

## Supporting Information

### **All-in-One Hyperbranched Polypeptides for Surgical Adhesive and Interventional Embolization of Tumor**

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#### **Synthesis of monomer**

##### **Synthesis of EG<sub>2</sub>-Glu-NCA <sup>[1]</sup>**

##### **Synthesis of DOPA-NCA**

L-DOPA (200 mg, 1.01 mmol) and triphosgene (200 mg, 0.67 mmol) were dissolved in anhydrous THF (50 mL) under argon and heated at 60 °C for 1 h with constant stirring. The reaction mixture was concentrated in vacuo to yield DOPA-NCA as a viscous yellow oil. DOPA NCA was synthesized and used immediately for each polymerization.

##### **Synthesis of Arg-NCA**

Anhydrous tetrahydrofuran (THF) of 200 mL was added rapidly to a suspension of 10.0 g (34.2 mmol) of N-benzyloxycarbonyl-L-arginine with stirring vigorously at room temperature. Next, a solution containing 10 mL of PBr<sub>3</sub> in 40 mL of THF was added to the reaction mixture placed in an ice bath. After stirring for 3 h at room temperature, THF was decanted from the product, which had deposited as a heavy oil. The heavy oil was washed by decantation with THF and dried in vacuo, yielding a faint yellow oil.

##### **Synthesis of Cys-NCA**

L-Cysteine NCA was synthesized by treating L-cysteine with triphosgene in THF. To a solution of triphosgene (1.47 g, 4.95 mmol) in THF (10 mL) was added L-cysteine (1.0 g, 8.25 mmol) in THF (30 mL), and the mixture was stirred at 50 °C under a nitrogen atmosphere. After 2.5 h, the mixture became a clear and yellowish solution, and then the reaction was cooled to room temperature. After removing the solvent on a rotary evaporator, the yellowish

precipitate obtained by adding n-hexane into the viscous solution was collected by filtration, successively recrystallized completely by adding n-hexane and ethyl acetate, and then white crystal was obtained.

### **Synthesis of Ac-Lys-NCA**

Ac-Lys-NCA was synthesized by treating  $\epsilon$ -N-acryloyl lysine with triphosgene in THF. To a solution of triphosgene (0.79 g, 2.66mmol) in THF(10 mL) was added  $\epsilon$ -N-acryloyl lysine (1.0 g, 4.42mmol)in THF (30 mL), and the mixture was stirred at 50 °C under a nitrogen atmosphere. After 1 h, the mixture became a clear and yellowish solution, and then the reaction was cooled to room temperature. After removing the solvent on a rotary evaporator, the yellowish precipitate obtained by adding n-hexane into the viscous solution was collected by filtration, successively recrystallized completely by adding n-hexane and ethyl acetate, and then white crystal was obtained.

**[1]** Y. Liao, C.-M. Dong, *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 1834-1843.

### **NMR Spectra**

NMR spectra were recorded on VARIAN JNM-ECP 600 MHz instruments using deuterium dimethyl sulfoxide (DMSO) as the solvents.

### **Molecular Mass Testing**

The molecular weight distribution of the polymers was characterized by light scattering (DAWN EOS, laser wavelength: 690.0nm) and gel permeation chromatography (GPC) (H<sub>2</sub>O as eluent).

### **Lower Critical Solution Temperature (LCST)**

The lower critical solution temperature (LCST) at 500nm was measured by UV-VIS spectrophotometer and the transmittance was measured. It is one of the important characteristics of polymer temperature sensitive performance parameters. When the

transmittance decreases to 50% of the initial transmittance, the measured temperature is defined as LCST.

### **Contact Angle Measurement**

The static contact angle was obtained on the SL200KB instrument at ambient temperature (25 °C) and normal body temperature (37 °C). In all contact angle measurements, the volume of a single droplet is 5 L. The average water contact angle is obtained by measuring the same sample in at least five different positions. All contact angles were measured with water droplets on the surface for about 5 seconds of residence time.

### **Degradation Study**

The degradation of HPEDAC-HPEDAL was studied by dialysis at 37 °C; the size of the dialysis membrane was 3000, the polymer was divided into two groups and dissolved in 50mL buffer solution of PBS (pH = 7.4). Protamex is added to a group. At different times, the dialysis bag was washed with water and dried at room temperature and weighed. Mass loss is calculated by comparing the initial mass with the quality measured at a predetermined time point.

### **The degree of branching (DB)**

The degree of branching (DB) was calculated from the intensity of the <sup>13</sup>C NMR using equation 1. DB represents the degree of branching, D, L<sub>13</sub>, and L<sub>14</sub> represent the fractions of dendritic, linear 1,3-units, and linear 1,4-units, respectively.[2]

$$DB = \frac{2D}{2D + L_{13} + L_{14}}$$

[2] A. Sunder, R. Hanselmann, H. Frey, R. Mulhaupt, *Macromolecules* 1999, 32, 4240-4246.

