

Supporting Information

A water-soluble hyperbranched copolymer based on dendritic structure for low-moderate permeability reservoir

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Optimum synthesis conditions of monomer DA

The effect of raw materials molar ratio on dendritic macromolecules was investigated as displayed in Fig. S1. It was found that the yield of whole dendritic macromolecules (GA0.5-GA2.0) initially increased, and then turned to be stable gradually with increasing the raw materials molar ratio. Therefore, with the purpose of reducing the obstruction of the subsequent purification process and economic cost, the optimal molar ratio were 1:8, 1:24, 1:35 and 1:48 for GA0.5, 1.0, 1.5 and GA2.0, respectively.

The effect of solvent methanol dosage on the yield and purity was equally important for dendritic macromolecules. In the hood, GA2.0 was studied as a representative and results were listed in Table S1. The best loading of C₂H₅OH was 30 wt. % (Table I, Entry 3). As the methanol content was increased or decreased, the higher yield and purity of macromolecules product could not be obtained.

Fig. S2 presented the effect of the molar ratio of GA2.0 to MAH to production state during

the modified process. Primarily, 1:8, 1:14 and 1:16 were selected in terms of the theoretical arithmetic. As results, sample no.1 exhibited a state of insolubility, and sample no.2 and no.3 showed a state of intense color due to the excessive overdose of MAH (Fig. S2a). Further changing the ratio to 1:10, 1:12 and 1:13 excellent solubility could be clearly observed and the sample of 1:13 molar ratio appeared more compromised color (Fig. S2b). Thus, the greatest molar ratio of GA2.0 to MAH was 1:13 utilizing to synthesis modified dendritic monomer (DA).

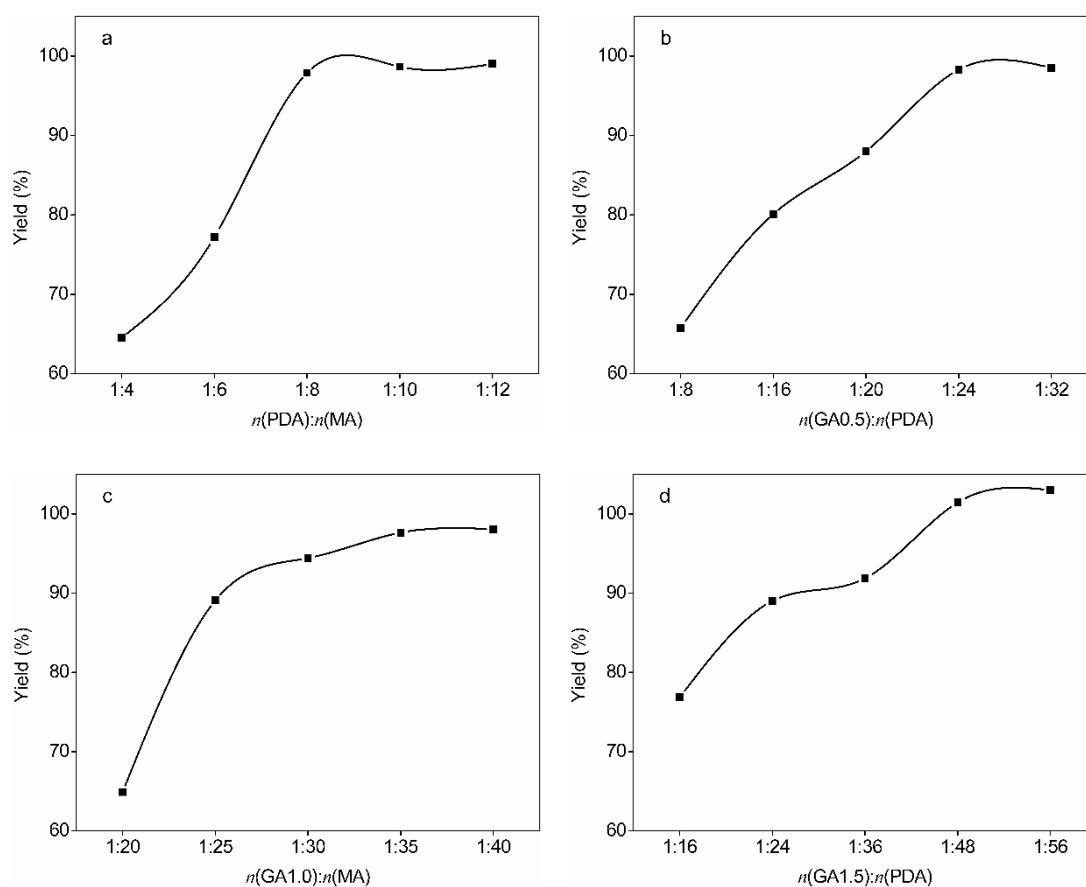


Fig. S1 Effect of the raw materials molar ratio (Temperature = 25 , reaction time = 24 h)

