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Synthesis and evaluation of a novel hydrophobically associating polymer based on acrylamide for enhanced oil recovery

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A novel polymerizable hydrophobic monomer 1-(4-dodecyloxy-phenyl)-propenone (DPP) was synthesized by esterification, Frise rearrangement and Williamson etherification; then, the obtained DPP was copolymerized with 2-(acrylamido)-dodecanesulfonic acid (AMC₁₂S) and acrylamide (AM) initiated by a redox initiation system in an aqueous medium to enhance oil recovery (EOR). AM/AMC₁₂S/DPP (PADP) was characterized by FT-IR, ¹H NMR spectroscopy, environmental scanning electron microscopy (ESEM), DSC-TG, fluorescent probe, core flood test, etc. Results of ESEM and fluorescent probe indicate that hydrophobic microdomains and associating three-dimensional networks were formed in the aqueous solution of PADP. Results of DSC-TG demonstrated that long carbon chains, aromatic groups and sulfonic groups were incorporated into the PADP polymer, which can lead to a significant increase of the rigidity of molecular chains. Performance evaluation of experiments showed superior properties in regard to temperature-tolerance, shear-tolerance and salt-tolerance. In the Sandpack Flooding Test, PADP brine solution showed a significant increase in EOR at 65° C because of its high thickening capability. All these features indicate that PADP has a potential application in EOR at harsh conditions. (© 2015 Institute of Chemistry, Slovak Academy of Sciences

Keywords: 1-(4-dodecyloxy-phenyl)-propenone, associating, acrylamide, enhanced oil recovery, hydrophobically associating polymer

Introduction

Polymer flooding is one of the most efficient ways to enhance oil recovery (EOR), and partially hydrolyzed polyacrylamide (HPAM) is the most frequently used compound in EOR (Samanta et al., 2010; Veerabhadrappa et al., 2013). In the process of chemical flooding, HPAM showed a series of useful abilities including viscoelasticity, thickening and rheological capability. However, the poor salt tolerance, low shear resistance and poor temperature resistance limit the application of traditional polyacrylamide in highsalinity or high-temperature oil reservoirs (Thomas, 2008; Zhou et al., 2011; Zou et al., 2013). Consequently, in order to exploit this kind of harsh reservoirs, a novel water-soluble acrylamide polymer system with high temperature, salt and shear resistance becomes the focus of world-wide oil industry scientists. In recent decades, many researches (Hourdet et al., 2013; Roy et al., 2014) have suggested that hydrophobically associating acrylamide copolymers consisting of hydrophobic side groups are a novel class of water-soluble polymers offering a more satisfying polymer with higher thickening capability, and better

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Fig. 1. Preparation of 1-(4-dodecyloxy-phenyl)-propenone (III).

salt, shear and temperature resistance. By introducing a very low amount of hydrophobic groups to polyacrylamide, the copolymer chain assemble together to generate a transitory three-dimensional network at certain polymer concentration through strong intermolecular hydrophobic interactions, thus providing particular transient rheological properties (Siano et al., 1989). A considerable number of publications has been reported regarding the hydrophobically watersoluble polymers with potential applications, including those associated with agriculture (Koromilas et al., 2014), water treatment (Volpert et al., 1998), cosmetics (Jiménez-Regalado et al., 2000) and oil industry (Wu et al., 2006; Bera et al., 2014a).

Surface-active monomer (surfmer), which contains a hydrophobic-tail or a head group and polymeric vinyl double bonds, has been widely used in biological simulations, cereals and water-soluble hydrophobically associating polymers. However, the ester and amide monomers can be hydrolyzed under alkali conditions limiting their utilization (Stähler et al., 1998; Zhu et al., 2006; Friedrich et al., 2011). Thus, research on molecules containing a phenyl monomer may be worthy as hydrolyzation of phenyl in alkali and acidic solutions was not observed. The group is a hydration group with a large steric hindrance and its particular structure makes it insensitive to high temperatures (Eastoe et al., 2001). Consequently, hydrophobically associating polymers containing a sulfonic group have superior salt and temperature resistance properties (Nishida et al., 2010; Morales & Rivas, 2015).

