

Electronic Supplementary Information (ESI)

A novel water-soluble hydrophobically associating polyacrylamide based on oleic imidazoline and sulfonate for enhanced oil recovery

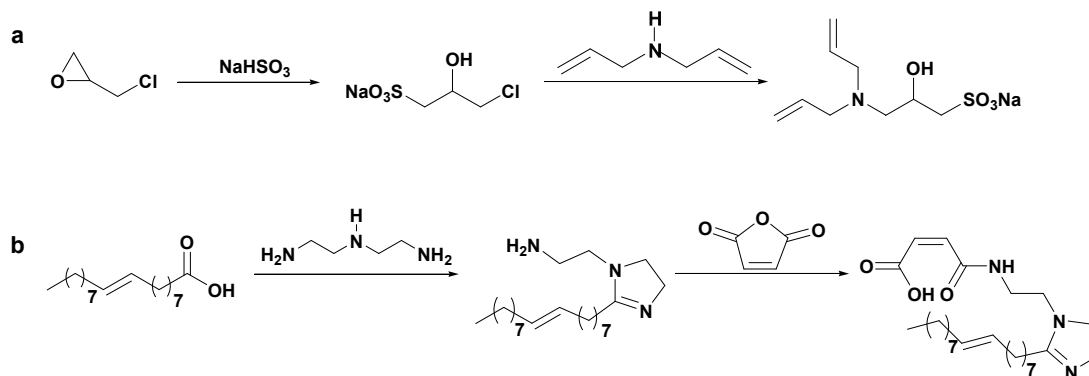
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Experimental

Synthesis

Preparation of the comonomer NIMA. The comonomer NIMA was synthesized by the following processes: oleic acid (56.48 g, 0.2 mol), xylene (27-43 g) and diethylenetriamine (24.8 g, 0.24 mol) were sequentially added to a reactor. Mixed well and heated to 142-162 °C with stirring. Refluxed for 2.5 h, wherein, arising out water of the reactor was carried out by the water-separator. The mixture, after refrigerated to 120 °C, was evaporated 0.5 h under reduced pressure. Heated again up to 200-220 °C and the crude product, after extracted and purified, was obtained while mechanical stirring continued for 2 h. Then maleic anhydride (2.35 g, 0.024 mol) in 20 ml of anhydrous ethanol was slowly added dropwise to above crude product (6.99 g, 0.02 mol) with predissolved in ethanol solution (20 ml). The reaction was still kept to 50 °C for 4-5 h, and then the mixture was extracted with dichloromethane after the organic phase was washed three times with saturated brine. Finally, the product, light brown oil-soluble thick liquid, 3-(2-(2-heptadec-8-enyl-4,5-dihydro-imidazol-1-yl)ethylcarbamoyl)acrylic acid (NIMA), could be purified and distilled the third filtrate through a rotary evaporator.

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 °C in 2 h. The resulting pure white precipitate, which was cooled sharply below 10 °C, was recovered by recrystallization, suction filtration and dried at 45-55 °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 °C for 4-6 h and adjusted to alkaline 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 monomer (a) NDS and (b) NIMA

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 samples 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. The composition of synthesized brine for dissolving polymer particle samples in the rheological experiments is revealed in Table S1.

Table S1 Composition of synthetic brine

ion	concentration (mg/L)
Na ⁺	1115
K ⁺	35
Ca ²⁺	47
Mg ²⁺	113
Cl ⁻	2013
HCO ₃ ⁻	14
SO ₄ ²⁻	274
Total	3612

Characterization

The synthesized copolymer samples were individually characterized by using WQF-520 Infrared spectroscopy (Beijing Rayleigh Analytical Instrument (Group) Co.Ltd, China) in 4400-400 cm⁻¹ optical range. The ¹H NMR spectra analysis of AM/AA/NIMA and AM/AA/NDS/NIMA, dissolved in deuterium oxide (D₂O) solvent, were measured by a Bruker AV III-400MHz spectrometer (Bruker BioSpin, Switzerland). The [η] of polymer solutions, at various desired concentrations (predissolved a certain quality of polymer molecules in distilled water with stirring by a mechanical agitator), were gauged via an Ubbelohde viscometer at 30 °C. Copolymer samples were dissolved and diluted to the required concentration by way of the 1.0 mol/L NaCl solution at a constant temperature bath (30 °C). The flux time of solutions were faintly registered with an accuracy of 0.05 s.

