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Supporting Information

Anti-biodegradable hydrophobic sulfonate-based acrylamide copolymer containing 2,4-dichlorophenoxy for enhanced oil recovery

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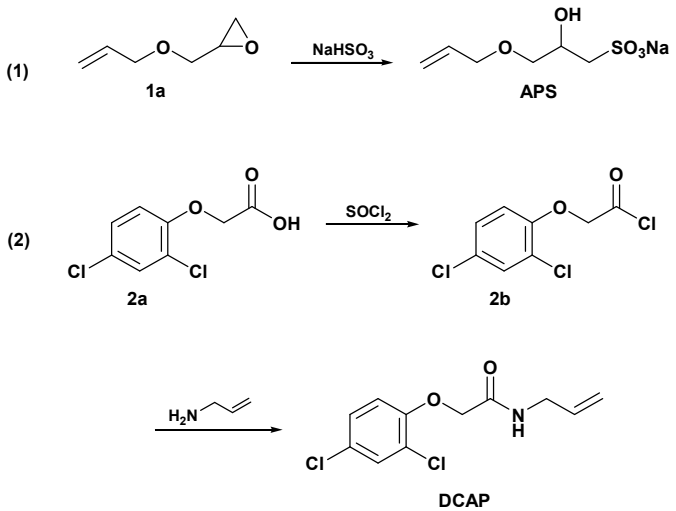
Synthesis routes of APS and DCAP

The synthesis routes of APS and DCAP was shown in Scheme S1.



Scheme S1 The synthesis routes of APS and DCAP.

^{1}H NMR and ^{13}C NMR of DCAP

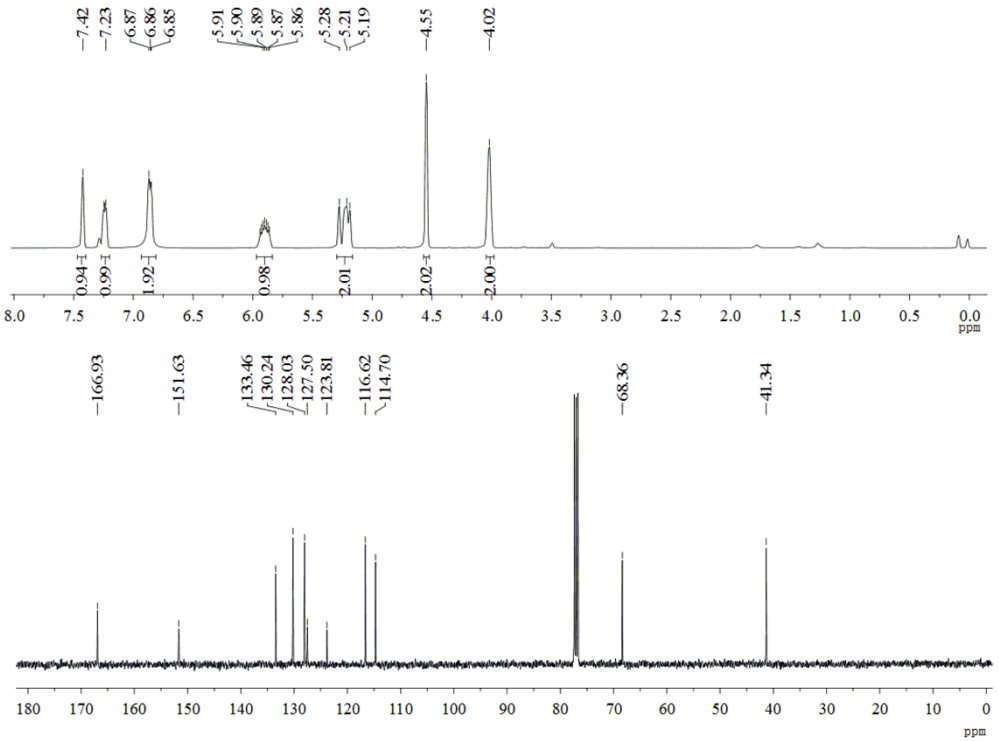


Fig. S1 ^{1}H NMR and ^{13}C NMR of DCAP

Optimum of copolymerization conditions

Initiator content. The initiator content was studied and shown in Fig. S2a. Along with the initiator content increasing, the apparent viscosity of the copolymer solution increased firstly and then reduced gradually after reaching a peak value. When the initiator content was 0.2 wt% of the total monomer weight, the peak value was the maximum apparent viscosity that was 401.3 mPa·s.