In the present work, hydrophobic monomer 1-(4-dodecyloxy-phenyl)- propenone (DPP) and polar monomer 2-(acrylamido)-dodecanesulfonic acid (AMC₁₂S) were synthesized. Then, they were copolymerized with AM to synthesize a hydrophobically associating polymer (PADP) by introducing phenyl ether hydrophobic groups, long chain and sulfonic groups to AM. Where AM acts as the backbone, DPP as a functional monomer for the preparation of a hydrophobically associating copolymer, AMC₁₂S as a hydration monomer to ensure the formation of a water-soluble hydrophobically associating polymer with salt, shear and temperature resistance. The two monomers and the water-soluble hydrophobically associating polymer were characterized by FT-IR and ¹H NMR spectroscopy, PADP was also characterized by ESEM, a fluorescent probe, DSC-TG and the sandpack flooding test (SFT).

Experimental

Dimethylformamide (dried over calcium hydride for 1 day and then distilled under reduced pressure prior to use), 1-dodecene (95 mass %), acrylamide, acrylic acid, SOCl₂, AlCl₃, CS₂, (NH₄)₂S₂O₈, KOH, NaOH, NaHSO₃, 1-bromododecane, acrylonitrile, acetic anhydride, ethyl alcohol (absolute) and phenol, were all of analytical reagent grade and purchased from Kelon Chemical Reagent Factory (Chengdu, China).

Preparation of 1-(4-dodecyloxy-phenyl)propenone (DPP)

DPP was prepared from phenol, thionyl chloride, acrylic acid, aluminum trichloride, carbon disulfide, bromododecane and dimethylformamide by the procedure described below (see Fig. 1). I and II were prepared based on the reported method (Ma et al., 2014). III was prepared as follows: in a dry flask fitted with a reflux condenser and a sealed stirrer unit, 29.6 g (0.2 mol) of the product of the previous step, 49.8 g (0.2 mol) of bromododecane and 100 mL of dimethylformamide (DMF) were placed under argon atmosphere at room temperature. Then, the mixture was stirred at $150 \,^{\circ}$ C for 10 h. The reaction mixture was gradually warmed to room temperature and stirred for additional 2 h. The solvent was removed on a rotary evaporator, and the mixture was washed thoroughly with water and extracted with ether. The organic layer was collected and dried using MgSO₄ overnight, filtered and the solvent was evaporated. DPP (56 %), isolated in form of white crystals, did not require further purification. DPP: ¹H NMR (400 MHz, CDCl₃), δ: 1.48–1.52 (m, 3H, CH₃), 1.58 (s, 20 H, $CH_2(CH_2)_{10}CH_3$), 1.69 (s, 2H, PhOC H_2), 5.71 (s, 1H, H—C*H*=), 5.59 (s, 1H, *H*—CH=), 5.9 (s,



Fig. 2. Preparation of 2-(acrylamido)-dodecanesulfonic acid (AMC₁₂S).



Fig. 3. Preparation of the AM/AMC₁₂S/DPP copolymer (PADP).

1H CH₂=C*H*), 5.95–6.22 (m, 4H, aromatic ring). IR (KBr), $\tilde{\nu}$ /cm⁻¹: 1045, 1202, 1467, 1597, 1679, 2851, 2927.

