcium hydride for 2 days and then distilled under reduced pressure prior to use), AM (CP), acrylate (AA, AR), 1-llyl-3-oil acyloxyimidazole-1-ammonion bramide (AOAB, CP), sodium sulfite ($NaHSO_3$, AR), and ammonium persulfate ($(NH_4)_2S_2O_8$, AR) were purchased from Chengdu Kelon Chemical Reagent Factory Co. (Sichuan, China). Sodium montmorillonite (MMT, Xinjiang Xiazijie Bentonite, Xinjiang/China), partially hydrolyzed polyacrylamide (HPAM, hydrolysis degree = 30%, $M_w = 1.5 \times 10^8$).

2.2. Synthesis of N-β-CD and O-β-CD

β-CD (60.0 g, 52.9 mmol) was suspended in 500 mL of water, and NaOH (6.57 g, 164.0 mmol) in 20 mL of water was added dropwise over 6 min. The suspension became homogeneous and slightly yellow before the addition was complete. 4-Toluene sulfonyl chloride (10.08 g, 52.9 mmol) in 30 mL of acetonitrile was added dropwise over 8 min, causing immediate formation of a white precipitate. After 2 h of stirring at 23 °C, the precipitate was removed by suction filtration and the filtrate refrigerated overnight at 4 °C. The resulting white precipitate was recovered by suction filtration and after drying for 12 h (0.005 mmHg) afforded a pure white solid (β-CD-OTS). The previous product (2.578 g, 2 mmol) was dissolved in excess allylamine (5.7 g, 0.1 mol), and trace amounts of *p*-dihydroxybenzene was added. The reaction was allowed to proceed at 80 °C in the next 2 days. After the reaction was ended, the extra allylamine was removed by vacuum rotary evaporation. And the crude product was dissolved by DMF. Adding massive acetone, precipitate was obtained after air pump filtration 3 times. Dried in 40 °C vacuum the faint yellow powder (*N*-β-CD) which was water-soluble was afforded (Liu et al., 1997; Petter, Salek, Sikorski, Kumaravel, & Lin, 1990).

NaOH (1.5 g) was dissolved in 100 mL deionized water. After the alkali liquor cooled to room temperature, 34.05 g β-CD was added into the flask under constant stirring until the paste turning to clear. Drip 3.4242 g AGE slowly into the flask in 5 min. After that, the mixture system changed into white paste again. Then the reaction was allowed to occur at 10–15 °C about 5–8 h until the mixture is clear. Next, the solution was neutralized by 85% phosphoric acid, the system changed into paste since the β-CD remaining after reaction which would be filtrated later. After the filtrate was dissolved by the ethanol, certain salt could be observed at the bottom which would also be filtrated. Finally, the product, faint yellow water-soluble thick liquid, mono-2-*O*-(allyl oxygen radicals-2-hydroxyl propyl)-β-cyclodextrin (*O*-β-CD) could be carried out through the reduced pressure distillation of the second filtrate (Ishimam, Masuda, & Lida, 1997).

2.3. Synthesis of copolymers (AM/AA/AOAB/N-β-CD and AM/AA/AOAB/O-β-CD)

The appropriate amounts of AM, AA, AOAB, *N*-β-CD and/or *O*-β-CD were placed in a beaker while stirred in distilled water under an inert nitrogen atmosphere, and NaOH was added into the solution to adjust the pH stirring for 10 min to achieve a certain temperature, then the copolymerization proceeded being thermally insulated for 8–10 h until the reaction ended. After the products were cooled to room temperature (25 °C), it was separated by precipitation using ethanol and dried at 45 °C vacuum retrieving the powdered copolymer samples. The synthesis routes were show in Fig. 1a and b.

2.4. Measurement of the intrinsic viscosity

Intrinsic viscosity of copolymer solutions, at five different concentrations (0.0010, 0.00067, 0.00050, 0.00033, 0.00025 g/L) (diluted in the 1.0 mol/L sodium chloride solution to meet the required concentration), was measured using an Ubbelohde viscometer at 30 °C. The flux time was recorded with an accuracy of 0.05 s. At each concentration, both reduced viscosity, η_{sp}/c, and inherent viscosity, $\ln \eta_r/c$, were determined from the apparent (kinematic) viscosity of polymer solutions, and plotted against the concentration of polymer solutions, which is known as dual Huggins Kraemer plot. Extrapolation of both data sets led to a unique *y*-intercept which is known as the intrinsic viscosity of the polymer (Lana, Wang, Xu, & Jacob, 2011; Yang, Li, He, Ren, & Wang, 2009).

2.5. Characterization

The *N*-β-CD, *O*-β-CD, AOAB, and synthesized copolymers were individually characterized by WQF-520 Infrared spectroscopy. ^1H

