

Supplementary material

Modified acrylamide copolymers based on β -cyclodextrin and twin-tail structure for enhanced oil recovery through host-guest interactions

Chuan Peng^a, Shaohua Gou^{a,b*}, Qi Wu^a, Lihua Zhou^a, Huichao Zhang^a, Yumei Fei^a

^aCollege of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu 610500, P.R. China

^bState Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, P.R. China

Correspondence to: S. Gou (E-mail: shaohuagou@swpu.edu.cn)

1. Synthesis of modified β -CD monomer (O- β -CD)

1.1 Synthesis of β -CD-TosCl

β -cyclodextrin (20 g) was dispersed in 125 mL of deionized ice water, and p-toluenesulfonyl chloride (4.2 g) was dissolved in 10 mL acetonitrile and added dropwise to the aqueous phase. After rapidly stirring the reaction at room temperature for 2 hours, 2.18 g NaOH was dissolved in 10 mL deionized water and added dropwise. After 30 min of stirring at room temperature, the pH of the solution was adjusted to 8.5 with solid ammonium chloride, and the solution was cooled with ice to collect precipitates. The product was washed three times with iced deionized water and acetone successively and dried under vacuum. β -CD-TosCl was obtained (~30%).

1.2 Synthesis of β -CD-EDA

β -CD-TosCl (4.4 g) was added to 20 mL ethylenediamine (EDA). The reaction was carried out for 12 hours with stirring at 70 °C and cooled to room temperature. After the reaction was completed, it was cooled to obtain a pale yellow viscous liquid, and the liquid was precipitated with iced anhydrous ethanol. The precipitant was collected and dried under vacuum to obtain the product (β -CD-EDA).

1.3 Synthesis of O- β -CD

β -CD-EDA (1.8 g) was added to 80 mL dichloromethane (CH_2Cl_2) and stirred to disperse evenly, and 0.138 g acryloyl chloride diluted with CH_2Cl_2 was added to the liquid phase under ice-water bath.

* Corresponding author

E-mail address: shaohuagou@swpu.edu.cn (S. Gou)

Then the reaction was performed at room temperature for 24 h, and then filtered to obtain a filter cake. The filter cake was washed three times with CH_2Cl_2 and dried under vacuum to obtain the final product ($\text{O-}\beta\text{-CD}$).

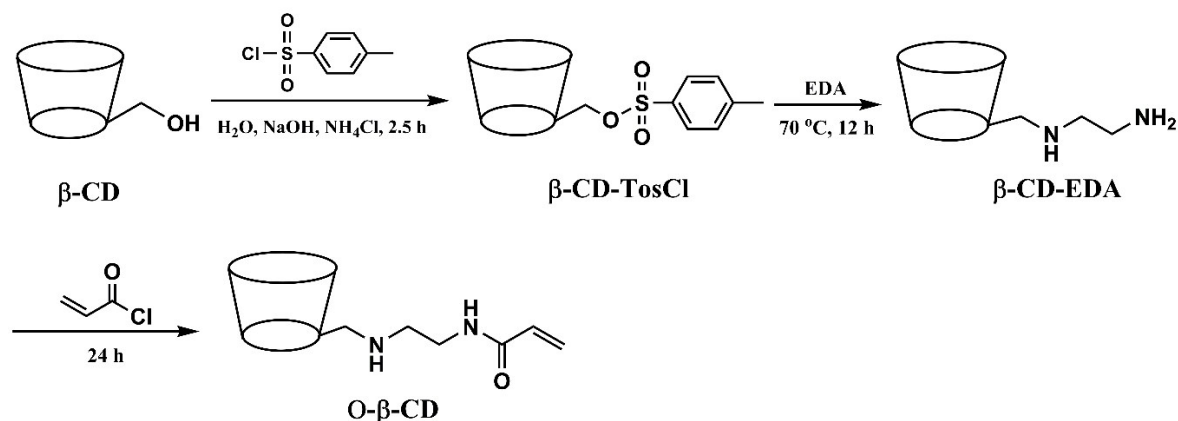


Fig. S1. The synthetic route of $\text{O-}\beta\text{-CD}$.