Preparation of 2-(acrylamido)dodecanesulfonic acid $(AMC_{12} S)$

 $AMC_{12}S$ was prepared by the following procedure (see Fig. 2) (Gao et al., 2007a): acrylonitrile (2 g), 1dodecene (4 g) and acetic anhydride (1 g) were added to a 100 mL three-necked flask fitted with a reflux condenser and a constant funnel. When the temperature of the flask decreased to -5 °C, sulfur trioxide (4 g, 20 %) was slowly added into the flask using the constant funnel. During the dropwise addition, the temperature could not exceed 0 °C. After the dropwise addition was completed, stirring was continued for 30 min at low temperature. Then, the mixture was stirred at 25 °C for 24 h. The resulting product was isolated by filtration, washed with a large amount of acetone and white powder samples of $AMC_{12}S$ were obtained. AMC₁₂S: ¹H NMR (400 MHz, CDCl₃), δ : 0.735–0.767 (m, 3H, C H_3 CH₂(CH₂))₇CH₂CH), 1.236 (s, 2H, $CH_3CH_2(CH_2))_7CH_2CH$), 1.155 (s, 14H, CH₃CH₂(CH₂))₇CH₂CH), 1.511–1.545 (m, 2H, $CH_3CH_2(CH_2)_7CH_2CH$, 3.026–3.125 (m, 1H, CH₃) $CH_2(CH_2)_7CH_2CH$, 2.99 (d, 2H, $CHCH_2SO_3H$), 2.95 (m, 1H, CHCH₂SO₃**H**), 6.249–6.291 (m, 1H, $CHNH(O)CHCH_2)$, 6.147 (d, 1H, J = 16.4Hz, $CHNH(O)CHCH_2)$, 5.721 (d, 2H, J = 9.6 Hz, CHNH(O)CHC H_2). IR (KBr), $\tilde{\nu}$ /cm⁻¹: 721, 1103, 1620, 1654, 3085, 3286.

Preparation of PADP

The PADP terpolymer was synthesized by redox free radical copolymerization (see Fig. 3). Appropriate amounts of DPP (0.240 g) and AMC₁₂S (0.638 g)were dissolved in deionized water (19.665 g). pH was adjusted to the indicated value of 7-8.5 using a 30 mass % NaOH solution. The mixture was stirred for about 10–15 min, AM was added to the flask under stirring at constant temperature and nitrogen atmosphere for approximately 30–35 min. Then, the initiator, $K_2S_2O_8/NaHSO_3$ (1.1–1.4 : 1, eq.), aqueous solutions with the initiator concentration of 0.2 mass % relative to the total monomer amount were added. Polymerization was carried out at 45 °C for approx. 4.5–6 h under stirring. The resulting products were obtained by repeated washing with ethanol to remove monomers and the initiator. PADP was further dried in a vacuum oven at $40 \,^{\circ}$ C for 24 h.

Characterization

¹H NMR spectra were measured on a Bruker AV-400 nuclear magnetic resonance spectrometer with chemical shift values in ppm downfield from TMS using CDCl₃ as solvents. FT-IR spectra of products were acquired via a WQF-520 Fourier transform infrared spectrometer in the optical range of 4500– 400 cm⁻¹. DSC-TG was carried out on a STA-409 Simultaneous DSC-TG instrument under nitrogen flow (100 mL min⁻¹) with the heating rate of 10 °C min⁻¹. Environmental scanning electron microscopy (ESEM) analysis of PADP solutions was obtained with a FEI Quanta 450 (FEI, USA), in the magnifying multiple ranges from $3 \times$ to $30000 \times$, the copolymer was dissolved in degassed and distilled water forming a solution (mass $\% \approx 5$ g L⁻¹). The images were obtained at 120–500 Pa and the acceleration of 20 kV.

Intrinsic viscosity measurement

Intrinsic viscosity (η) of PADP was determined by an Ubbelohde viscometer at the constant temperature of (30.0 ± 0.1) °C in a 1.0 M NaCl aqueous solution, and the relative and specific viscosities of copolymer solutions at different concentrations were measured. Viscosity average molecular mass of PADP was obtained from the intrinsic viscosity value by employing the Mark–Houwink equation together with the dilution extrapolation method (Zou et al., 2014).