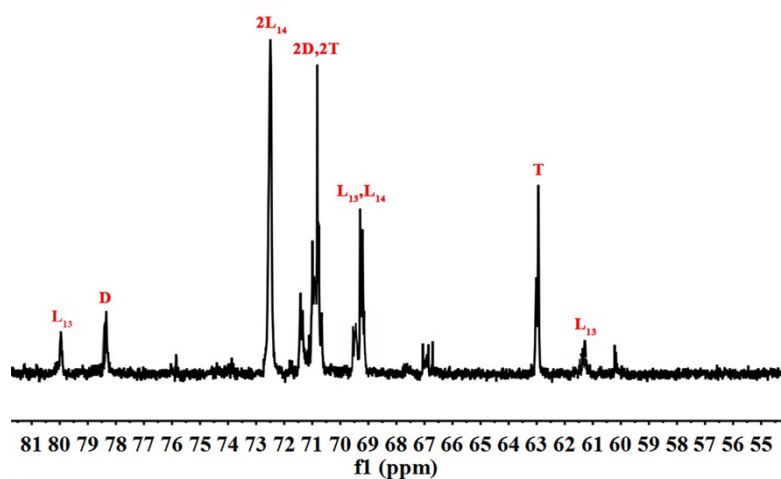


Fig. S1.  $^{13}\text{C}$  NMR spectra of HPG.

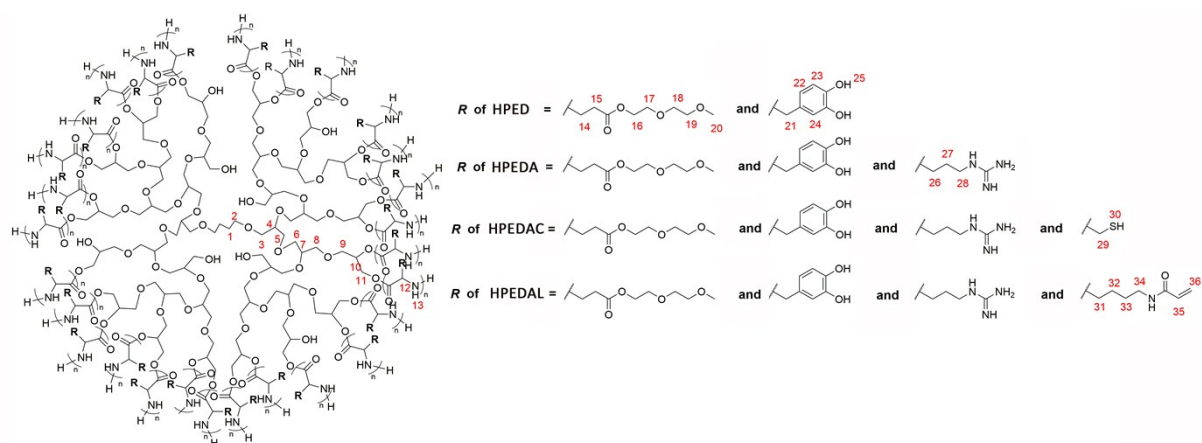


Fig. S2. numbering of copolymeric carbon.