Table S1 Effect of solvent methanol dosage

Entry ^a	C ₂ H ₅ OH (wt. %)	Yield (%)	Purity (%)
1	25	88.8	85.3
2	28	93.1	91.2
3	30	97.0	97.4
4	35	89.6	87.3
5	38	83.5	82.3

^aCondition: n(GA1.5):n(PDA) = 1:48, Temperature = 25°C and reaction time = 24 h.

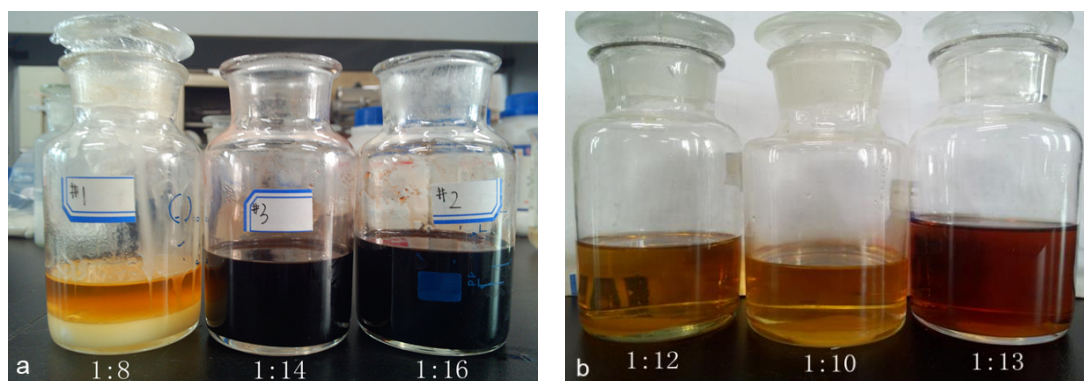


Fig. S2 Effect of the molar ratio between GA2.0 and maleic anhydride

Characterization of GA0.5-GA2.0

The chemical structure of GA0.5-GA2.0 were confirmed with IR and ¹H-NMR spectroscopy as shown in Fig. S3 and S4. It is obvious that both of the IR spectra of GA.0.5, GA1.5 (Fig. S3a) and the IR spectra of GA.1.0, GA2.0 (Fig. S3b) existed homologous absorption peak. The absorptions peaks at 2950 cm⁻¹, 2815 cm⁻¹ were assigned to C–H of methylene of GA0.5. The peak at 1737 cm⁻¹ was attributed to the stretching vibration of C=O, while 1174 cm⁻¹ peak was the result of the stretching vibration of C–O. In addition, we could find the appearance of new characteristic absorption peaks of N–H at 3288 cm⁻¹ from the spectrum curve of GA1.5 in comparison to GA0.5. Similarly, from Fig. S3b, the characteristic absorption peaks of C=O, C–O and C–H in methylene could be observed readily. Meanwhile, the broad peak ranged from 3260 cm⁻¹ to 3421 cm⁻¹ was the overlap of primary amine and secondary amide. From the ¹H-NMR spectrogram of GA0.5-GA2.0 (Fig. S4), it is clear that the chemical shift of –CH₂–CH₂–N–, –CH₂–CH₂–N– and –CH₂–C=O displayed 1.5 ppm, 2.3 ppm and 2.6 ppm, respectively. Particularly, the proton peak of –NH– bonded with the

carbonyl C=O in the GA1.0-GA2.0 was obtained at 7.1-7.8 ppm. The signal observed at 3.1 ppm contributed to the proton peak of $-NH_2$ as seen in Fig. S4b. Therefore, the structures of GA0.5-GA2.0 were consistent with initial design by means of IR and 1H -NMR data.