Temperature. And then, we investigated the influence of temperature on the copolymerization as shown in Fig. S2b. As the temperature increased to 50 from 40 ^{o}C, the apparent viscosity of the copolymer reached the maximum. With the rising of the reaction temperature, higher apparent viscosity could not be gained.

Total concentration of monomers. The total concentration of monomers was also an important factor affecting apparent viscosity of the copolymer, and the results were shown in Fig. S2c. It was found that the maximum apparent viscosity could be obtained when the concentration of monomers for the

copolymerization was 20 wt%. As the concentration of monomers changed to 30 from 20 wt%, a decreasing trend could be observed in the result.

pH. The influence of pH on the copolymerization was researched. It could be seen from Fig. S2d that the apparent viscosity showed increase under the changing from 5 to 7 of the pH value. The apparent viscosity decreased slightly when pH changed from 7 to 8, and then the apparent viscosity was reduced dramatically with further increase of the pH value.

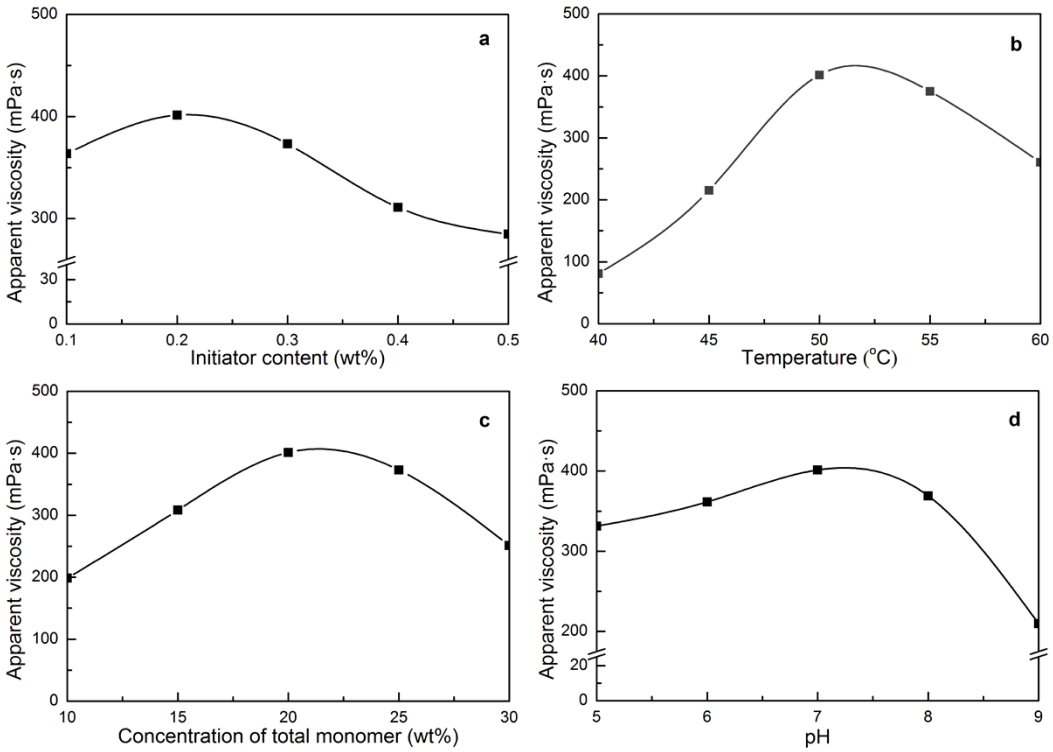


Fig. S2 The effect of initiator content, temperature, concentration of total monomer, and pH on the copolymerization.