2. Synthesis of hydrophobic twin-tailed monomers (DLMA and DLMB)

Di-*n*-butylamine (6.5 g) and triethylamine (5.3 g, TEA) (molar ratio of 1: 1.05) were added to 100 mL CH_2Cl_2 and stirred evenly. 5.2 g methacryloyl chloride diluted with CH_2Cl_2 was added dropwise to the liquid phase under ice-water bath. Then the reaction was performed with stirring at room temperature for 12 h. The product was extracted with saturated ammonium chloride and sodium carbonate solution, respectively, and the organic layer was collected. The organic layer was dried over anhydrous sodium sulfate for 12 hours and then distilled under reduced pressure to give a pale yellow viscous liquid (DLMA).

The synthetic route of DLMB is the same as that of DLMA, except that it is only necessary to replace di-*n*-butylamine with di-*n*-octylamine.

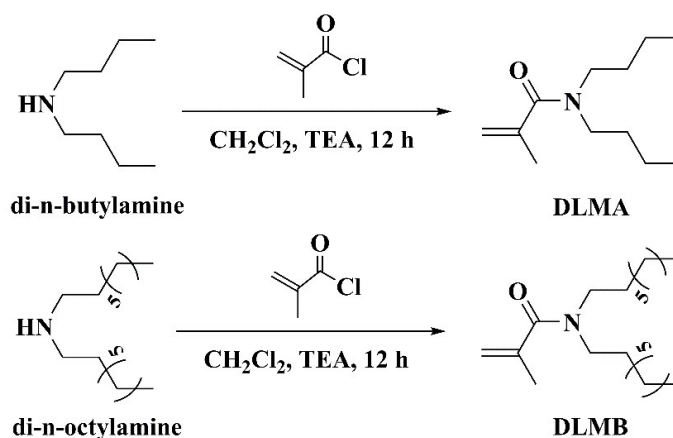


Fig. S2. The synthetic routes of DLMA and DLMB.

3. Effect of the Synthesis Conditions

All copolymerization of ratio of monomers was in Table S1 with the same conditions (initiator loading, 0.04 g; pH value, 8; temperature, 45 °C; total monomer concentration, 25%).

Table S1. The effects of the ratio of monomers on Poly-A and Poly-B.

Entry	AM (g)	AA (g)	O- β -CD (g)	DLMA/DLMB (g)	η^a/η^b (mPa·s)
1	7.0	2.0	0.5	0.5	264.5/298.6
2	6.0	3.0	0.5	0.5	324.5/358.7
3	5.0	4.0	0.5	0.5	375.6/425.2
4	4.0	5.0	0.5	0.5	405.8/476.6
5	3.0	6.0	0.5	0.5	382.1/462.3
6	2.0	7.0	0.5	0.5	344.0/411.8
7	4.0	5.0	0.6	0.4	412.2/483.2
8	4.0	5.0	0.7	0.3	391.1/456.0
9	4.0	5.0	0.8	0.2	372.4/427.3
10	4.0	5.0	0.4	0.6	418.8/487.6
11	4.0	5.0	0.3	0.7	436.8/504.5
12	4.0	5.0	0.2	0.8	409.5/487.3
13	4.0	5.0	0.1	0.9	371.8/444.1

^aApparent viscosity of Poly-A: copolymer solution=2000 mg/L.

^bApparent viscosity of Poly-B: copolymer solution=2000 mg/L.

Table S2. Effects of the initiator concentration, pH, and temperature on Poly-A and Poly-B.

Entry	Initiator (g)	pH	Temperature (°C)	η^a/η^b (mPa·s)
1	0.01	8	45	184.5/234.4
2	0.02	8	45	279.6/312.2
3	0.03	8	45	371.4/421.7
4	0.04	8	45	436.8/504.5
5	0.05	8	45	418.5/479.6
6	0.06	8	45	288.8/346.7
7	0.04	9	45	422.4/494.2
8	0.04	10	45	— ^c /122.8
9	0.04	7	45	345.6/431.8
10	0.04	8	50	416.5/489.6
11	0.04	8	55	398.7/466.9
12	0.04	8	40	232.3/267.2
13	0.04	8	35	— ^c /— ^c

^csituation: obvious copolymerization was not observed.

4. Analysis of intrinsic viscosity

The measurement of intrinsic viscosity on Poly-A and Poly-B was conversion Eq 1 and 2. Fig. S3 illustrated the relationships of η_{sp}/C_r or $\ln\eta_r/C_r$ that straight lines of η_{sp}/C_r or $\ln\eta_r/C_r$ following concentration almost converged at a point on ordinate by 849.4 and 932.5 mL/g for Poly-A and Poly-B, respectively.