¹H NMR analysis of the commoners

Depicted in Fig.S1(a) was the ¹H NMR spectra of copolymer NDS. The chemical shift value appeared at 5.83-5.91 ppm is assigned to the CH protons of [=CHCH₂N], and the characteristic peak due to the CH₂= protons of [CH₂=CHN] was detected at 5.47-5.50 ppm. Then the peak at 3.03-3.08 ppm representing the -CH- protons of [-CH(OH)CH₂SO₃Na]. The chemical shift value due to the -NCH₂ protons is appearing at 2.70-2.72 ppm, and the -CH₂- protons of [=CHCH₂N] were appointed at 3.15-3.19 ppm. The chemical shift value around 3.66-3.76 ppm is the protons of the aliphatic -CH₂- of [-CH₂SO₃Na].

From the ¹H NMR spectra in Fig.S1(b), the chemical shift value appeared at 7.81 ppm is assigned to the NH protons of [CONHCH₂-]. The chemical shift value owing to the =CHCON protons is appearing at 7.29 ppm, and the =CHCOO protons were appointed at 6.24-6.26 ppm. The chemical shift value at 5.91-5.94 ppm is attributed to -NCH₂- of [(CH₂)NCH₂CH₂N=] of the heterocycle of NIMA. The characteristic peak due to -CH₂N= of the imidazoline ring was detected at 3.39-3.50 ppm. The chemical shift value around 5.32-5.33 ppm is the protons of the aliphatic -CH=CH- of [-CO(CH₂)₇CH=CH(CH₂)₇CH₃]. The chemical shift value at 1.26 ppm was appointed to the -CH₃ proton of the aliphatic chain. The -CH₂- protons of the aliphatic chain appeared at 1.58 ppm and 1.99-2.20 ppm.

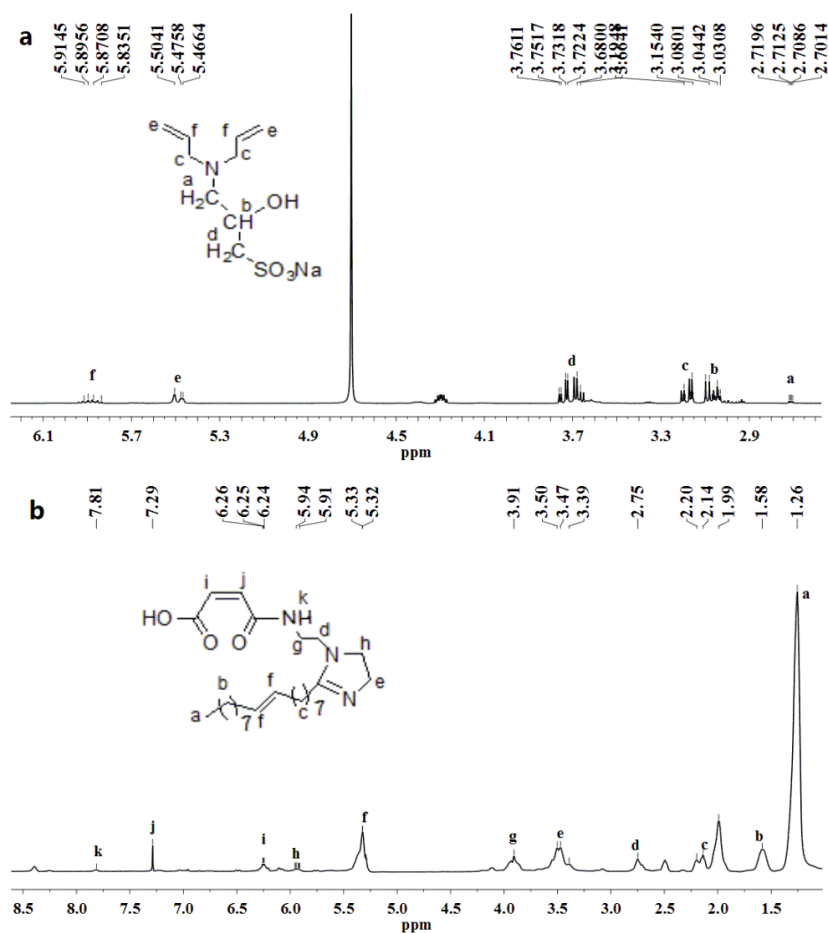


Fig. S1 ¹H NMR of comonomer (a) NDS and (b) NIMA

Critical association concentration

Pyrene probe fluorescence spectroscopy was employed to examine the critical association concentration of obtained copolymers. The ratio (I_1/I_3) of the intensities of the first and the third peaks in the fluorescence spectrum of pyrene could be used to estimate the micropolarity sensed by pyrene in its solubilization site. Fluorescence spectra of the copolymers are as shown in Fig. S2. The excitation wavelength was 335 nm. The emission spectra of pyrene probe fluorescence sequences was in about 372, 378, 382, 392 and 412 nm.