Apparent viscosity measurement

Apparent viscosity studies were conducted on a rotational viscometer (NDJ-79/7, the range of $1-10^6$ mPa, Shanghai Changji Geological, China) at $25 \,^{\circ}$ C. In the process, polymer samples were weighed accurately, swelled in distilled water and left at a constant temperature for 24 h to make sure the polymers can dissolve entirely.

Fluorescence spectroscopy

The appropriate amount of pyrene (10.112 mg) was added into a 50 mL volumetric flask and diluted to the mark to 10^{-3} M with methanol. A certain amount of polymer and 250 µL of pyrene stock solutions were added to a 50 mL volumetric flask, the mixture was diluted to different concentrations with deionized wa-





Fig. 4. IR spectrum of DDP, AMC₁₂S, PADP (a), scheme of PADP (b) and ¹H NMR spectra of PADP (c).



Fig. 5. ESEM images of copolymers: PADP, $1000\times$, scale bar $100 \ \mu m$ (a), PADP, $2000\times$, scale bar $50 \ \mu m$ (b); PADP, $5000\times$, scale bar $20 \ \mu m$ (c); PADP, $10000\times$, scale bar $10 \ \mu m$ (d) (polymer concentration = 5 g L⁻¹).

ter. The pyrene solution was stirred for 48 h before the fluorescence measurements were made. Fluorescence spectroscopy measurements were conducted on an F-4500 spectrofluorimeter at 25 °C, using 5 nm bandpass settings for emission and excitation, respectively. The excitation wavelength was 335 nm, and the scanning range was 350–550 nm. Pyrene was used as the fluorescent probe (Gao et al., 2007b).

Results and discussion

Characterizations

Purified DPP, AMC₁₂S and PADP were prepared in KBr pellets and characterized on a Fourier transform infrared spectrometer. Structures of the functional monomer and copolymer were confirmed by IR spectra as illustrated in Fig. 4. Functional monomer DPP was confirmed by strong absorptions at 2927 cm⁻¹ (Ar—H stretching vibration), 1679 cm⁻¹ (C=O stretching vibration), 1597 cm⁻¹ (C=C stretching vibration), 1200 cm⁻¹ (C-O-C stretching vibration) in its IR spectra. Pure AMC₁₂S exhibited a very strong absorption at 3286 cm⁻¹, 1597 cm⁻¹, 1100 cm⁻¹, which reflect the N—H, C—C and SO₃H stretching vibrations, respectively. PADP has both functional groups of DPP and AMC₁₂S, and the C—C was not detected in the IR spectrum. The IR spectrum showed that the polymer was successfully synthesized.

¹H NMR of PADP is shown in Fig. 4. The chemical shift at 1.04 ppm was assigned to the long chain methyl protons (j). The chemical shift at 1.52 ppm was ascribed to the methylene (a, i) protons of —CH₂CH₃. The protons of —CH==C(O) (b, d) appeared at 1.63 ppm and 1.64 ppm. The chemical shift at 3.38 ppm was assigned to the —CH protons of —CH—NH (l). The protons of —CH₂—SO₃H (m) appeared at 3.49 ppm and those of Ar—O—CH₂ (h) appeared at 3.54 ppm. The chemical shift at 5.70 ppm was assigned to the NH (e) protons of —CONH₂. The protons of Ar (f) appeared at 6.88–6.90 (J = 8 MHz) and the chemical shift at 7.61–7.69 (J = 38 MHz) was assigned to the protons of Ar (g).



Fig. 6. DSC and TG of PADP.

ESEM images provided in Fig. 5 reveal that an obvious gel-network microstructure of PADP was formed and is clearly visible. The microscopic nets indicated that intramolecular and intermolecular interactions are accrued during the copolymerization process (Patterson et al., 2013; Zhu et al., 2014). Hydrophobic interactions between copolymers due to the hydrophobic bonds of DPP, sulfonamide structures of AMC₁₂S and amide groups of AM were also observed.

