Electronic Supplementary Information (ESI)

Thermally stable imidazoline-based sulfonated copolymers for enhanced oil recovery

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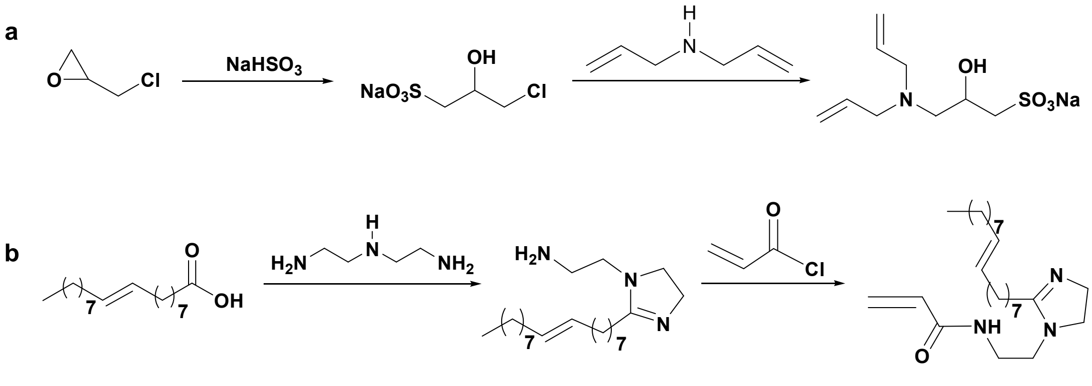
Experimental

Synthesis

Synthesis of the comonomer NDS. Another comonomer NDS was prepared by following procedure: Sodium bisulfite (9.57 g, 0.092 mol) with predissolved water (20 ml) was added into a reaction and epichlorohydrin was titrated slowly under constant stirring. After titration, the system temperature was kept to proceed at 85 ^{o}C in 2 h. The resulting pure white precipitate, which was cooled sharply below 10 ^{o}C, was recovered by recrystallization, suction filtration and dried at 45-55 ^{o}C for 10-15 h. Then the product was dissolved in 20 ml of deionized water and slowly added drop wise to the diallylamine solution with water (20 ml) for 10-20 min. The reaction system was permitted to proceed at 60 ^{o}C for 4-6 h and adjusted to alkalescent pH to maximize the reaction yield. After completion of the reaction, the precipitate was concentrated and recrystallized from methanol-water. Filtered repeatedly, then the white powdery water-soluble substance, 3-(diallyl-amino)-2-hydroxypropyl sulfonate (NDS) could be obtained through the reduced pressure distillation and dried in 10-20 h.



Scheme S1 Synthesis routes of the monomers (a) NDS and (b) ACEIM

Synthesis of copolymers PAMDSCM and PAMPSCM

The indicated amounts of raw materials AM, AA, ACEIM and NDS/AMPS were added into a flask with mechanical stirring in deionized water under an inert nitrogen atmosphere. NaOH solution was utilized to regulate the pH to a given value with magnetic stirring for 10-15 min. Copolymerization could be allowed to initiate by the addition of $(NH_4)_2S_2O_8$ and $NaHSO_3$ (molar ratio 1:1) at a stated temperature for a minimum of 6 h. The white granular copolymers, after purified repeatedly through ethanol, were dried at 45-55 ^{o}C under vacuum for approximately 8-12 h. The synthesis routes of PAMDSCM and PAMPSCM were shown in Scheme S2.

Apparent viscosity

The apparent viscosity, as one of the most important characteristic of the polymers, is dependent on the molecular weight and hydrolysis degree of the polymers. In addition, the external conditions (such as temperature, pressure and shear rate), also influence greatly the apparent viscosity of the polymers. Hence apparent viscosity of the polymers is often devoted to choose the best polymerization conditions.[1-3]