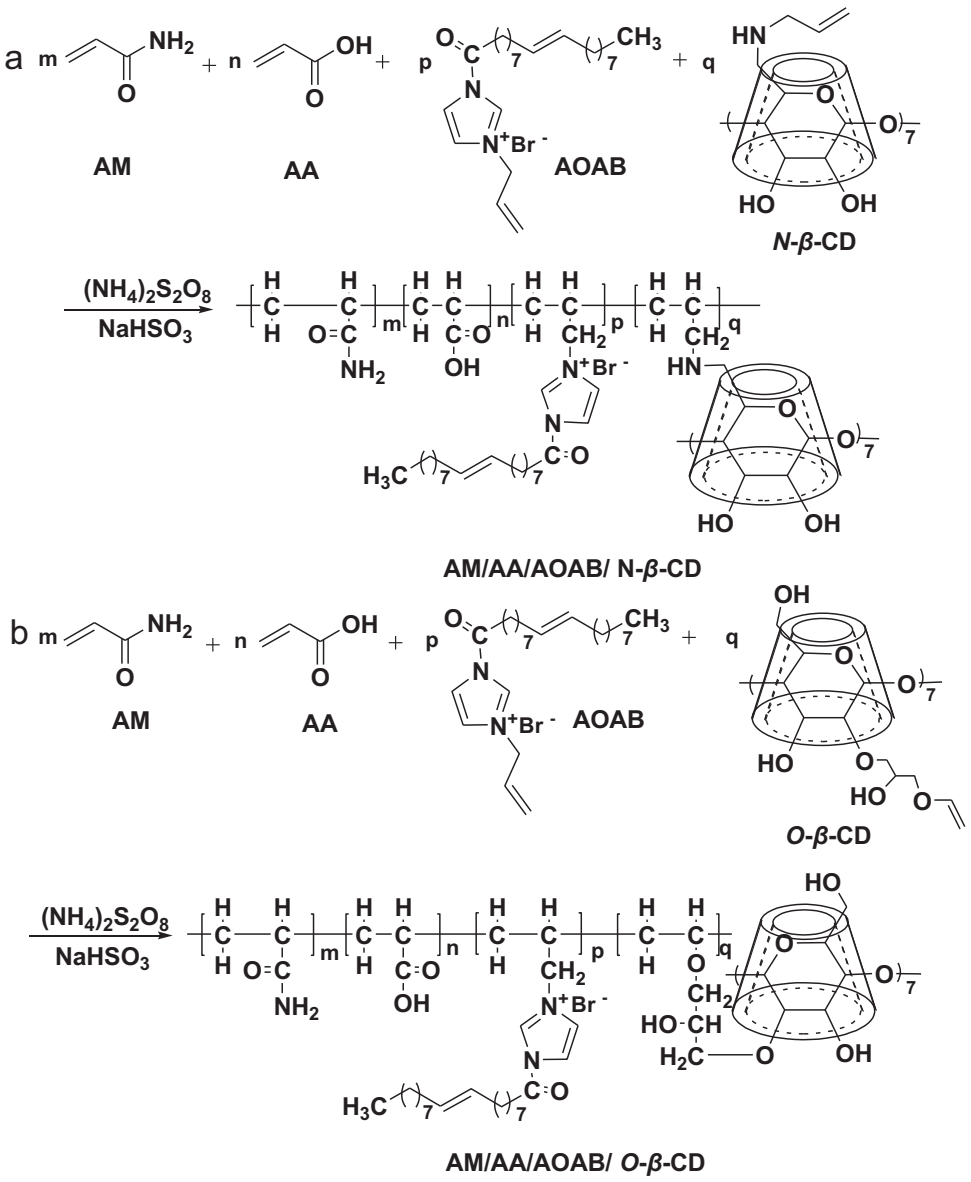

Fig. 1. (a) synthesis route of AM/AA/AOAB/*N*-β-CD; (b) synthesis route of AM/AA/AOAB/*O*-β-CD.

NMR spectra of AM/AA/AOAB/*N*-β-CD and AM/AA/AOAB/*O*-β-CD were recorded on Bruker AC-E 200 (Bruker BioSpin, Switzerland) spectrometer by dissolving the samples in D_2O and operating at 200 MHz (Ye, Gou, Gou, Jiang, & Liu, 2013).

And the microscopic structures of copolymer solutions of AM/AA/AOAB/*N*-β-CD and AM/AA/AOAB/O-β-CD were investigated by scanning electron microscope (SEM, Quanta 450, USA). Sample solutions (copolymers concentration = 5000 mg/L, HPAM concentration = 5000 mg/L) for SEM were prepared by placing 20 mL copolymer drops on 20 mm × 40 mm glass slides of 1.5 mm in thickness. Samples were allowed to cure either under infrared light or at room conditions. Before SEM, samples were freeze fractured using liquid nitrogen. Sample cross sections were coated with gold (300 Å) to increase conductivity. The sample cross sections were imaged with a SEM. The SEM was operated at an accelerating voltage of 20 kV at a working distance of 10–50 μm.

2.6. Shear-resistance tests

HAAKE RheoStress 6000 rotational rheometer (Thermo Fisher Scientific, Waltham/Massachusetts) was utilized to study the rheological character of copolymer solutions (2000 mg/L) of AM/AA/AOAB/*N*-β-CD and AM/AA/AOAB/*O*-β-CD. Compared with HPAM (2000 mg/L), the shear-resistance test was carried out at 30 °C varying with different shear rates.

2.7. Temperature-resistance and salt-tolerance evaluation

With the depth of oil or gas well/reservoir increasing, the high temperature makes the viscosity of polymer flood agent decrease badly. The salts such as NaCl, $CaCl_2$, and $MgCl_2$ exist in the formation water. And the high reservoir water salinity has been a crucial problem for EOR exploitation. Firstly, the apparent viscosity of copolymer solutions (2000 mg/L) was tested with temperature increasing compared with HPAM (2000 mg/L). Then the anti-salt ability was tested by increasing salt concentration. Finally the long-term salt-tolerance and temperature-resistance of obtained copolymers in transparent glass bottles were studied by apparent viscosity change (copolymer: 2000 mg/L, HPAM: 2000 mg/L, NaCl: 10,000 mg/L, $CaCl_2$: 2000 mg/L, $MgCl_2$: 2000 mg/L) at 100 °C for 10 days.

2.8. Core flood

The core flood tests were carried out to investigate the enhancing oil recovery ability of synthesized copolymers (for the details of core flood device, see supporting information). The cores used in tests were washed by 18% hydrochloric acid solution to remove the influence of impurities, for example, carbonate and argillaceous minerals. And then the cores were washed again with massive water until the pH value was 7. Finally, the cores were dried at 45 °C vacuum. The apparent viscosity of simulation of crude oil: 70.34 mPa s at 60 °C; ISCO 260D syringe pump, maximum injection pressure: 50 MPa, single pump flow rate of 0.01–107 mL/min; pressure sensor: range 0–0.1, 0–1, and 0–5 MPa, accuracy of 0.1% FS (Liu, Jiang, Gou, Ye, & Xie, 2012).