DSC-TG (Casarano et al., 2009) was used to investigate the thermal stability of copolymers and the thermal gravimetric curve is presented in Fig. 6.

The diagram in Fig. 6 suggests that the process of weight loss can be divided into four main steps. To begin with, in the range of 25-128 °C, the weight decreased by about 14.34 mass % because of the evaporation of intermolecular and intramolecular moisture combined with oxygen. In the second step, in the range of 128-250 °C, with a mass loss of 8.25 % can be divided into two parts: i) a gentle decrease from $128 \,^{\circ}{\rm C}$ to $210 \,^{\circ}{\rm C}$ corresponding to the evaporated water combined with the sulfonamide structure and amide groups through hydrogen bonds; ii) a rapid decrease in the 210–250 $^{\circ}\mathrm{C}$ temperature range which can be ascribe to the decomposition of amide groups. The third step occurred between 250–420 °C, where the C—C backbone and the side chains began to fracture resulting in a PADP decomposite and with the significant loss of 35.65 mass %. The main structure was destroyed mostly in the fourth stage at temperatures above 420 °C.

Intrinsic viscosity measurements of PDAP

Intrinsic viscosity of PADP at five different concentrations (250 µg L⁻¹, 330 µg L⁻¹, 500 µg L⁻¹, 670 µg L⁻¹, 1 mg L⁻¹) was measured using a Ubbelohde viscometer. The solvent efflux time was over 100 s reproducible to 0.2 s. At each concentration, reduced viscosity (η_{sp}/c) and inherent viscosity ($\ln(\eta_r/c)$) were



Fig. 7. Intrinsic viscosity of PADP.

both determined from the apparent viscosity of PADP. The η was obtained by extrapolation of the plot of reduced specific viscosity $(\eta_{\rm sp}/c)$ vs. concentration to the concentration of 0 µg L⁻¹. To obtain the viscosity molecular mass, the following equations have to be applied: $\eta = K M_{\eta}^{\alpha}$, where η is the intrinsic viscosity in mg L⁻¹; M_{η} is the viscosity-average molecular mass in g mol⁻¹ and K and α are constants related to the copolymer.

In this paper, the equation used is: (Zou et al., 2013). The result is shown in Fig. 7, where the intrinsic viscosity was 1147 mL g^{-1} and the viscosity molecular mass was $5.26 \times 10^6 \text{ g mol}^{-1}$.

Effect of temperature, shear rate and salt on apparent viscosity

Influence of shear rate, temperature, and salt on the apparent viscosity of PADP was studied and the results were shown in Fig. 8. Since high viscosity improves the sweep efficiency during the enhanced oil recovery, the polymers should have excellent anti-shear abilities (Pu et al., 2015). The shear resistance of PADP (3000 mg L^{-1}) and HPAM (3000 mg L^{-1}) was measured at a shear of $0-500 \text{ s}^{-1}$ at $30 \,^{\circ}\text{C}$. Fig. 8a presents the apparent viscosity versus shear rate for PADP and HPAM. Viscosity of HPAM decreased with the increase of the shear rate; however, viscosity of PADP increased with the increasing shear rate, and it reached a maximum at 0.05 s^{-1} , when it started to decrease. Following from the balance between the disassociation and intermolecular association, viscosity of PADP varied slightly, which showed a pseudoplastic behavior. Shear thickening behavior at low shear rates was attributed to the expansion of the polymer chains and the shear thinning behavior at high shear rates was due to the disruption of the hydrophobic domains. Therefore, when a PADP solution flowed through the pores of the shale



Fig. 8. Effect of shear rate on apparent viscosity (30 °C, 3000 mg L⁻¹) (a); effect of temperature on apparent viscosity (15.8 s⁻¹, 3000 mg L⁻¹) (b); effect of NaCl on apparent viscosity (15.8 s⁻¹, 30 °C, 3000 mg L⁻¹) (c); effect of CaCl₂ and MgCl₂ on apparent viscosity (15.8 s⁻¹, 30 °C, 3000 mg L⁻¹) (d).

at low shear rates, copolymer chains associated with each other via molecular interactions of hydrophobic groups to enhance oil recovery (Zhong et al., 2009).