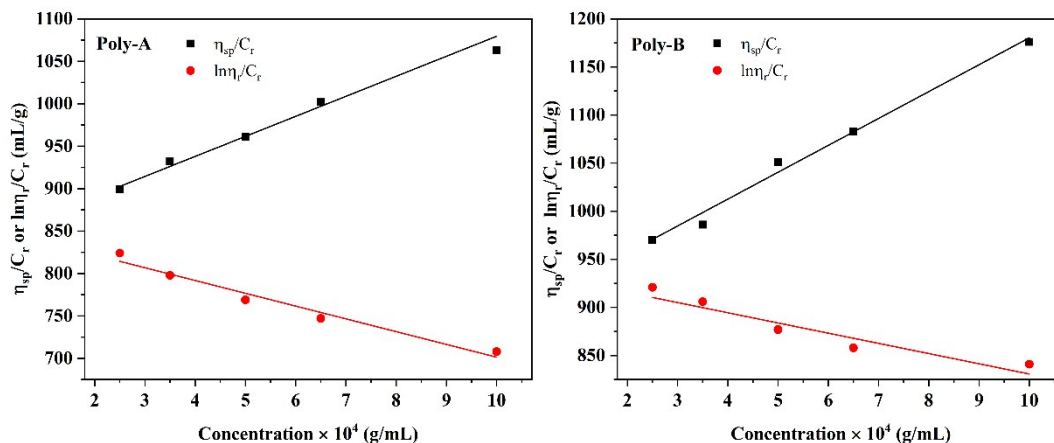


Fig. S3. Relationship of η_{sp}/C_r ($\ln\eta_r/C_r$) and copolymer concentrations.

5. Conversions of monomers

The conversion of each monomer in the copolymer was analyzed by using 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 of Poly-A and Poly-B 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 is the conversion rate for different monomers, %; W is the total quality of the feed; A is the peak area of different residual monomers in ethanol; C₀ is the concentration of the corresponding monomer; A₀ is the peak area of the corresponding monomer; V is the volume of ethanol used to purify the copolymer.

The proportion of each monomer in Poly-A or Poly-B was investigated by the conversion rate, which illustrates the actual situation of copolymerization. The actual feed ratio and the ratio of the monomer of the copolymer via the final calculation are listed in Table S3 and Table S4. For Poly-A,

the calculated conversion rates of AM, AA, O- β -CD, and DLMA are 95.98%, 96.20%, 96.35%, and 96.02%, respectively. For Poly-B, the calculated conversion rates of AM, AA, O- β -CD, and DLMB are 96.06%, 96.27%, 96.82%, and 96.28%, respectively.

Table S3. Composition of Poly-A.

Feed ratio (wt %) ^d				Measured content (wt %) ^e			
AM	AA	O- β -CD	DLMA	AM	AA	O- β -CD	DLMA
40.0	50.0	3.0	7.0	41.24	48.76	2.83	7.17

^dThe mass of original monomers is 5.0226 g. ^eThe mass of purified copolymer is 4.8268 g.

Table S4. Composition of Poly-B.

Feed ratio (wt %) ^f				Measured content (wt %) ^g			
AM	AA	O- β -CD	DLMB	AM	AA	O- β -CD	DLMB
40.0	50.0	3.0	7.0	41.47	49.14	2.52	6.87

^fThe mass of original monomers is 5.0244 g. ^gThe mass of purified copolymer is 4.8336 g.

6. Determination of host-guest interactions by dissolution time

In order to prove the host-guest interactions between β -CD and hydrophobic twin-tailed structure, comparative experiments were carried out. As shown in Fig. S4a, the dissolution time of Poly-A, Poly-AM/AA/DLMA and Poly-AM/AA/O- β -CD were 70 min, 84 min and 72 min, respectively. The above results indicated that host-guest inclusion was formed by self-assembly between hydrophobic twin-tail chains and β -CD in Poly-A to reduce the dissolution time. Likewise, similar results were observed in Fig. S4b, the dissolution time of Poly-B, Poly-AM/AA/DLMB and Poly-AM/AA/O- β -CD were 78 min, 90 min and 72 min, respectively. These results once again demonstrated that the hydrophobic twin-tail chain was embedded in the hydrophobic cavity of β -CD to reduce the dissolution time of the copolymer.

