

Supplementary material

**Hyper-branched structure—an active carrier for copolymer
with surface activity, anti-polyelectrolyte effect and
hydrophobic association in enhanced oil recovery**

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1. Synthesis of monomer MMPES

Into a solution of DAPMAA (40 mmol, 6.82 g) in 1,4-dioxane (30 mL) was added hydroquinone (0.54 mmol, 0.06 g) at room temperature, then the mixture of MES (48 mmol, 5.18 g) and 1,4-dioxane (40 mL) was dribbled into the system within 30 min and refluxed for 2h. After the solvent removed under reduced pressure, the crude product was recrystallized with acetonitrile, then the light yellowish-white product MMPES was obtained with 92% yield. ¹H NMR (400 MHz, D₂O): δ 7.83 (s, 1H, -C(O)N(CH₂)-H), 5.72–5.78 (s, 2H, CH₂=C(CH₃)-), 3.95 (t, 2H, -CH₂-OSO₂⁻), 3.39 (t, 2H, -CH₂-CH₂-OSO₂⁻), 3.21–3.30 (m, 10H, -C(O)NH-CH₂-CH₂-CH₂-N⁺(CH₃)₂-), 1.98 (m, 3H, CH₂=C(CH₃)-).

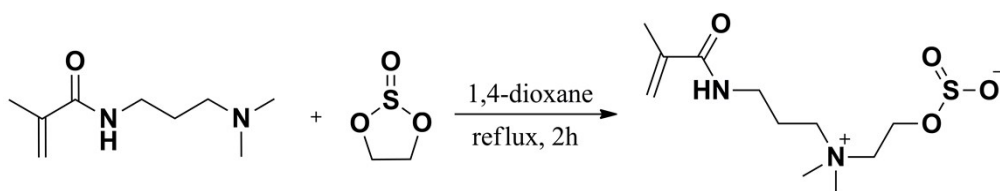


Fig. S1. The synthetic route of MMPES.

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2. Synthesis of monomer DMBSA

Into a 100 mL flask, P-Tosyl Chloride (40 mmol, 7.62g) was dissolved in dichloromethane (20mL) at 0-5°C, the N,N-diallylamine (48 mmol, 4.66g) and triethylamine (80 mmol, 8.08g) were mixed with dichloromethane (10mL) and then added dropwise to the flask. Upon addition, the reaction was kept at 30 °C for 6h. The reaction solution was washed successively with deionized water (100 mL), 1 wt% hydrochloric acid (100 mL), 1 wt% sodium hydroxide solution (100 mL) and saturated brine (100 mL), the organic phase was dried by anhydrous sodium sulfate, then the light yellow viscous liquid DMBSA was obtained via distillation under vacuum (87% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, 2H, Ar-*H*), 7.40 (t, 2H, Ar-*H*), 5.72 (m, 2H, -CH₂-CH=CH₂), 5.22 (dd, 4H, -CH₂-CH=CH₂), 3.90 (d, 4H, -CH₂-CH=CH₂), 2.52 (s, 3H, Ar-CH₃).

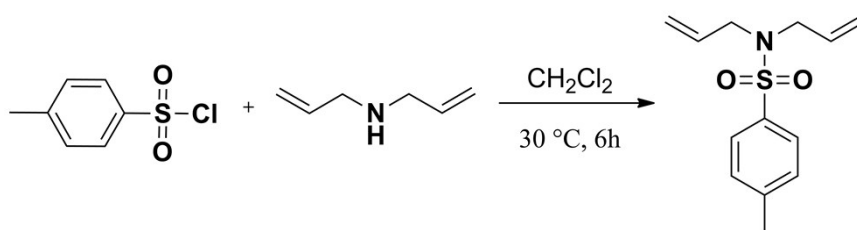


Fig. S2. The synthetic route of DMBSA.