Fig. 8b shows the impact of temperature on the apparent viscosity of PADP (3000 mg L⁻¹) and HPAM (3000 mg L⁻¹) at 15.8 s⁻¹. Viscosity of HPAM decreased with the temperature increased; however, viscosity of PADP initially increased from $25 \,^{\circ}$ C to $35 \,^{\circ}$ C, and then it decreased. The hydrophobic association behavior is an endothermic process of entropy increase in a certain temperature range. Thus, under low-temperature conditions, intermolecular associations can benefit from a temperature increase. Over $35 \,^{\circ}$ C, apparent viscosity decreased when the temperature increased due to the movement of molecular chains and the destruction of the hydration sphere of hydrophobic groups (Zhong et al., 2009).

The influence of salts (NaCl, CaCl₂ and MgCl₂) on the apparent viscosity of PADP (3000 mg L^{-1}) and HPAM (3000 mg L^{-1}) was studied at 30 °C. As

shown in Figs. 8c and 8d, apparent viscosities of PADP and HPAM displayed similar phenomena. With the increasing NaCl, $CaCl_2$ and $MgCl_2$ concentration, the hydrophobic microstructures became firm and condensed forming large aggregates, and the phase separation generated and the apparent viscosity decreased finally. However, the PADP solutions showed a better anti-salt ability than HPAM due to their higher apparent viscosity under the same conditions, which is well explained by the sturdy network structure of PADP.

Hydrophobic microdomains of PADP

A change of PADP viscosity reflected in its hydrophobic association properties, which can be illustrated by the fluorescence probe at molecular level (Deng et al., 2014). As shown in Fig. 9a, five peaks (around 368 nm, 379 nm, 390 nm, 411 nm and 436 nm) were found in the pyrene emission spectrum; the intensity ratio of the first peak to the third (I_1/I_3) is



Fig. 9. Fluorescence spectra of pyrene in PADP aqueous solution (a); I_1/I_3 ratio vs. PADP concentrations (b).



Fig. 10. Estimated oil recovery (EOR) (a) and water cut (WC) (b) vs. cumulative injection volume (CIV) capability of polymer solution at 65 °C.

sensitive to the polarity of the solution, the stronger the polarity the higher the value of (I_1/I_3) ; therefore, this property of pyrene fluorescence emission spectrum was called "polarity staff".

Fig. 9b shows the relationship between I_1/I_3 and C_p , with the following conclusions: (1) with the increasing C_p , the value of I_1/I_3 decreased continuously. At low concentrations ($C_p < 0.2 \text{ g dL}^{-1}$), the value of I_1/I_3 was close to the value of water (1.8), and only little changes with the increasing polymer concentration were observed. This information indicates that the pyrene probe was in a high polarity environment, where the distance between two macromolecules was large and only little chances in the hydrophobic groups forming hydrophobic associations

occurred at low concentrations. In addition, the electrostatic repulsion between the sulfonamide groups of the polymer chain results in extended state. (2) Values of I_1/I_3 diminished abruptly at $C_p = 0.2$ g dL⁻¹ indicating the presence of a large number of hydrophobic microdomains in the water solution. (3) After the concentration ($C_p = 0.2$ g dL⁻¹), the type of the association changed from intramolecular to intermolecular. In this case, the hydrophobic groups of polymer molecules associated with each other generated supramolecular aggregates and formed a hydrophobic microarea. (4) With the increasing polymer concentration, the number of hydrophobic domains increased gradually. As the polarity of the pyrene probe microenvironment continued to decrease, the