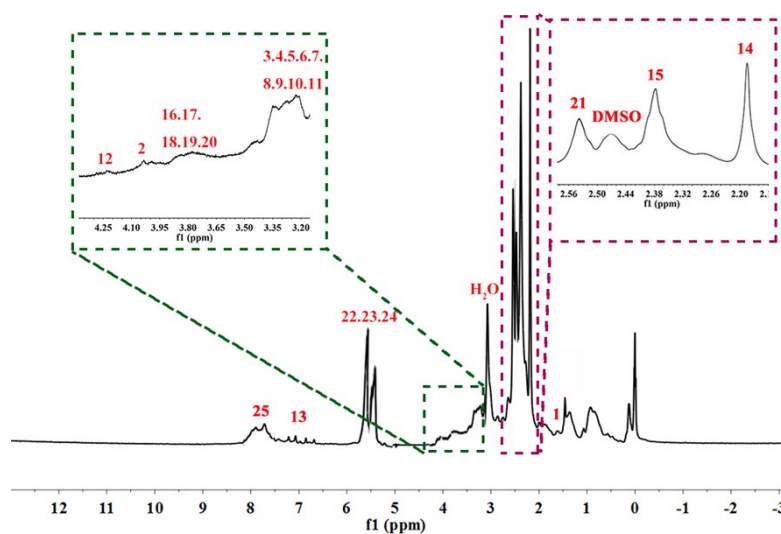
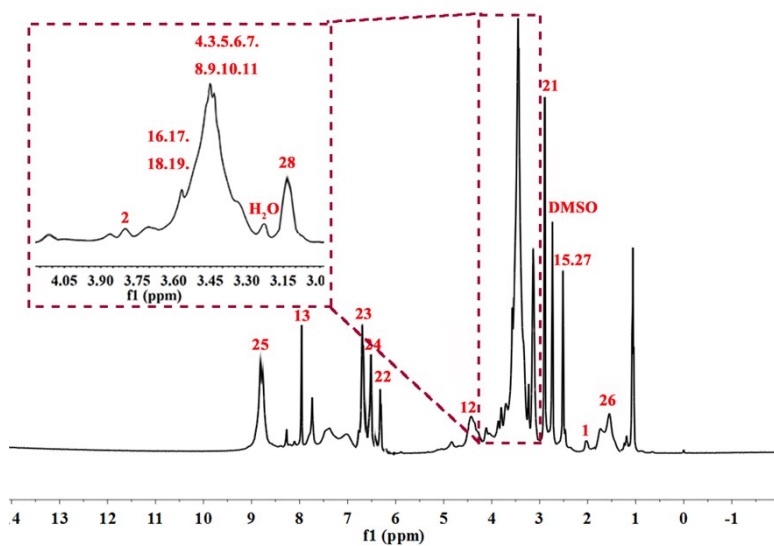
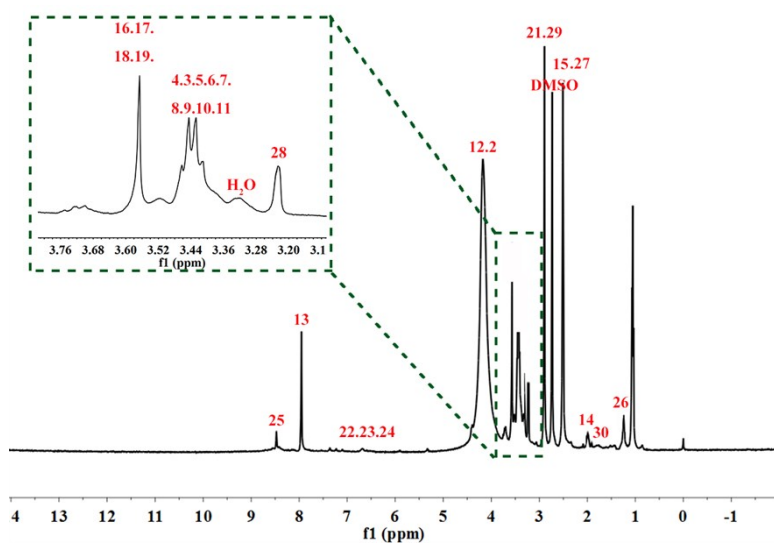


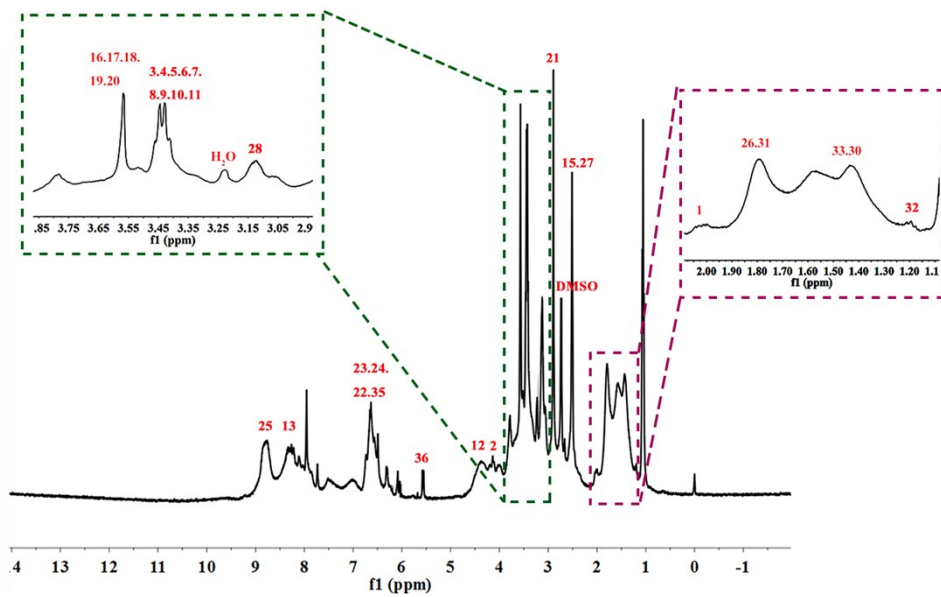
Fig. S3.  $^1\text{H}$  NMR spectra of HPED