Initiator Content. *m*(AM): *m*(AA): *m*(APS): *m*(DCAP) = 7.96:1.5:0.5:0.04, concentration = 20wt%, pH = 7, T = 50 °C.

Temperature. *m*(AM): *m*(AA): *m*(APS): *m*(DCAP) = 7.96:1.5:0.5:0.04, concentration = 20 wt%, pH =7, initiator content = 0.2 wt%.

The Total Concentration of Monomers. *m*(AM): *m*(AA): *m*(APS): *m*(DCAP) = 7.96:1.5:0.5:0.04, pH = 7, initiator content = 0.2 wt%, T = 50°C.

pH. *m*(AM): *m*(AA): *m*(APS): *m*(DCAP) = 7.96:1.5:0.5:0.04, concentration = 20 wt%, initiator content = 0.2 wt%, T = 50 °C.

Monomer Ratio. Initiator content = 0.2 wt%, T = 50 °C, concentration = 20 wt%, pH = 7.

Monomer ratio. The effect of monomer ratio on the apparent viscosity of HPAM, AM/AA/APS, and AM/AA/APS/DCAP solution was shown in Table S1. From entries 1-5, with the increasing contents of hydrophobic monomer (DCAP), AM/AA/APS/DCAP demonstrated a tendency that its apparent viscosity rapidly raised at first, and then the apparent viscosity decreased lightly, and last the copolymer was insoluble. So the maximum of hydrophobic monomer (DCAP) was 0.1 g. From entries 4, 6-8, it was found that the satisfying content of APS was 0.5 g, and the results could not be improved when increasing or decreasing APS contents. A satisfying monomer ratio was *m*(AM): *m*(AA): *m*(APS): *m*(DCAP) = 7.9: 1.5: 0.5: 0.1.

Table S1 Effect of the pH, Temperature and Initiator Concentration

Entries[a]	AM (g)	AA (g)	APS (g)	DCAP (g)	Apparent viscosity (mPa·s)[b]
1	7.96	1.50	0.50	0.04	401.3
2	7.94	1.50	0.50	0.06	466.5
3	7.92	1.50	0.50	0.08	488.2
4	7.90	1.50	0.50	0.10	410.5
5	7.88	1.50	0.50	0.12	-[b]
6	8.10	1.50	0.30	0.10	350.2
7	8.00	1.50	0.40	0.10	390.6
8	7.80	1.50	0.60	0.10	384.2

[a]Condition: Initiator= 0.2 wt%, Concentration of monomers= 20 wt%, pH=7, temperature= 50 °C, and reaction time= 8 h.

[b]Apparent viscosity: concentration of copolymer solution was 2000 mg·L^{-1}, tested by Brookfield DV-III Programmable Rheometer with a 62# rotor at 25 °C.

The optimum copolymerization conditions were listed in Table S2.

Table S2 The copolymerization conditions of AM/AA/APS and AM/AA/APS/DCAP

Copolymer	Initiator / wt%	Temperature / °C	Concentration / wt%	pH	Monomer / g			
					AM	AA	APS	DCAP
AM/AA/APS/DCAP	0.2	50	20	7	7.9	1.5	0.5	0.1
AM/AA/APS	0.2	50	20	7	7.9	1.5	0.5	0

Composition of copolymers

The composition for copolymers AM/AA/APS was obtained by elemental analysis. And the composition of AM/AA/APS/DCAP was determined by ^{1}H NMR and elemental analysis. For AM/AA/APS/DCAP, it is seen from Fig. S3 that the ratio of number of $\boldsymbol{H}_{(j)}$ in functional pendent benzene groups to number of $\boldsymbol{H}_{(a)}$ in –CH_2– of the copolymer chain was 1.0 : 798.3, which means that the content of the functional monomer DCAP was 0.25% in the copolymer AM/AA/APS/DCAP. Combined with elemental analysis, the composition results of AM/AA/APS and AM/AA/APS/DCAP are listed in Table S3.