Simulated crude oil was poured into the prepared core sample, which had been saturated at 0.1 mL/min 12 h, at flow rate of 0.2 mL/min about 6 h. Only the oil flowed from the discharge end of core flood device without water, the core saturated at 0.3 mL/min. Then the valves of device were closed and sealed up.

Water flooding was conducted by using brine to displace simulated oil at 0.5 mL/min. The water ratio of produced fluid was recorded by means of automatic sampling instrument every 20 min. When water ratio began to exceed 98%, the polymer solution was ready to be injected by rearranging valves.

Afterwards, the prepared synthesized copolymer solution (2000 mg/L, 4000 mg/L, and 6000 mg/L) and/or HPAM (2000 mg/L) was injected to displace. And the water ratio was recorded in the same way. The injection rate of polymer solution was noted too. After the injection rate reached at 0.3 PV (pore volume), the valves were rearranged again to continue water flooding which was proceeded at 0.5 ml/min until the water ratio was above 98%.

2.9. Measurement of MMT crystalline interspace

The influence of obtained copolymer solutions (2000 mg/L) on clay was evaluated using crystalline interspace changes of MMT after hydration and expansive. The crystalline interspace of MMT was investigated by means of X-ray diffractometry (XRD, X' pert PRO, PANalytical B.V., The Netherlands).

3. Results and discussion

3.1. Optimal synthesis conditions of copolymerization

The relationship between apparent viscosity of copolymer solutions and synthesis conditions was studied. The apparent viscosities of copolymers produced with different conditions were copolymer solution tested by Brookfield DV-II + Pro Viscometer at 30 °C at 1000 mg/L. For synthesis of copolymer AM/AA/AOAB/*N*-β-CD, the results shown in Fig. 2 reveal that the maximum apparent viscosity of copolymer solution is 387 mPa s at 1000 mg/L. The corresponding optimal synthesis conditions are established, the initiator concentration is 0.7 wt%, the solution pH value is 7, the reaction temperature is 40 °C, the ratio of AM and AA on weight is 8.31:1.66, the monomer AOAB and *N*-β-CD concentrations are 0.1 wt% and 0.2 wt%, respectively (for the details, see supporting information).

And for copolymer AM/AA/AOAB/*O*-β-CD, the optimal conditions were confirmed in the same way as pervious in Fig. 2. The initiator concentration is 0.5 wt%, the solution pH value is 7, the reaction temperature is 45 °C, the ratio of AM and AA on weight is 8.31:1.66, the monomer AOAB and *O*-β-CD concentrations are 0.1 wt% and 0.1 wt%, respectively (for the details, see supporting information). In addition, the maximum apparent viscosity of copolymer solution is 399.5 mPa s at 1000 mg/L.

The thickening ability of AM/AA/AOAB/*N*-β-CD and AM/AA/AOAB/*O*-β-CD was investigated comparing with HPAM under different magnifications. The result in Fig. 2 indicated that the copolymers showed better viscosification property than HPAM.

3.2. IR spectroscopy analysis

The obtained copolymers structures were confirmed by IR spectroscopy. The IR spectra were showed in Fig. 3a. The IR spectra indicated that monomers AOAB, *N*-β-CD and *O*-β-CD were copolymerized successfully onto the backbone of PAM chains since the observation of peaks at 3415.06 cm^{-1}, 3184.29 cm^{-1}, 1455.12 cm^{-1}, 1405.45 cm^{-1}, and 1120.19 cm^{-1} in AM/AA/AOAB/*N*-β-CD IR spectrum and peaks at 3142.62 cm^{-1}, 1339.03 cm^{-1}, and 1120.23 cm^{-1} in AM/AA/AOAB/*O*-β-CD IR spectrum (Ye et al., 2013).

3.3. ^1H NMR analysis

The ^1H NMR spectra were shown in Fig. 3b and c, respectively. In Fig. 3b, the chemical shift value at 6.95–7.03 ppm was assigned to the NH protons of the imidazole ring. The chemical shift value at 6.2–6.3 ppm is due to the NH protons of [—$CONH_2$]. The protons of the aliphatic —CH=CH— of [—$CO(CH_2)_7CH$=$CH(CH_2)_7CH_3$] appeared at 5.87 ppm. And the chemical shift value at 1.22 ppm was assigned to the —CH_3 protons of [—$CO(CH_2)_7CH$=$CH(CH_2)_7CH_3$]. The protons of the aliphatic —CH_2— of polymeric chain appeared at 1.66–1.64 ppm. The proton of the aliphatic —CH— of polymeric chain appeared at 2.24 ppm. And the characteristic peak due to —CH— of the hexatomic ring of β-CD was observed at 5.70 and 3.70 ppm. The ^1H NMR spectrum of AM/AA/AOAB/*N*-β-CD in Fig. 3c indicated the similar characteristic peaks to AM/AA/AOAB/*O*-β-CD. And the distinct peak at 7.84 ppm due to NH protons of [—$NHCHCH_2$] (the substituent group of *N*-β-CD). Due to the synthesis method (NaOH was used to regulate the pH), the OH protons of [—COOH] could not be found. Since the loading of monomer (*N*-β-CD or *O*-β-CD) was quite low, the typical peaks of copolymer were not obvious.