3. The synthetic route of monomer N-TETA

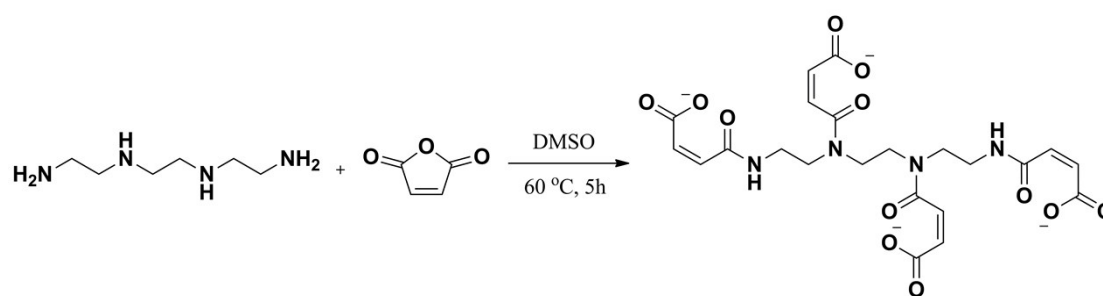


Fig. S3. The synthetic route of N-TETA.

4. Synthesis of copolymer MMPES/AM/AA/DMBSA (PMAD)

Into a 100 mL three necked flask, the certain amount of MMPES, DMBSA, OP-10 and MPS were well mixed with 18mL DI water, then the AM, AA was added in order. After stirring for 15 min, sodium hydroxide solution was used to adjust the pH

of the system. Next, the flask was kept in water bath at certain temperature under nitrogen atmosphere for 15 min, then the $\text{NaHSO}_3\text{-(NH}_4)_2\text{S}_2\text{O}_8$ (1/1 mol ratio) initiator was added and dispersed rapidly, the reaction was at certain condition for 10h. At last, the copolymer gels was precipitated with ethanol and dried in 45 °C vacuum retrieving the powdered sample, the optimum synthesis conditions for PMAD were exhibited in Table S1.

Table S1. The optimum synthesis conditions for copolymer PMAD

Feed ratio (g)				pH	Initiator (g)	Tem. (°C)
AM	AA	MMPES	DMBSA			
7	3	0.3	0.03	7	0.03	45

5. The optimization of synthesis conditions of copolymer h-PMAD

The monomer ratio of all polymerizations were showed in Table S2 with the same conditions (initiator 0.03 g, pH 7, temperature 45 °C, total monomer concentration 25%).

Table S2. The optimization of ratio of monomers on h-PMAD

Group	AM (g)	AA (g)	N-TETA (g)	MMPES (g)	DMBSA (g)	η^a (mPa·s)
1	5	5	0.3	0.3	0.04	542.5
2	6	4	0.3	0.3	0.04	650.2
3	7	3	0.3	0.3	0.04	709.8
4	8	2	0.3	0.3	0.04	631.5
5	9	1	0.3	0.3	0.04	466.0
6	7	3	0.1	0.3	0.04	462.2
7	7	3	0.2	0.3	0.04	589.5
8	7	3	0.3	0.3	0.04	675.9
9	7	3	0.4	0.3	0.04	739.1
10	7	3	0.5	0.3	0.04	695.1
11	7	3	0.4	0.1	0.04	686.5
12	7	3	0.4	0.2	0.04	761.2
13	7	3	0.4	0.3	0.04	739.1
14	7	3	0.4	0.4	0.04	666.5
15	7	3	0.4	0.5	0.04	598.8
16	7	3	0.4	0.2	0.01	499.4
17	7	3	0.2	0.2	0.02	617.5
18	7	3	0.2	0.2	0.03	789.5

19	7	3	0.2	0.2	0.04	761.2
20	7	3	0.2	0.2	0.05	721.7

^aApparent viscosity of h-PMAD: copolymer solution 2000 mg/L.

The initiator ratio, pH and temperature of all polymerization were showed in Table S3 with the same conditions (AM:AA=7:3, N-TETA 0.4 g, MMPES 0.2 g, DMBSA 0.03 g, total monomer concentration 25%).