Table S3 Elemental analysis of AM/AA/APS and AM/AA/APS/DCAP

Copolymer	Theoretical elements mass			Actual elements mass (%)			Molar composition of copolymer			
	C	N	S	C	N	S	AM	AA	APS	DCAP
AM/AA/APS/DCAP	49.69	13.39	0.73	47.26	14.59	0.65	80.93	17.25	1.57	0.25
AM/AA/APS	49.68	13.48	0.74	47.21	15.00	0.69	83.06	15.26	1.68	-

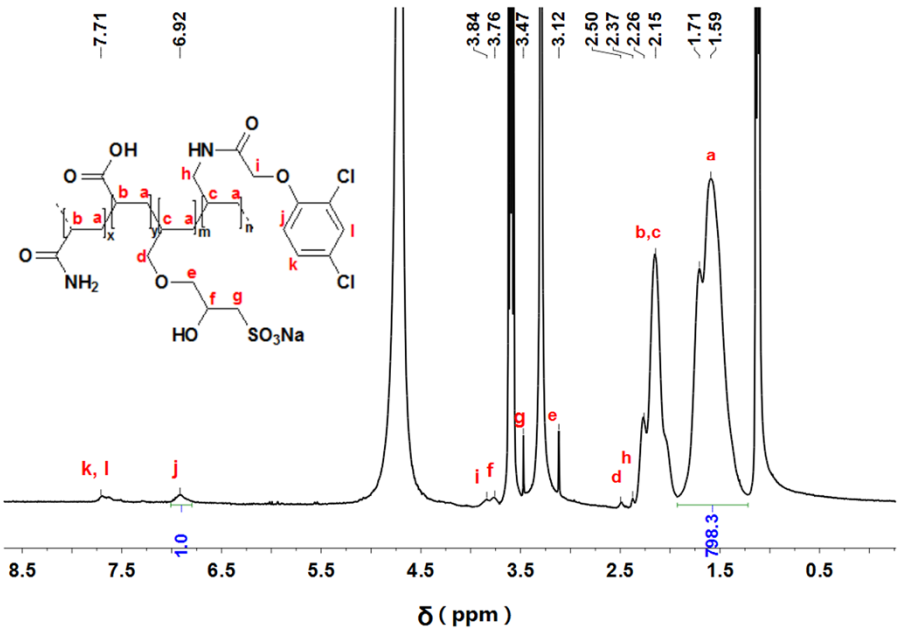


Fig. S3 The ^{1}H NMR of AM/AA/APS/DCAP

Intrinsic viscosity of copolymers

The intrinsic viscosity ([η]), which reflects the expanded extent of the polymer chain, is a measurement of the hydrodynamic volume of macromolecules. The flux time of HPAM, AM/AA/APS, and AM/AA/APS/DCAP solutions with different polymer contents was determined, and then η_{sp}/C versus C relationship was plotted in Fig. S4. According to the eqn (2) (see Manuscript), the three y-intercepts are the [η] of the AM/AA/APS/DCAP, AM/AA/APS and HPAM. The result revealed that the [η] of AM/AA/APS/DCAP, AM/AA/APS and HPAM were respectively 1317 mL·g^{-1}, 1326 mL·g^{-1} and 1342 mL·g^{-1}.

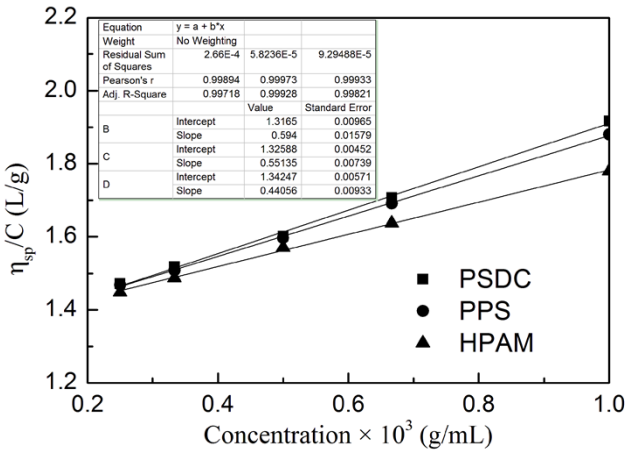


Fig. S4 The relationship between η_{sp}/C of HPAM, AM/AA/APS, and AM/AA/APS/DCAP.