3.4. Microcosmic configuration analysis by SEM

The scanning electron microscopy images of HPAM, AM/AA/AOAB/*O*-β-CD, and AM/AA/AOAB/*N*-β-CD solutions were shown in Fig. 4. Among these images, Fig. 4a–c were HPAM solution at different scan sizes (50 μm, 2000×; 40 μm, 2500×; 100 μm, 1000×; respectively). Fig. 4d (50 μm, 2000×), Fig. 4e (20 μm, 5000×), and Fig. 4f (10 μm, 10,000×) were images of copolymer AM/AA/AOAB/O-β-CD solution. Similarly, the images of copolymer AM/AA/AOAB/*N*-β-CD solution were displayed in Fig. 4g (50 μm, 2000×), Fig. 4h (20 μm, 5000×), and Fig. 4i (10 μm, 10,000×). Significantly reticular structures could be found in every image; however, we could also observe that in the same scan size copolymers' microcosmic nets are much more compact than those of HPAM, for instance, the comparison of Fig. 4a, d and g. Comparing images of the obtained copolymers, much denser networks could be found in than AM/AA/AOAB/*N*-β-CD which could be the proof of higher thickening ability of AM/AA/AOAB/*O*-β-CD. These remarkable networks make it possible to be excellent EOR chemicals by accelerating the apparent viscosity of displaying fluid for the synthesized copolymers.

3.5. The intrinsic viscosity of copolymers

Carrying the measurement of intrinsic viscosity as the previous experimental plan, the results of final copolymers AM/AA/AOAB/*N*-β-CD and AM/AA/AOAB/*O*-β-CD were

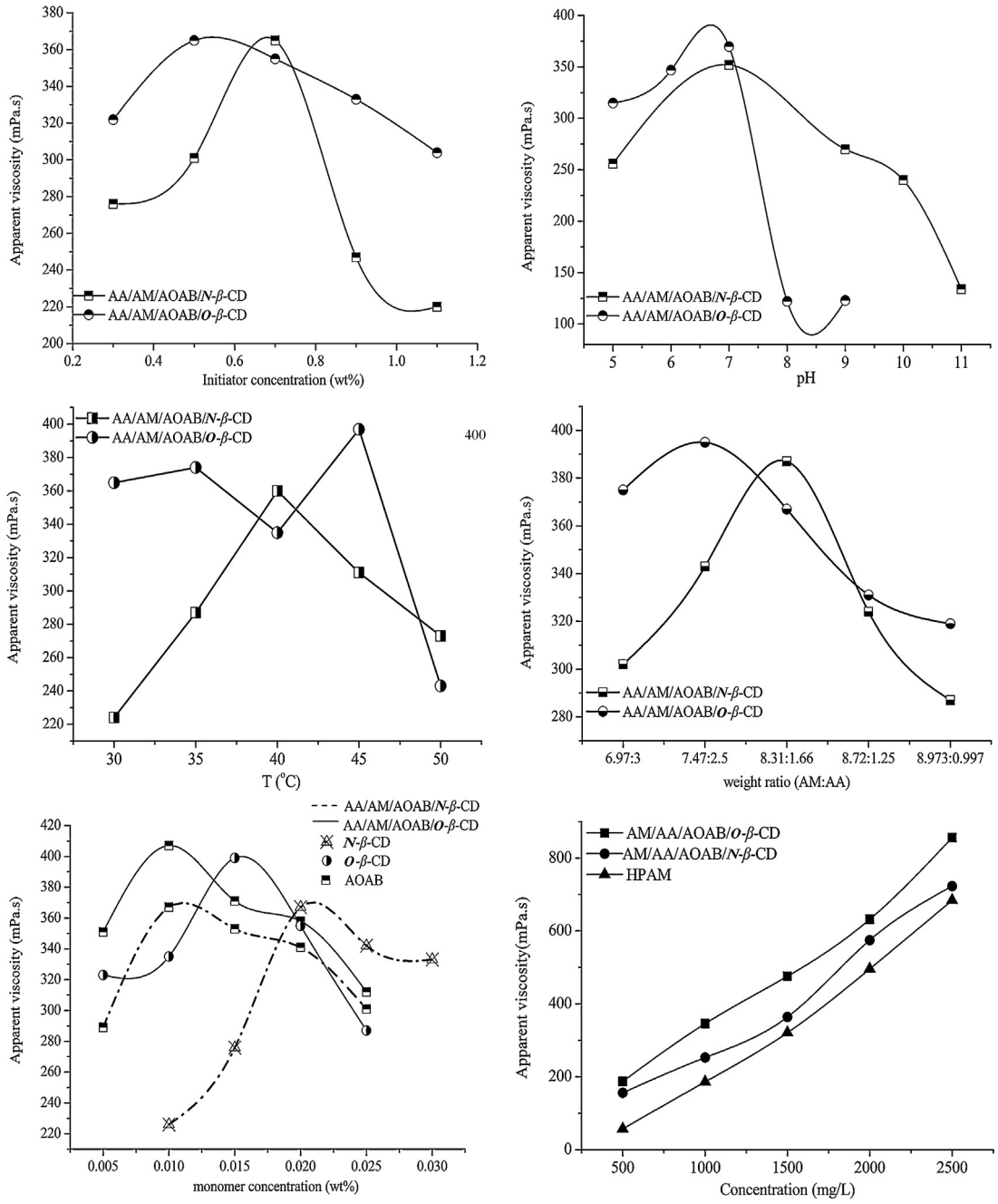

Fig. 2. The effects of optimal synthesis conditions on copolymerization.

922.42 mL/g and 537.09 mL/g, respectively (for the details, see supporting information).

3.6. Effect of temperature, shear rate, and salt on the apparent viscosity

The influences of temperature, shear rate, and salt on apparent viscosity of aqueous solutions of AM/AA/AOAB/*O*-β-CD, and AM/AA/AOAB/*N*-β-CD were carried out. The results were shown in Fig. 5.