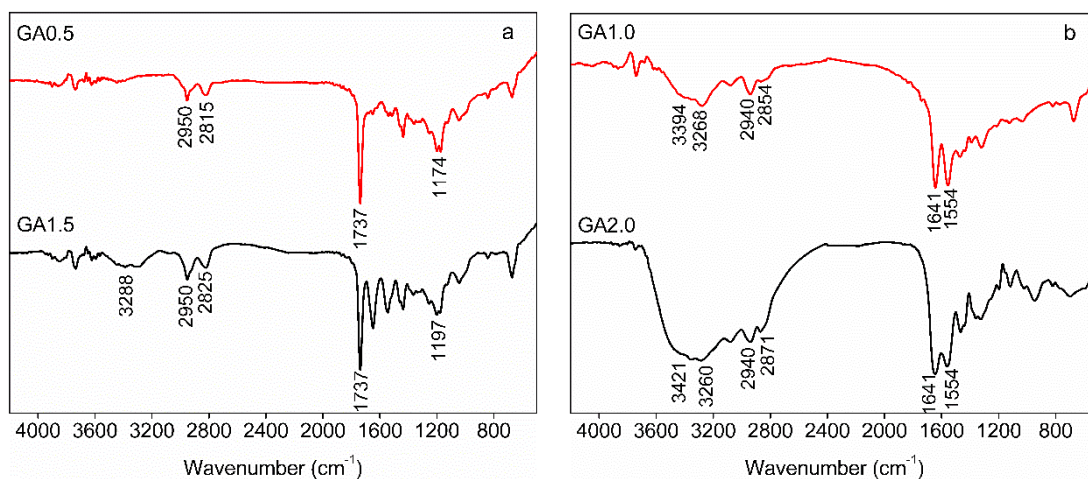


Fig. S3 IR spectra of dendritic macromolecules (GA0.5-2.0)

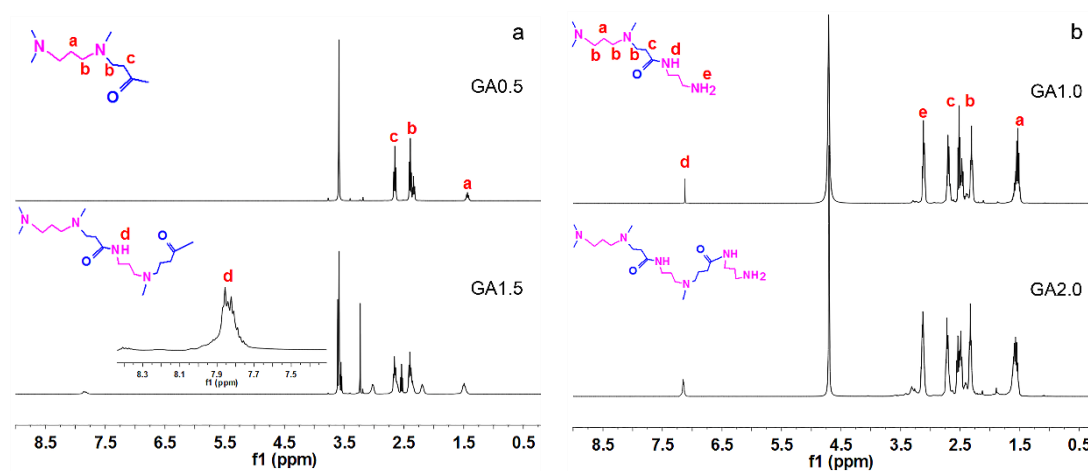


Fig. S4 1H -NMR spectra of dendritic macromolecules (GA0.5-2.0)

Optimum of copolymerization conditions

Given the significance of the ratios of AM to AA for final polymer properties, it was first investigated under fixed others conditions as summarized in Table II (Entries 1-5). It was found that when the feeding ratio of AM to AA was increased to 7:3, the

viscosity retention rate of polymer solution increased abruptly to 85.2% with 439.3 mPa s apparent viscosity (Entry 5), which was the highest among all of the samples and other's ratios only gave 75.7- 81.1% in spite of highly viscosity (Entry 1-4).

Then the effect of DA loading on copolymerization was studied (Entry 3, 6-9). With the increase of DA, the apparent viscosity and retention rate of the polymer solution also increased. However, the dissolving time of polymer solution continued to increase as well that indicated the dissolving power gradually becomes poor. Thus the best dosage of DA was 0.4 wt. % (Entry 8).