Table S3. The optimization of ratio of monomers on h-PMAD

Group	initiator (g)	pH	temperature (°C)	η^a (mPa·s)
1	0.01	7	40	446.5
2	0.02	7	40	655.2
3	0.03	7	40	739.5
4	0.04	7	40	687.1
5	0.05	7	40	430.9
6	0.03	5	40	326.2
7	0.03	6	40	634.5
8	0.03	7	40	739.5
9	0.03	8	40	591.9
10	0.03	9	40	442.0
11	0.03	7	30	462.5
12	0.03	7	35	556.2
13	0.03	7	40	739.5
14	0.03	7	45	789.4
15	0.03	7	50	755.7

^aApparent viscosity of h-PMAD: copolymer solution 2000 mg/L.

6. Conversion rate of monomers and actual composition of h-PMAD

The conversion rate of monomers in the copolymer was analyzed via high performance liquid chromatography (HPLC; Shimadzu Co., Japan) with an ODS column (mobile phase: H₂O/CH₃OH=1:9; UV detection wavelength, 210 nm; column temperature: 40 °C; flow rate: 1.0 mL/min). The conversion rate was obtained by the residual monomers from ethanol used to purify the copolymer with Eq. S1:

$$\alpha = \frac{W - \frac{AC_0}{A_0} \times V}{W} \times 100\% \quad (S1)$$

where α was the conversion rate of different monomers, %; W was the total quality of the feed; A was the peak area of different residual monomers in ethanol; C_0 was the

concentration of the corresponding monomer; A_0 was the peak area of the corresponding monomer; V was the volume of ethanol used to purify the copolymer. The results were listed in Table S4.

Table S4. The conversion rate of monomers and actual composition of h-PMAD

Conversion rate (wt %)					Actual composition (wt %)				
AM	AA	N-TETA	MMPES	DMBSA	AM	AA	N-TETA	MMPES	DMBSA
95.58	95.87	97.21	97.55	96.34	65.73	28.25	3.82	1.92	0.28

7. Intrinsic viscosity and molecular weight of h-PMAD

7.1 Intrinsic Viscosity Measurement

Intrinsic viscosity $[\eta]$ was decided with a NCY automatic Ubbelohde capillary viscometer (0.55 mm) (Shanghai Sikeda scientific instruments Inc., Shanghai, China) at 30 ± 0.1 °C. The copolymers were dissolved and diluted to five different concentrations ($C=1.0, 0.67, 0.50, 0.33, 0.25$ mg/L) with 1 mol/L NaCl solution. The flux times of the copolymer solutions had to be accurate to ± 0.2 s. The specific viscosity and intrinsic viscosity were calculated via the following Eq. S2 and S3¹.

$$\eta_{sp} = \frac{t - t_0}{t_0} \quad (S2)$$

$$[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c \quad (S3)$$

where η_{sp} is the specific viscosity of polymer; c is pure polymer solution concentration, mg/L; t_0 is flux time of 1 mol/L NaCl brine, s; and t is flux time of polymer brine solution, s.

The specific calculations of the measurement of intrinsic viscosity were according to the Eq. S2 and S3. From Fig. S4, the values of the η_{sp}/C_r and $\ln\eta_r/C_r$ with the concentration being extrapolated to zero were 1284.62 and 1196.44 mL/g, respectively. Therefore, the intrinsic viscosity of copolymer h-PMAD was 1240.53 mL/g (12.41 dL/g).