Entry	Polymer solution	$P_{\mathbf{w}}$	Q	$V_{\rm v}$	arphi	$S_{ m o}$	EOR
		MPa	${\rm K}\;\mu{\rm m}^{-2}$	mL	%		
1-1	HPAM	0.0025	1.7356	47	32.12	8992	6.23
2-2	PADP (0.5 g L^{-1})	0.0024	1.8223	52	35.33	89.86	11.26
3-3	PADP (1.5 g L^{-1})	0.0023	1.7769	49	33.56	89.79	15.67

Table 1. Results of sandpack flooding tests of copolymer flooding: injection pressure of the water saturation process (P_w) , permeability (Q), void volume (V_v) , porosity (φ) , oil saturation (S_o) and enhanced oil recovery (EOR)

non-polar molecules of pyrene entered the hydrophobic microarea.

Core flooding test

The core flooding tests (Samanta et al., 2011; Bera et al., 2013; Bera et al., 2014b) were employed to investigate the enhanced oil recovery ability of the copolymer (500 mg L⁻¹, $\eta = 56$ mPa s; 1500 mg L⁻¹, $\eta = 72$ mPa s) and HPAM (500 mg L⁻¹, $\eta = 43$ mPa s) solutions.

In this work, the one-dimensional sand packed model was 500 mm long with the diameter of 25 mm; η of the simulated crude oil was 45.6 mPa s at 65 °C; ISCO 260D syringe pump with the maximum injection pressure of 50 MPa, accuracy of 0.1 %. The total amount of dissolved solids was 5210 g L⁻¹, $\rho(\text{Na}^+) = 1770 \text{ mg L}^{-1}$, $\rho(\text{Ca}^{2+}) = 102 \text{ mg L}^{-1}$, $\rho(\text{Mg}^{2+}) = 17 \text{ mg L}^{-1}$, $\rho(\text{Cl}^-) = 2270 \text{ mg L}^{-1}$, $\rho(\text{CO}_3^{2-}) = 71 \text{ mg L}^{-1}$, $\rho(\text{HCO}_3^-) = 749 \text{ mg L}^{-1}$, $\rho(\text{SO}_4^{2-}) = 231 \text{ mg L}^{-1}$. Oil recovery tests were carried out according to the method published by Mandal et al. (2010) and oil recovery was determined via the following equation: , where EOR is the enhanced oil recovery in %, H_1 is the oil recovery of polymer flooding, H_2 is the oil recovery of water flooding. The parameter of cores and the results of the sandpack flooding test are shown in Table 2 and Fig. 10.

As indicated in Table 1 and Fig. 10, one of the commonly used flooding additives, PADP, provided oil recovery higher by 5.03 % than HPAM, at the same polymer concentration (500 mg L⁻¹). Furthermore, the increase of the PADP concentration (1500 mg L⁻¹) enhanced the oil recovery ratio continually up to 15.67 %. These results suggest that EOR under harsh condition is significantly improved by PADP, probably due to its supramolecular structure formed by the long carbon chains of AMC₁₂S and DPP. In conclusion, this phenomenon indicates that PADP has a potential application in enhanced oil recovery and may reduce the cost of oil industry to some extent.

Conclusions

A novel polymerizable hydrophobic monomer DPP was successfully synthesized using AMC₁₂S and AM in an aqueous medium. Results of DSC-TG indicate that the hydrophobic long carbon chains of DPP and the $-SO_3^-$ of AMC₁₂S enhance the thermal stability of copolymers. Results of systematical investigations showed that PADP possesses a series of superior properties regarding salt, temperature and shear resistance when compared with HPAM. ESEM images and the fluorescence probe revealed that an obvious gel-network microstructure of PADP is formed during the copolymerization process. In addition, the core flooding tests indicate that PADP has a potential application in enhance oil recovery(EOR) and can be used in some harsh reservoirs.

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