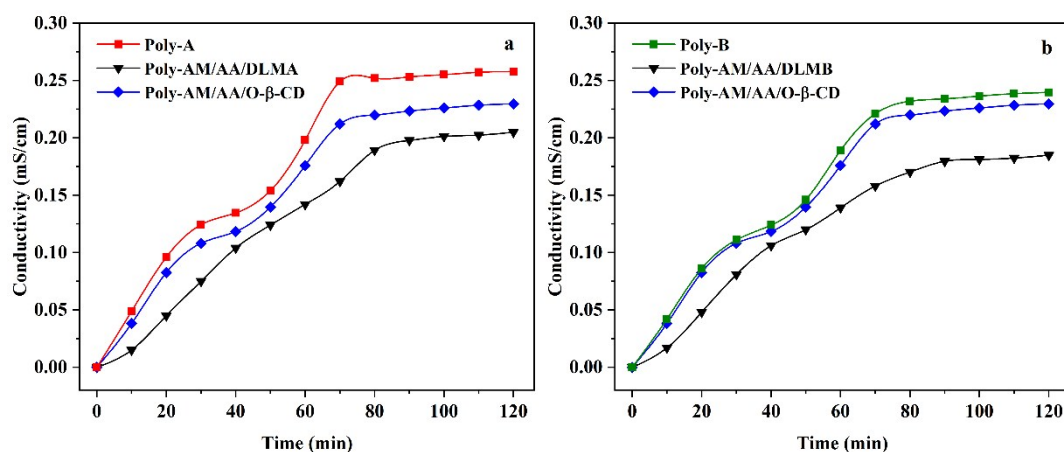


Fig. S4. The dissolution time curves of copolymers.

7. Effect of host-guest interactions on critical association concentration (CAC)

In order to prove the effect of host-guest interaction on CAC, comparative experiments were carried out. As shown in Fig. S5a, the apparent viscosity of all polymer solutions increased with increasing concentration. The apparent viscosity of Poly-AM/AA/DLMA solution increased slightly as the polymer concentration increased from 100 to 800 mg/L, and then the apparent viscosity increased sharply as the polymer concentration increased from 800 to 2000 mg/L, which exhibited typical viscometric behavior of hydrophobically associating polymers. The CAC of Poly-AM/AA/DLMA is 800 mg/L. The Poly-A, which simultaneously contained β -CD and hydrophobic twin-tail structure, also exhibited the same viscometric behavior as hydrophobically associating polymers. The CAC of Poly-A was 700 mg/L, which was lower than that of Poly-AM/AA/DLMA evidently, indicating intermolecular host-guest interactions could be generated more easily than intermolecular hydrophobic association. Likewise, similar results were observed in Fig. S5b, the CACs of Poly-AM/AA/DLMB and Poly-B were 800 mg/L and 700 mg/L, respectively. The characteristic of Poly-A and Poly-B is very useful in practical application because polymer solution will be continuously diluted and absorbed after being injected underground. Hence, Poly-A and Poly-B can maintain favorable thickening ability at relatively low concentration, which contributes to an effective mobility control role for a long period.

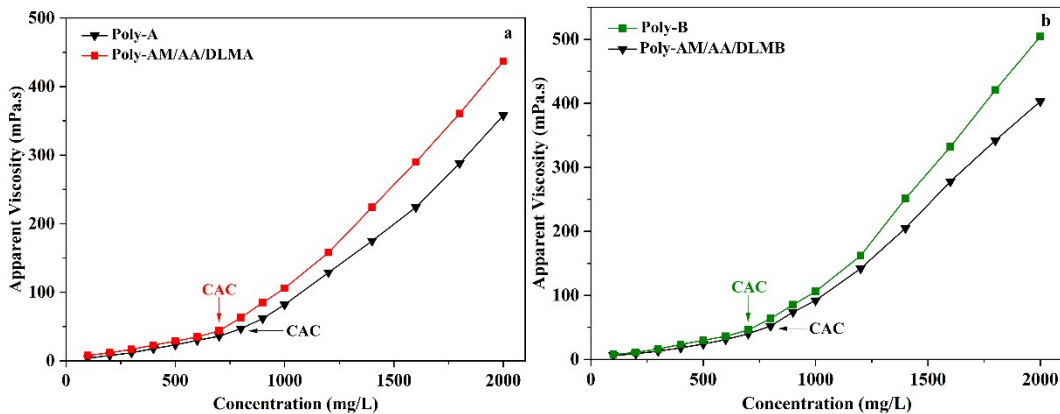


Fig. S5. The dissolution time curves of copolymers.