The temperature-resistance and shear-resistance were investigated by HAAKE RheoStress 6000 rotational rheometer (Fig. 5a and b). Comparing with HPAM, we could easily find that the obtained copolymers own better anti-temperature and anti-shear abilities. The data indicated that AM/AA/AOAB/*N*-β-CD could withstand higher temperature and higher shear rate. This characteristic may be explained by the cavity structure of β-CD which can improve the thermal ability of copolymer and the long carbon chain of AOAB which can sustain high shear stress.

The ability against Na^+ of synthesized copolymers was shown in Fig. 5c and the long term stability in brine (10,000 mg/L) at 100 °C was shown in Fig. 5d. The salt-tolerance of AM/AA/AOAB/*O*-β-CD and AM/AA/AOAB/*N*-β-CD was much more excellent than HPAM and the long term stability tests indicated that the apparent viscosity of copolymer solution in brine at 100 °C would decrease for 6 days and then remain unchanged with high viscosity retention rate (about 62%) while HPAM could not tolerate high temperature and long time with 15% viscosity retention.

The tests about Ca^{2+} and Mg^{2+} (2000 mg/L, 100 °C) gave similar phenomena (Fig. 5e and f). These results reveal that synthesized

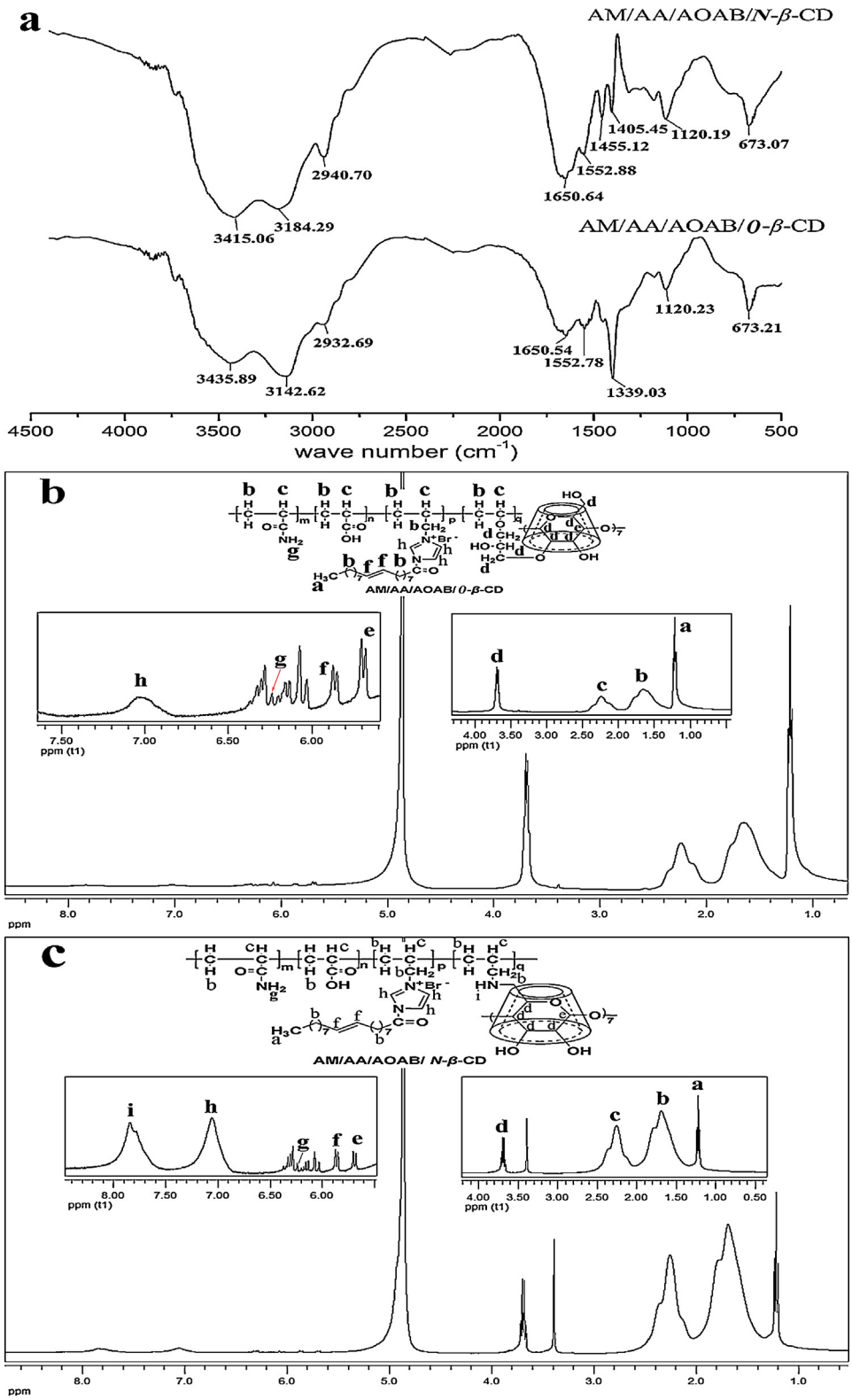

Fig. 3. (a) IR spectra of copolymers AM/AA/AOAB/*N*-β-CD and AM/AA/AOAB/*O*-β-CD; (b) ^{1}H NMR spectrum of AM/AA/AOAB/*O*-β-CD in D_2O; (c) ^{1}H NMR spectrum of AM/AA/AOAB/*N*-β-CD in D_2O.

copolymer can withstand high temperature and salinity. And this may be related to the long carbon-chain units on the chain of copolymer. Since the presence of salt causes a shielding of the electrostatic interactions and thus a collapse of the network with total loss of the solution viscosity. In this work, the solubility of the hydrophobic group of AOAB decreases with increasing salt concentration. This leads to the formation of aggregates, which enhances the interactions between the polymeric chains. The intermolecular association is enhanced leading to a stronger network and thus increased solution viscosity which represents better salt resistance.