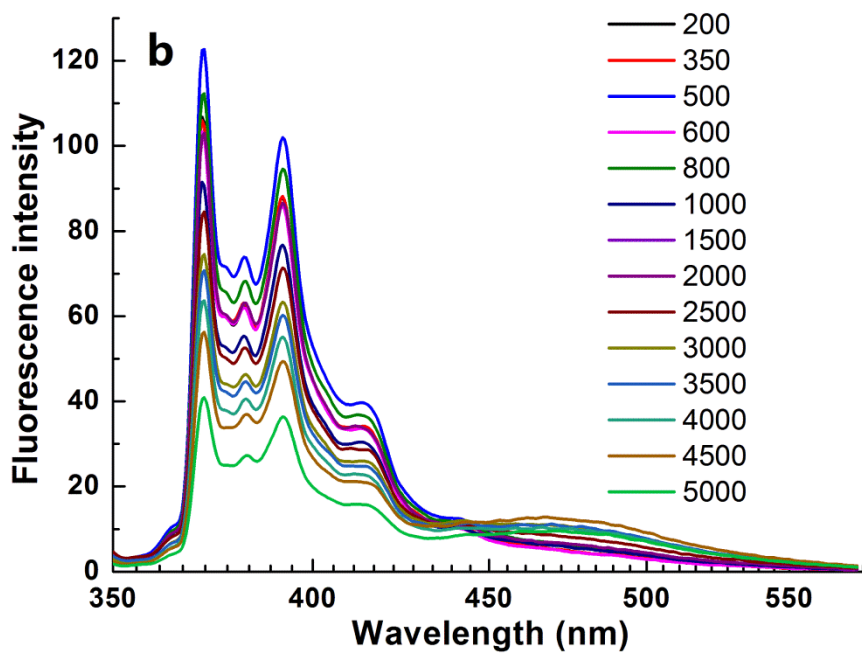
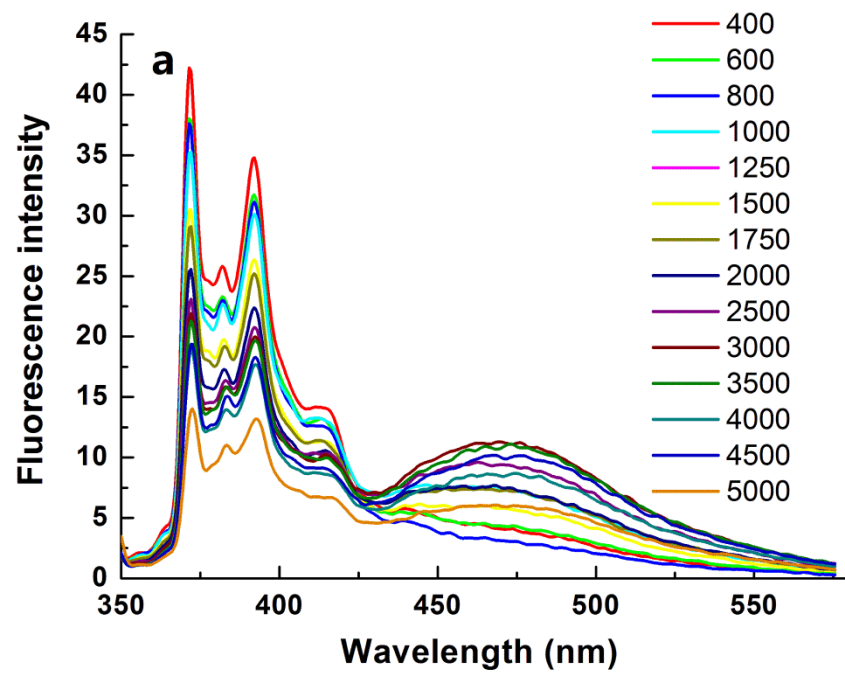


Fig. S2 Fluorescence spectra of different concentrations of (a) AM/AA/NIMA and (b) AM/AA/NDS/NIMA solutions