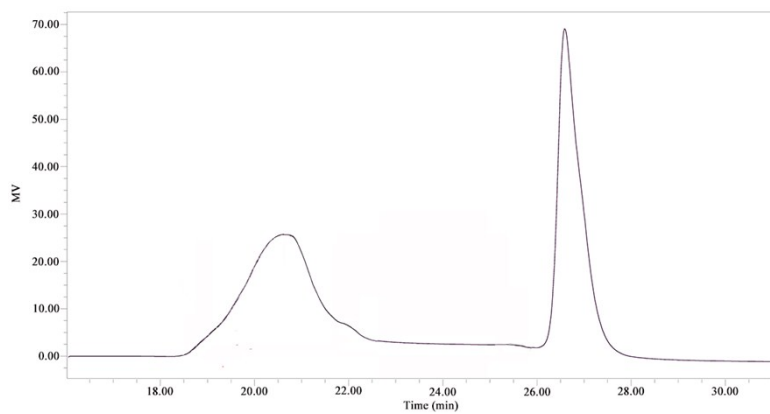
**Fig. S4.**  $^1\text{H}$  NMR spectra of HPEDA



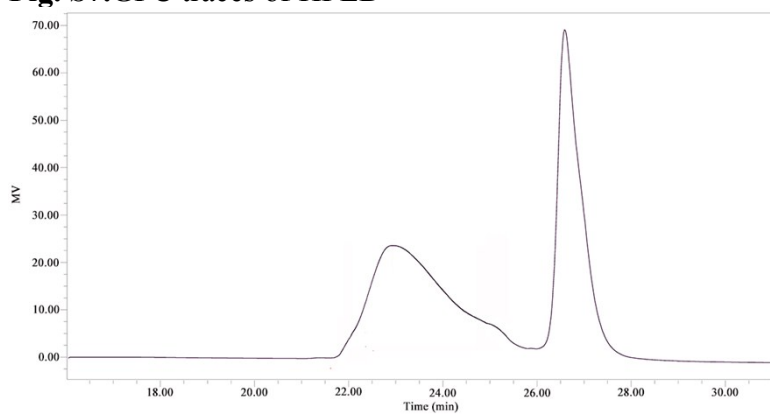
**Fig. S5.**  $^1\text{H}$  NMR spectra of HPEDAC



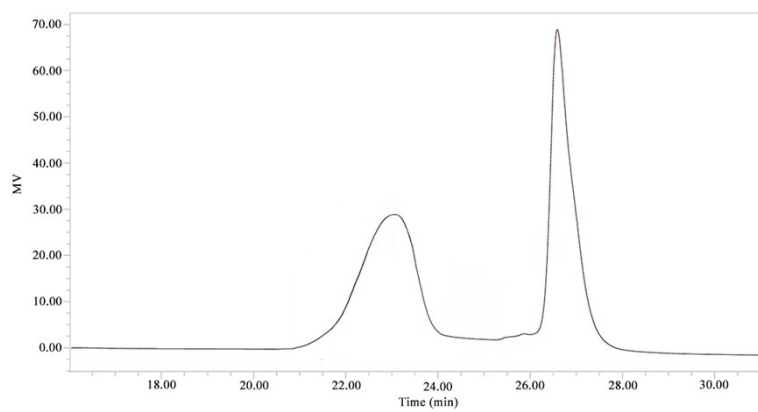
**Fig. S6.**  $^1\text{H}$  NMR spectra of HPEDAL



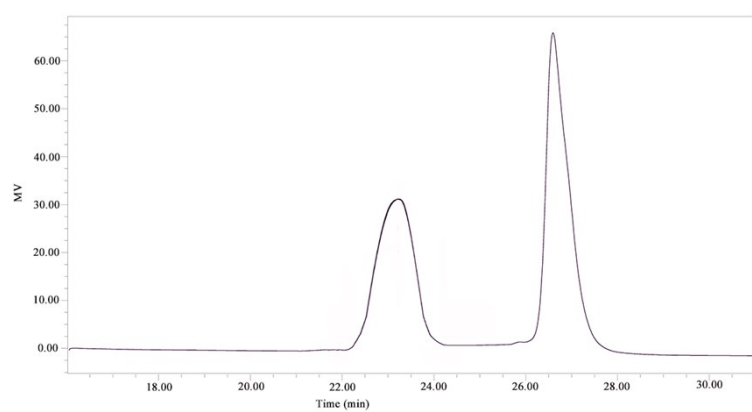
**Fig. S7.** GPC traces of HPED



**Fig. S8.** GPC traces of HPEDA.



**Fig. S9.**GPC traces of HPEDAC



**Fig. S10.**GPC traces of HPEDAL.