

## Supporting Information

# A Branching Point Thermo and pH Dual-Responsive Hyperbranched Polymer Based on Poly(*N*-vinylcaprolactam) and Poly(*N,N*-diethylaminoethyl methacrylate)

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### Synthesis of alkynyl-terminated linear polymers (PVCL-C≡CH and PDEAEMA-C≡CH)

**(a) Synthesis of PVCL-C≡CH.** PVCL-COOH (3.2 g, 0.3 mmol), DCC (0.62 g, 3 mmol) and NHS (0.35 g, 3 mmol) were completely dissolved in DMF (25 mL) under a N<sub>2</sub> atmosphere. Propargylamine (0.17 g, 3 mmol) dissolved in DMF (3 mL) was added dropwise to the above solution at ice-water bath. After the reaction was kept at ambient temperature for 24 h, the precipitate was filtered out and the crude product was left in filtrate. The solvent was evaporated under the reduced pressure at 80 °C/10<sup>-4</sup> bar. The product was obtained which was again dissolved in DMF, and then precipitated into cold diethyl ether for three times. The PVCL-C≡CH obtained was dried at 30 °C in a vacuum oven for 3 d. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ, ppm): 4.33 (—CH—); 1.67—1.70 (—CH<sub>2</sub>—, from the backbone); 3.34 (—CH<sub>2</sub>—N—); 2.44 [—(CO)—CH<sub>2</sub>—] 2.57 (—S—CH<sub>2</sub>—CH<sub>2</sub>—CO—); 2.73 (—S—CH<sub>2</sub>—CH<sub>2</sub>—CO—); 3.89 (—CH<sub>2</sub>—NH—). SEC/MALLS: *M*<sub>n</sub>=10610, *M*<sub>w</sub>=13350, *M*<sub>w</sub>/*M*<sub>n</sub>=1.26.

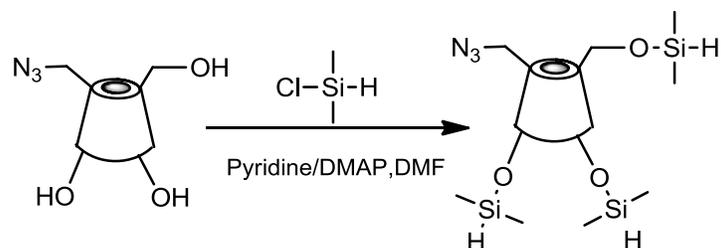
**(b) Synthesis of PDEAEMA-C≡CH.** The synthetic procedures were similar to PVCL-C≡CH. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ, ppm): 0.86—1.03 (—CH<sub>3</sub>); 1.91 (—CH<sub>2</sub>—, from the backbone); 4.36 (—O—CH<sub>2</sub>—CH<sub>2</sub>—); 3.40 (—O—CH<sub>2</sub>—CH<sub>2</sub>—); 3.18 [(CH<sub>3</sub>—CH<sub>2</sub>)<sub>2</sub>—N—]; 1.30 [(CH<sub>3</sub>—CH<sub>2</sub>)<sub>2</sub>—N—]; 2.67 (—S—CH<sub>2</sub>—CH<sub>2</sub>—COOH); 2.73 (—S—CH<sub>2</sub>—CH<sub>2</sub>—COOH). SEC/MALLS: *M*<sub>n</sub>=18590, *M*<sub>w</sub>=13580, *M*<sub>w</sub>/*M*<sub>n</sub>=1.37.

### Synthesis of hyperbranched polymers with PVCL or PDEAEMA chains at branching points, HBP(A<sub>2</sub>+B<sub>x</sub>)-*g*-PVCL and HBP(A<sub>2</sub>+B<sub>x</sub>)-*g*-PDEAEMA

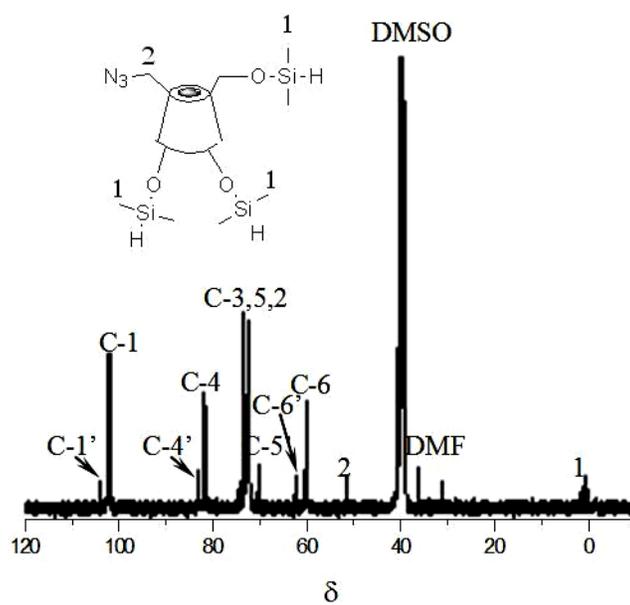
**(a) Synthesis of HBP(A<sub>2</sub>+B<sub>x</sub>)-*g*-PVCL.** PVCL-C≡CH (2.2 g, 2 mmol) was used instead of the mixture of PVCL-C≡CH and PDEAEMA-C≡CH, and the synthetic procedures were similar to HBP(A<sub>2</sub>+B<sub>x</sub>)-*g*-PVCL/PDEAEMA except that the pure water (pH=7.2) was used to dissolve the crude product instead of the acid water (pH<4). <sup>1</sup>H NMR (D<sub>2</sub>O, δ, ppm): 4.19 (—CH<sub>2</sub>—CH—N—); 3.25

(—N—CH<sub>2</sub>—); 2.38 (—CH<sub>2</sub>—CO—); 1.86 (—CH<sub>2</sub>—); 1.68 (—N—CH<sub>2</sub>—(CH<sub>2</sub>)<sub>3</sub>—). SEC/MALLS:  
 $M_n=202100$ ,  $M_w=242500$ ,  $M_w/M_n=1.20$ .