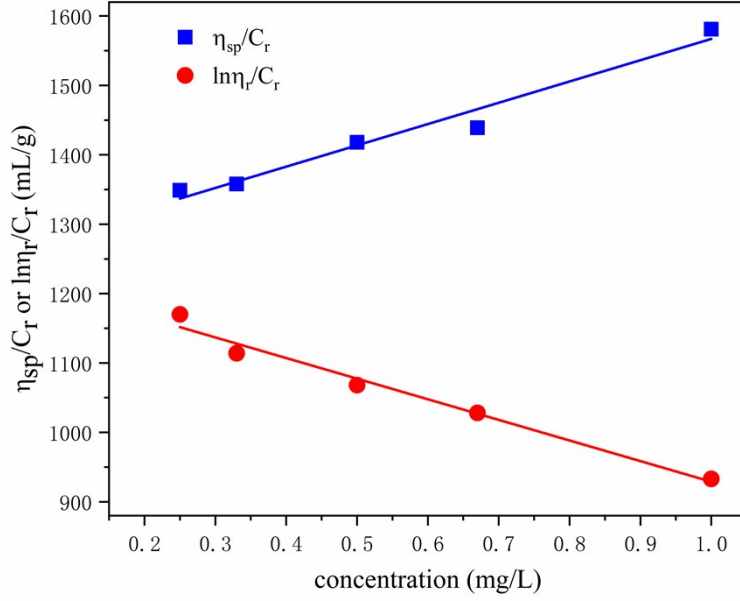


Fig. S4. Relationship of η_{sp}/C_r ($\ln\eta_r/C_r$) with copolymer concentrations.

7.2 Molecular Weight and Molecular Weight Distribution

Intrinsic viscosity measurement is a quick and simple method for determining molecular weight, which is almost exclusively used to study the polymerization kinetics of high molecular weight polyacrylamide-related polymers². Collinson et al.³ developed the most widely used equation to correlate the number average molecular weight of a polymer with its intrinsic viscosity in water at 25-30 °C, as follow Eq. S4.

$$[\eta] = 6.80 \times 10^{-4} \bar{M}_n^{0.66} \quad (S4)$$

where $[\eta]$ is Intrinsic viscosity, dL/g; \bar{M}_n is the number average molecular weight. Whereas the corresponding expression for the weight-average molecular weight was proposed by Scholtan⁴, as follow Eq. S5.

$$[\eta] = 6.31 \times 10^{-5} \bar{M}_w^{0.80} \quad (S5)$$

where $[\eta]$ is Intrinsic viscosity, dL/g; \bar{M}_w is the weight-average molecular weight.

Substituting the value 12.41 dL/g of the intrinsic viscosity $[\eta]$ into the Eq. S4 and Eq. S5 calculated the molecular weight, the results were as follow:

$$\bar{M}_n = 2.86 \times 10^6$$

$$\bar{M}_w = 4.14 \times 10^6$$

the molecular weight distribution D was calculated as follows:

$$D = \frac{\bar{M}_w}{\bar{M}_n} = 1.45$$

8. Parameters of simulated formation water

Table S5. Parameters of simulated formation water

Inorganic ions	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	CO ₃ ²⁻	HCO ₃ ⁻	TDS
Concentration (mg/L)	1988	1433	159	276	5733	85	14	312	10000

9. Parameters of sandstone cores for core flooding experiment

Table S6. Basic parameters of sandstone cores

Core No.	Diameter (cm)	Length (cm)	PV (mL)	Porosity (%)	Permeability (D) ^a	Oil saturation (%)
1	3.78	6.82	76.50	38.05	1.77	89.31
2	3.79	6.82	76.90	37.88	1.82	89.35
3	3.78	6.81	76.38	37.43	1.79	89.32

^aDetermined by Darcy's Law.

10. Experimental results of mobility control ability and EOR

Table S7. Experimental results of mobility control ability and EOR

Polymer	P ₀ (MPa)	P ₁ (MPa)	P ₂ (MPa)	RF ^a	RRF ^b	E ₁ (%)	E ₂ (%)	EOR ^c (%)
HPAM	0.012	0.095	0.020	7.92	1.66	56.82	50.94	5.88
PMAD	0.014	0.14	0.051	10.00	3.64	60.09	51.90	8.19
h-PMAD	0.014	0.20	0.071	14.29	5.07	64.11	52.5	11.61

^aRF, ^bRRF and ^cEOR were calculated via Eq. 6, 7 and 5, respectively.

References

- 1 M. E. Zeynali, A. Rabii and H. Baharvand, Iran. Polym. J., 2004, 13, 479–484.
- 2 S. M. Shawki and A. E. Hamielec, J. Appl. Polym. Sci., 1979, 23, 3323-3339.
- 3 E. Collinson, F. S. Dainton and G. S. McNaughton, Trans. Faraday SOC., 1957, 53, 489.
- 4 W. Scholtan, Makromol. Chem., 1954, 14, 169.