Optimal synthesis conditions of copolymerization

Variation of the viscosity of 1000 mg/L copolymers solutions with different synthesis conditions were measured by Brookfield DV-III+Pro Viscometer at room temperature at 30 °C, as shown in Fig.S1. It was found that the optimal synthesis conditions for copolymer PAMDSCM were given: the initiator concentration is 0.4 wt%; pH value of the solution is 7; the reaction temperature is 40 °C; loading of ACEIM is 1.0 wt‰; loading of NDS is 1.0 wt‰; the ratio of AM and AA on weight is 65:35. Then the result of copolymer PAMPSCM solution revealed that the maximum apparent viscosity was 309.6 mPa·s at 1000 mg/L, following the matching conditions: the initiator concentration is 0.4 wt%, pH value of the solution is 7, the reaction temperature is 35 °C, loading of ACEIM is 1.5 wt‰, the concentrations of monomer AMPS is 1.0 wt%, the ratio of AM and AA on weight is 70:30.

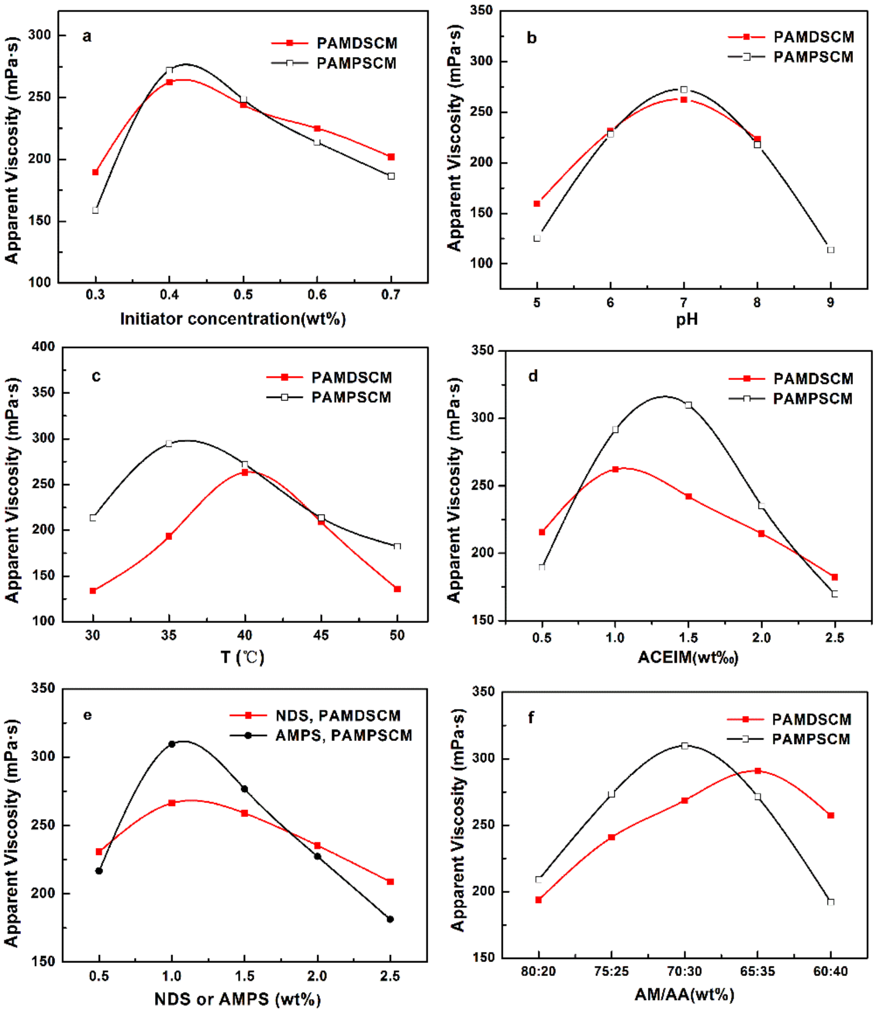


Fig. S1 The influence factors of optimum synthesis condition.

Solution preparation

A stock solution of 5000 mg/L was prepared to measure performance by dispersing dry polymer particles (HPAM and the obtained polymers) in distilled water/mineralized water at the ambient temperature (about 25 °C) and the stock polymer solutions were diluted to the desired concentrations by mechanical stirring for a minimum of 24 h under low speed. In core flooding system, the polymer solution samples were dissolved to the given concentrations in simulated formation water.