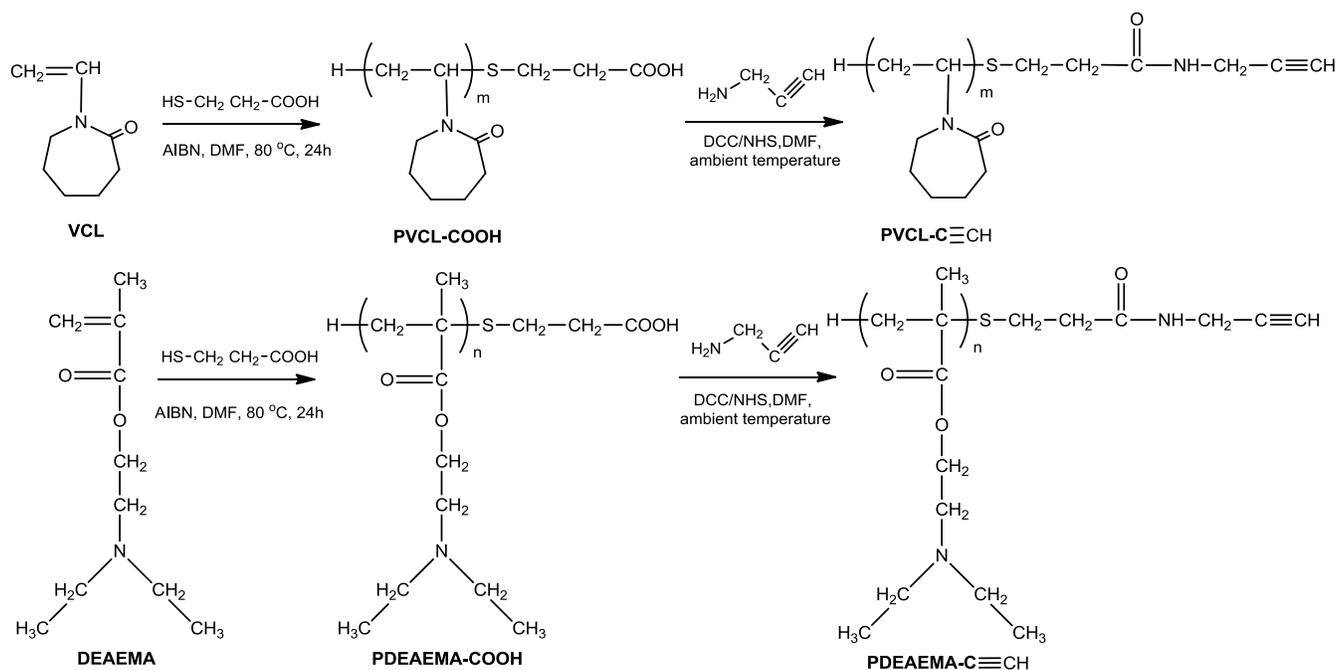
**(b) Synthesis of HBP(A<sub>2</sub>+B<sub>x</sub>)-g-PDEAEMA.** PDEAEMA-C≡CH (2.2 g, 2 mmol) was used instead of the mixture of PVCL-C≡CH and PDEAEMA-C≡CH, and the synthetic procedures were similar to HBP(A<sub>2</sub>+B<sub>x</sub>)-g-PVCL/PDEAEMA. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ, ppm): 0.81—0.98 (—CH<sub>3</sub>); 1.87 (—CH<sub>2</sub>—, from the backbone); 4.32 (—O—CH<sub>2</sub>—CH<sub>2</sub>—); 3.35 (—O—CH<sub>2</sub>—CH<sub>2</sub>—); 3.11 [(CH<sub>3</sub>—CH<sub>2</sub>)<sub>2</sub>—N—]; 1.18 [(CH<sub>3</sub>—CH<sub>2</sub>)<sub>2</sub>—N—]. SEC/MALLS:  $M_n=361400$ ,  $M_w=441000$ ,  $M_w/M_n=1.22$ .



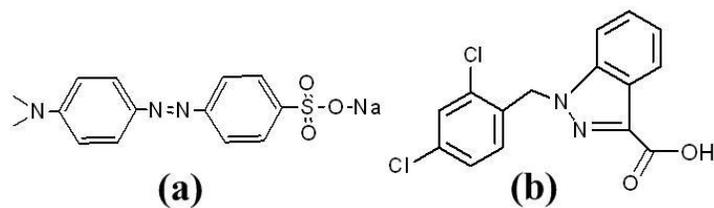
**Scheme S1.** Synthetic route for  $B_x-N_3$  monomer



**Figure S1.**  $^{13}C$  NMR spectrum of  $B_x-N_3$  monomer in  $DMSO-d_6$  and  $DMF-d_6$



**Scheme S2.** Synthetic routes for PVCL-C≡CH and PDEAEMA-C≡CH



**Scheme S3.** Chemical structures of MO (a) and LND (b)