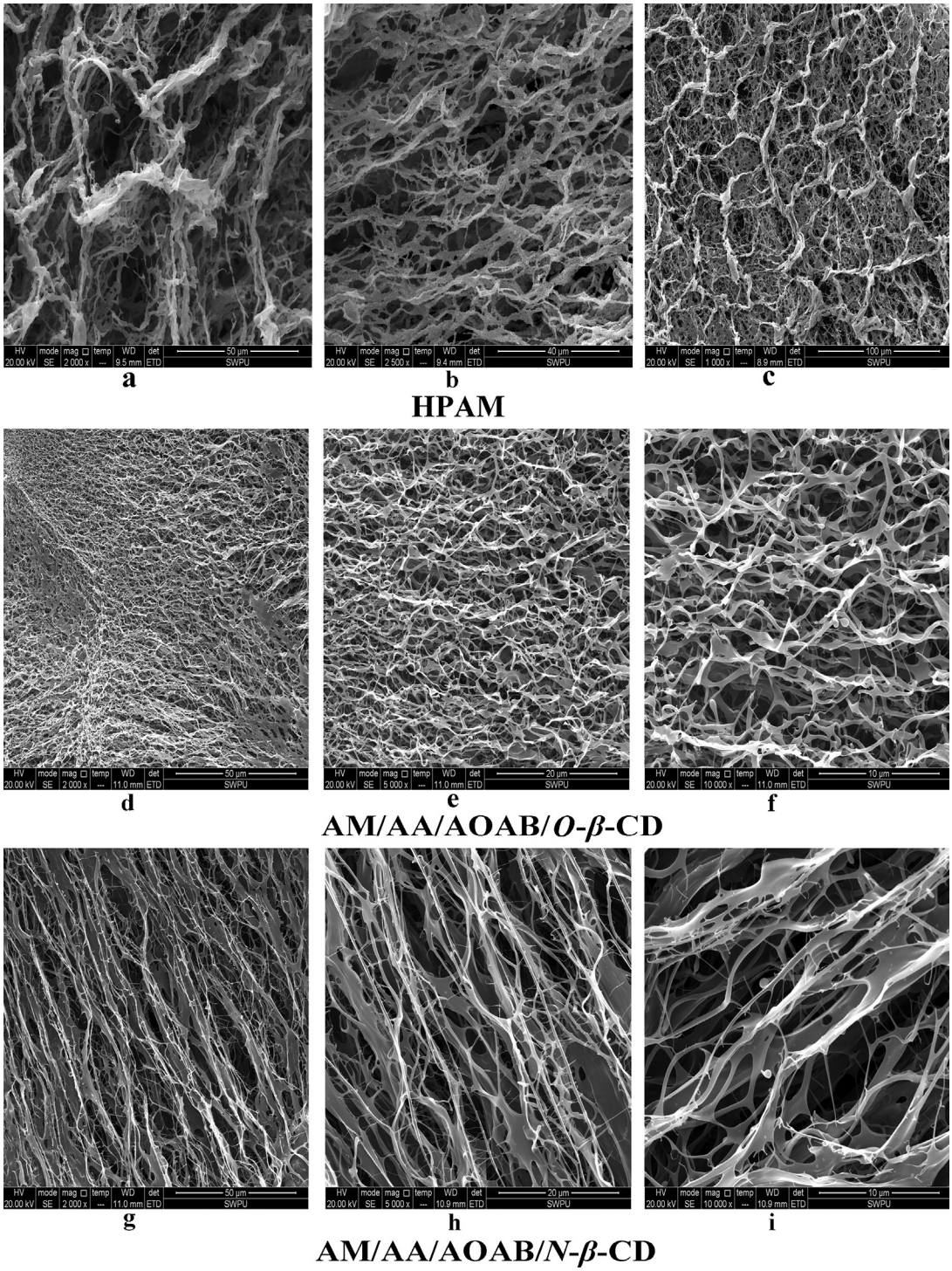

Fig. 4. The SEM images of polymers: (a) HPAM solution at 50 μm, 2000×; (b) HPAM solution at 40 μm, 2500×; (c) HPAM solution at 100 μm, 1000×; (d) AM/AA/AOAB/*O*-*β*-CD solution at 50 μm, 2000×; (e) AM/AA/AOAB/*O*-*β*-CD solution at 20 μm, 5000×; (f) AM/AA/AOAB/*O*-*β*-CD solution at 10 μm, 10,000×; (g) AM/AA/AOAB/*N*-*β*-CD solution at 50 μm, 2000×; (h) AM/AA/AOAB/*N*-*β*-CD solution at 20 μm, 5000×; (i) AM/AA/AOAB/*N*-*β*-CD solution at 10 μm, 10,000×.

3.7. Core flood analysis

The core flood device and results were displayed in Fig. 6. Compared with water flooding and HPAM flooding, AM/AA/AOAB/*N*-*β*-CD and AM/AA/AOAB/*O*-*β*-CD could enhance oil recovery significantly. In addition, comparing Fig. 6a with Fig. 6b, EOR effect of AM/AA/AOAB/*N*-*β*-CD was better than AM/AA/AOAB/*O*-*β*-CD which was 18.3–12.5%.