^{1}H NMR analysis

Depicted in Fig.S2 was the ^{1}H NMR spectrum of monomer NDS. The chemical shift value appeared at 5.83-5.91

ppm is assigned to the CH protons of [=C***H***CH_2N], and the characteristic peak due to the CH_2= protons of [CH_2=CHN] was detected at 5.47-5.50 ppm. Then the peak at 3.03-3.08 ppm representing the –CH– protons of [–C***H***(OH)CH_2SO_3Na]. The chemical shift value due to the –NCH_2 protons is appearing at 2.70-2.72 ppm, and the –CH_2– protons of [=$CHCH_2N$] were appointed at 3.15-3.19 ppm. The chemical shift value around 3.66-3.76 ppm is the protons of the aliphatic –CH_2– of [–C***H***$_2$ SO_3Na].

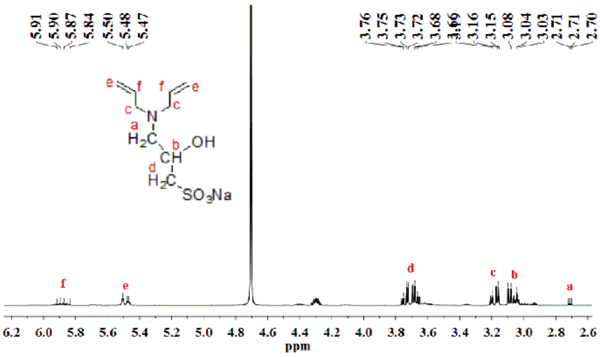


Fig. S2 ^{1}H NMR of commoner NDS

Fluorescence Investigation

Fig.S3 and Fig.S4 depicted the fluorescence spectra of 2×10^{-6} mol/L pyrene at different concentration polymers conditions, which were employed to measure the critical association concentrations of the copolymers. The ratio (I_1/I_3) of the first and the third vibronic peaks in the fluorescence spectra of pyrene could be sensitive to the micropolarity of the pyrene probe in their solubilization sites. The emission spectra of pyrene probe fluorescence sequences were in the vicinity of 372 nm, 378 nm, 382 nm, 392 nm and 412 nm, respectively.

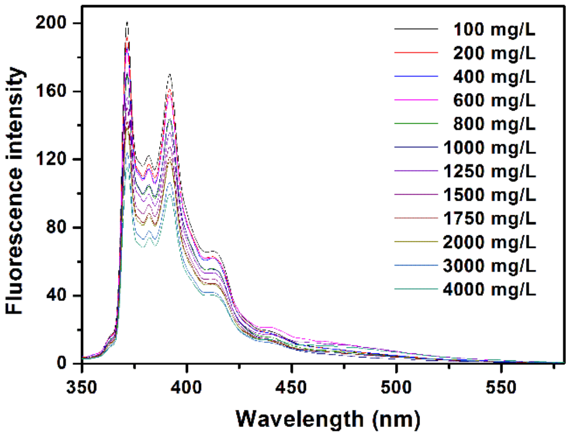


Fig. S3 Fluorescence spectra of different concentrations of PAMDSCM.

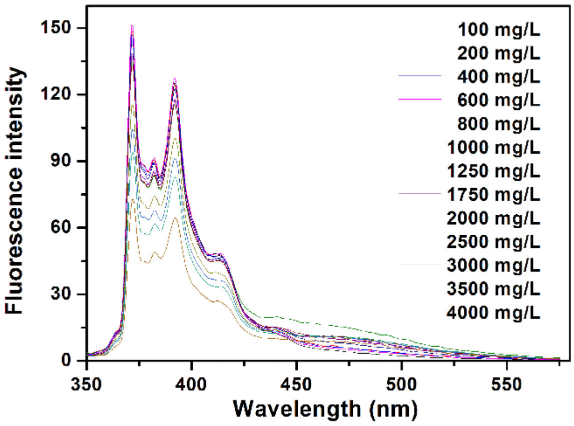


Fig. S4 Fluorescence spectra of different concentrations of PAMPSCM.

References

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