The concentration of total monomers were critical to the performances of polymer. Hence, the monomers content was investigated (Entry 8, 10 -13). It could be note that the apparent viscosity of polymer solution increased as the concentration was increased, yet the retention rate first increased and then decreased. So, the best result was obtained when the total monomers concentration was 25 % (Entry 11).

Finally, we research the effect of initiator concentration on polymer, which was equally significant factor for copolymerization (Entry 11, 14 -17). The most pleased loading of initiator was 0.2 wt. % (Entry 11). When the initiator concentration was increased or decreased, both of the higher apparent viscosity and retention of polymer could not be achieved.

Table S2 The Optimization of Monomers Ratio and Initiator Concentration

Entry ^a	AM:AA ^b	DA (wt. %)	Content (wt. %)	Initiator (wt. %)	Dissolving time (h)	Viscosity (mPa·s) ^c	Retention rate (%) ^d
1	5:5	0.5	20	0.2	24	290.4	75.7
2	6:4	0.5	20	0.2	24	350.2	77.8
3	7:3	0.5	20	0.2	24	439.3	85.2
4	8:2	0.5	20	0.2	24	456.6	81.1
5	9:1	0.5	20	0.2	24	465.6	80.8
6	7:3	0.2	20	0.2	4	387.1	70.6
7	7:3	0.3	20	0.2	6	396.7	80.8
8	7:3	0.4	20	0.2	12	423.0	84.7
9	7:3	0.6	20	0.2	36	454.1	86.4
10	7:3	0.4	15	0.2	12	377.5	79.2
11	7:3	0.4	25	0.2	12	436.8	86.9
12	7:3	0.4	30	0.2	12	445.0	83.0
13	7:3	0.4	35	0.2	12	451.3	80.6
14	7:3	0.4	25	0.1	12	417.7	83.7
15	7:3	0.4	25	0.3	12	374.4	80.1
16	7:3	0.4	25	0.4	12	299.9	72.5
17	7:3	0.4	25	0.5	12	167.3	58.4

^a Condition: pH = 7, Temperature = 45°C, AMPS = 0.5 (wt. %) and reaction time = 6 h.

^b AM: AA: the mass ratio of AM and AA.

^c Viscosity: concentration of copolymer solution = 2000 mg/L, tested by Brookfield DV-III Programmable Rheometer (Brookfield Co., America) at 65°C.

^d Retention rate: the polymer solution of 2000 mg/L was sheared by Mixing Speed Governor (WT-VSA2000B) at 3500 r/min for 20 s.