3.8. Effect of copolymer solutions on the crystalline interspace of MMT

Since the crystalline interspace of MMT would increase after hydration and swelling compared with dry MMT, the application of EOR chemicals might lead to dispersion and migration of clay minerals which would plug the pore in formation resulting in decrease of oil recovery (Liu, Jiang, Gou, Ye, & Xie, 2012;

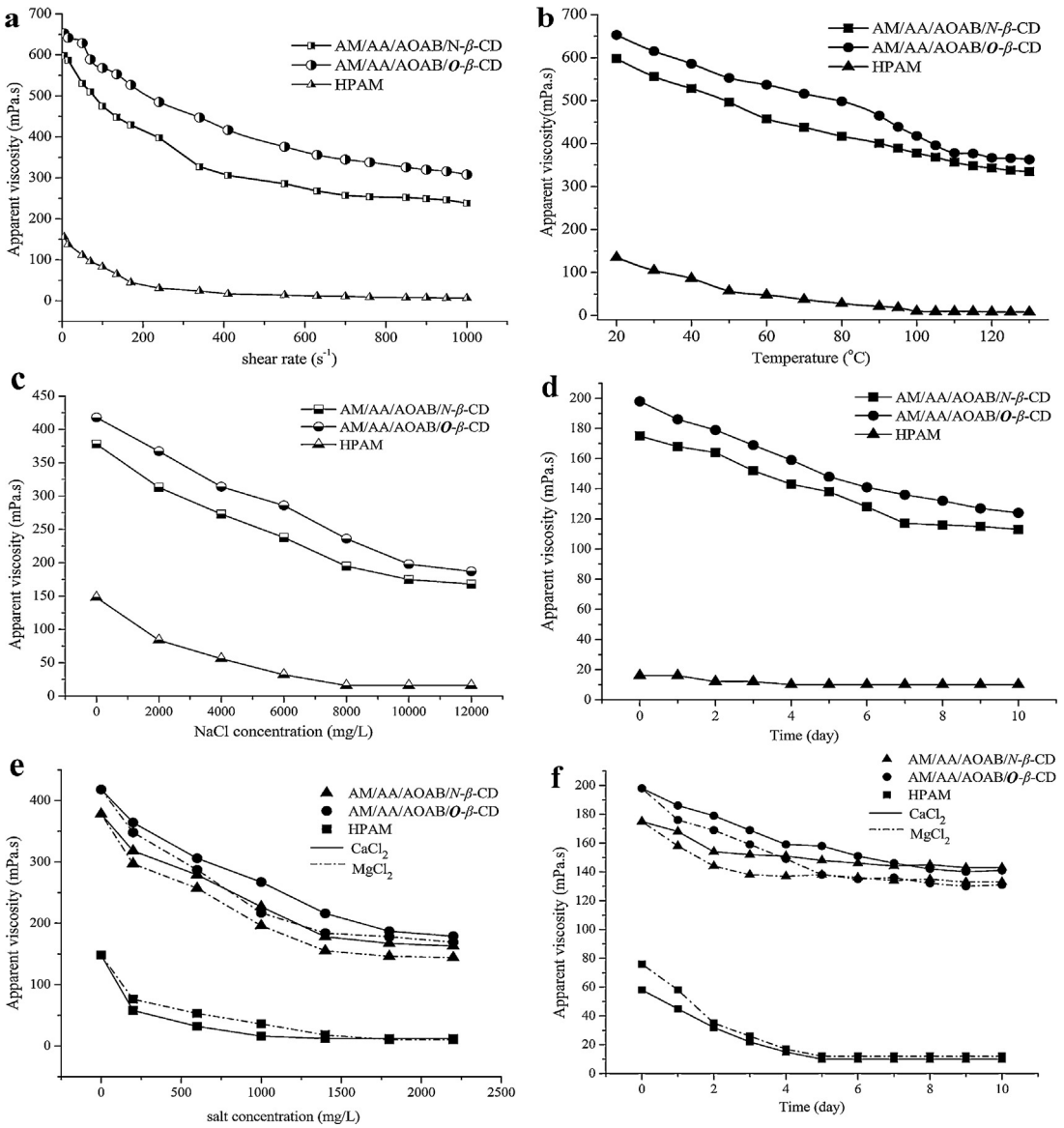

Fig. 5. (a) Effect of temperature on apparent viscosity; (b) effect of shear rate on apparent viscosity; (c) effect of NaCl on apparent viscosity; (d) long-term stability of copolymers in the presence of 10,000 mg/L NaCl at 100 °C for 10 days; (e) effect of $CaCl_2$ and $MgCl_2$ on apparent viscosity; (f) long-term stability of copolymers in the presence of 2000 mg/L $MgCl_2$ and/or $CaCl_2$ at 100 °C for 10 days.

Liu, Yuan, Liu, & Wu, 2011). The crystalline interspaces of MMT were investigated by X-ray diffractometry in different aqueous formulation of polymer. The result of XRD analysis was displayed in Table 1 and Fig. 7.

According to the data in Table 1, the obtained copolymers could stabilize MMT by preventing it from swelling resulting in reduction of crystalline interspace compared with condition of pure water. Comparing entries 2, 6 and 10 in Table 1, we could obviously find that the crystalline interspace of MMT had been decreased by copolymer solution from 18.9532 Å to 16.6657 Å and 16.0345 Å. What's more, the compound of salt (KCl, $CaCl_2$ and $MgCl_2$) and copolymers could exhibit more excellent clay stabilization of MMT. It was found that AM/AA/AOAB/*N*-β-CD and AM/AA/AOAB/*O*-β-CD had significantly inherent abilities of anti-swelling. According to Fig. 7, the peaks of MMT-copolymers were all between MMT and MMT-water which indicated that copolymer solutions could inhibit clay swelling. Especially, copolymers with $CaCl_2$ could afford better results than the previous researches (Liu, Jiang, Gou, Ye, & Luo, 2012; Liu, Jiang, Gou, Ye, & Xie, 2012; Liu et al., 2011).

Table 1
The clay stabilization results of obtained copolymers by XRD.

Entry	Formulation	Crystalline interspace (Å)[c]
1	MMT	12.6339
2	MMT-pure water	18.9532
3	MMT-KCl (10 wt%)	15.4582
4	MMT-$CaCl_2$ (10 wt%)	18.1523
5	MMT-NaCl (10 wt%)	15.8745
6	MMT-AM/AA/AOAB/*O*-β-CD[a]	16.6657
7	MMT-AM/AA/AOAB/*O*-β-CD[a]-KCl (10 wt%)	15.2804
8	MMT-AM/AA/AOAB/*O*-β-CD[a]-$CaCl_2$ (10 wt%)	17.6657
9	MMT-AM/AA/AOAB/*O*-β-CD[a]-NaCl (10 wt%)	15.7628
10	MMT-AM/AA/AOAB/*N*-β-CD[b]	16.0345
11	MMT-AM/AA/AOAB/*N*-β-CD[b]-KCl (10 wt%)	15.1346
12	MMT-AM/AA/AOAB/*N*-β-CD[b]-$CaCl_2$ (10 wt%)	16.8723
13	MMT-AM/AA/AOAB/*N*-β-CD[b]-NaCl (10 wt%)	16.3568

[a] AM/AA/AOAB/*O*-β-CD: 2000 mg/L copolymer AM/AA/AOAB/*O*-β-CD solution.
[b] AM/AA/AOAB/*N*-β-CD: 2000 mg/L copolymer AM/AA/AOAB/*N*-β-CD solution.
[c] Crystalline interspace: tested by X-ray diffraction in small angle scattering.

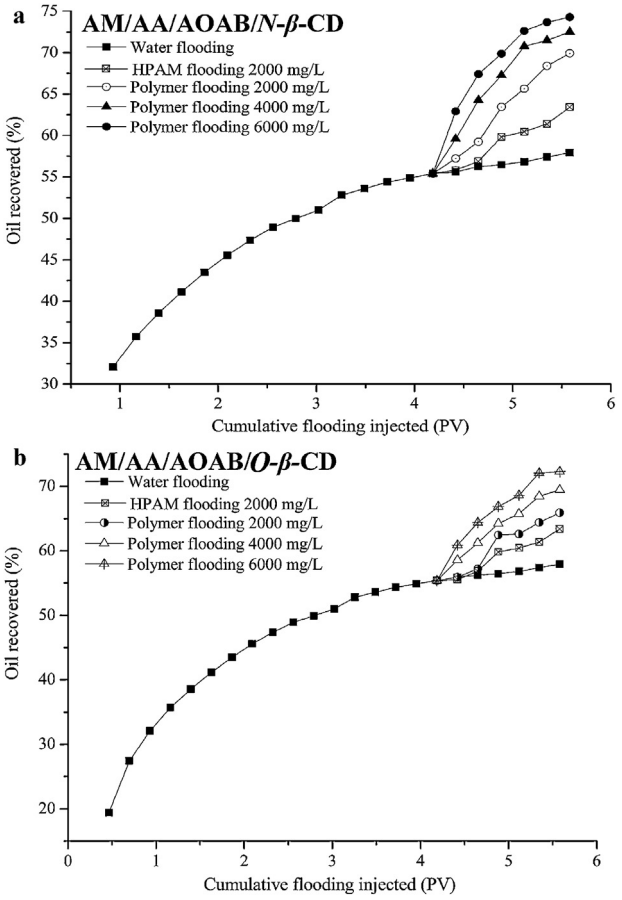

Fig. 6. (a) EOR result of copolymer AM/AA/AOAB/*N*-β-CD at 60 °C; (b) EOR result of copolymer AM/AA/AOAB/*O*-β-CD at 60 °C.

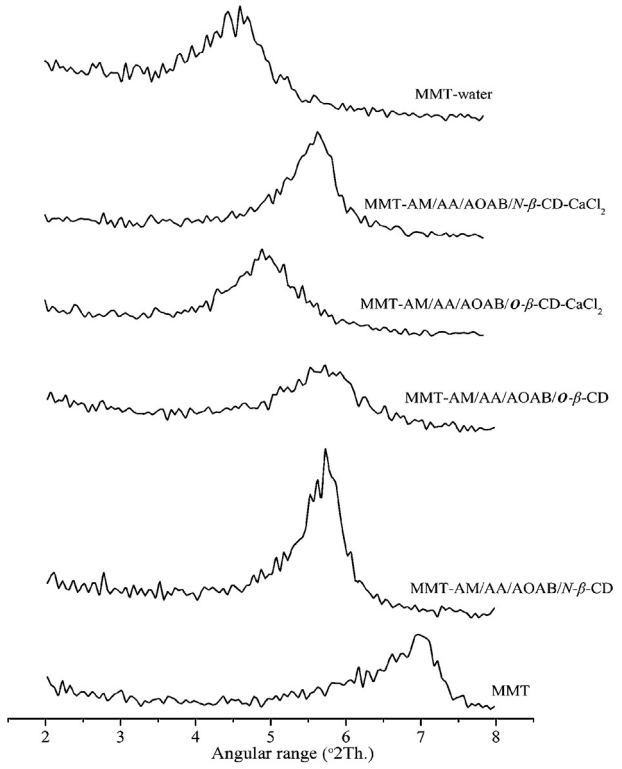

Fig. 7. XRD results of MMT in different conditions.

4. Conclusions

β-Cyclodextrin derivatives and 1-llyl-3-oil acyloxyimidazole-1-ammonion bramide have been successfully copolymerized onto PAM chain by using redox system as initiator in aqueous medium. Compared with HPAM the viscosity, heat-resistance, shear-resistance, salt-resistance and long-term stability of synthesized copolymers are improved greatly. The core flood test results indicate that AM/AA/AOAB/*N*-β-CD and AM/AA/AOAB/*O*-β-CD can afford enhanced oil recovery about 18.3% and 12.5% respectively compared with water flooding and HPAM flooding. XRD investigations prove that AM/AA/AOAB/*N*-β-CD and AM/AA/AOAB/*O*-β-CD will not worsen the swelling and migration of MMT but inhibit the progress since the crystalline interspaces was reduced from 18.9 Å to 15.3 Å.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.03.053.

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