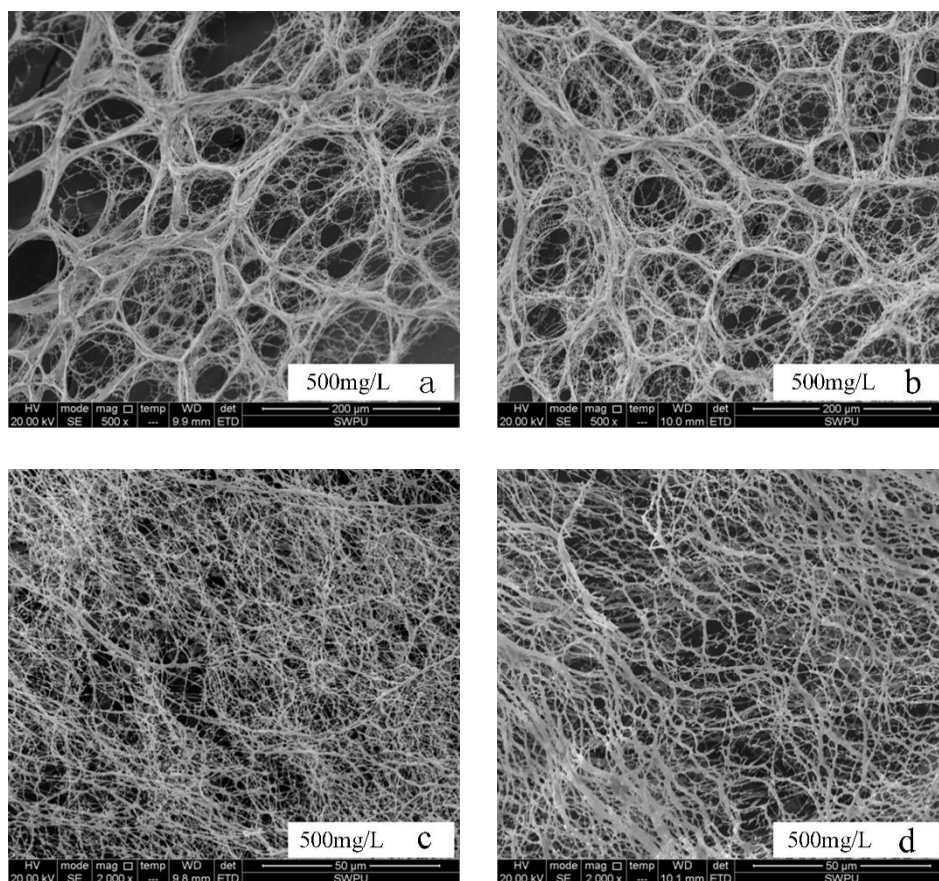


Fig. S5 SEM morphologies of (a) HPDA-unsheared, (b) HPDA-sheared, (c) Poly (AM/AA/AMPS)-unsheared, (d) Poly (AM/AA/AMPS)-sheared.

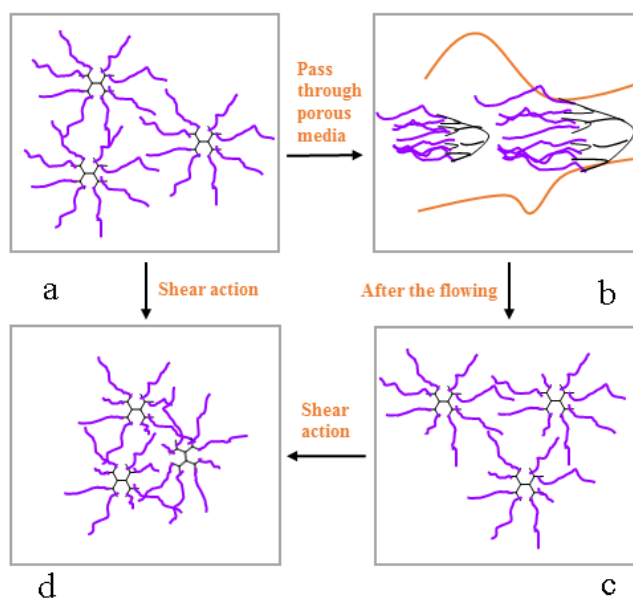


Fig. S6 Schematic representation of morphology of hyperbranched polymer HPDA passing

through porous media; (a) entanglement of terminal flexible chains to form network structure, (b) deformation of polymer construction to preferably pass through medium-low pore throat, (c) damage of partial branched chains and reformed network structure due to the entanglement of residual terminal flexible chains, (d) broke partial branched chains and formed more dense network structure due to the smaller steric hindrance between the branched chains.

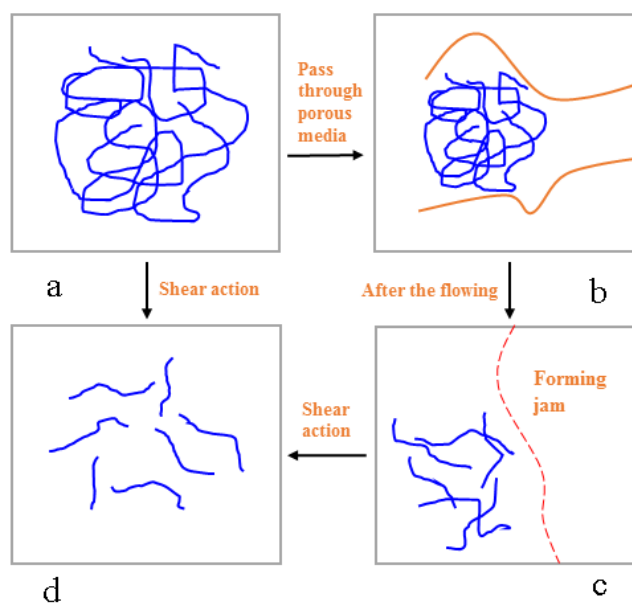


Fig. S7 Schematic representation of morphology of linear polymer passing through porous media; (a) entanglement of linear chains to form network structure, (b) cannot deformed meeting medium-low pore throat, (c) forming of stable jam or severe destruction of linear molecular structure, (d) destruction of linear molecular structure to form decentralized chain segment.