

# Supporting Information

## **Synthesis of Amphiphilic Copolymers with a Dendritic Polyethylene Core and Poly(ethylene oxide) Arms and Their Self-Assembled Nanostructures**

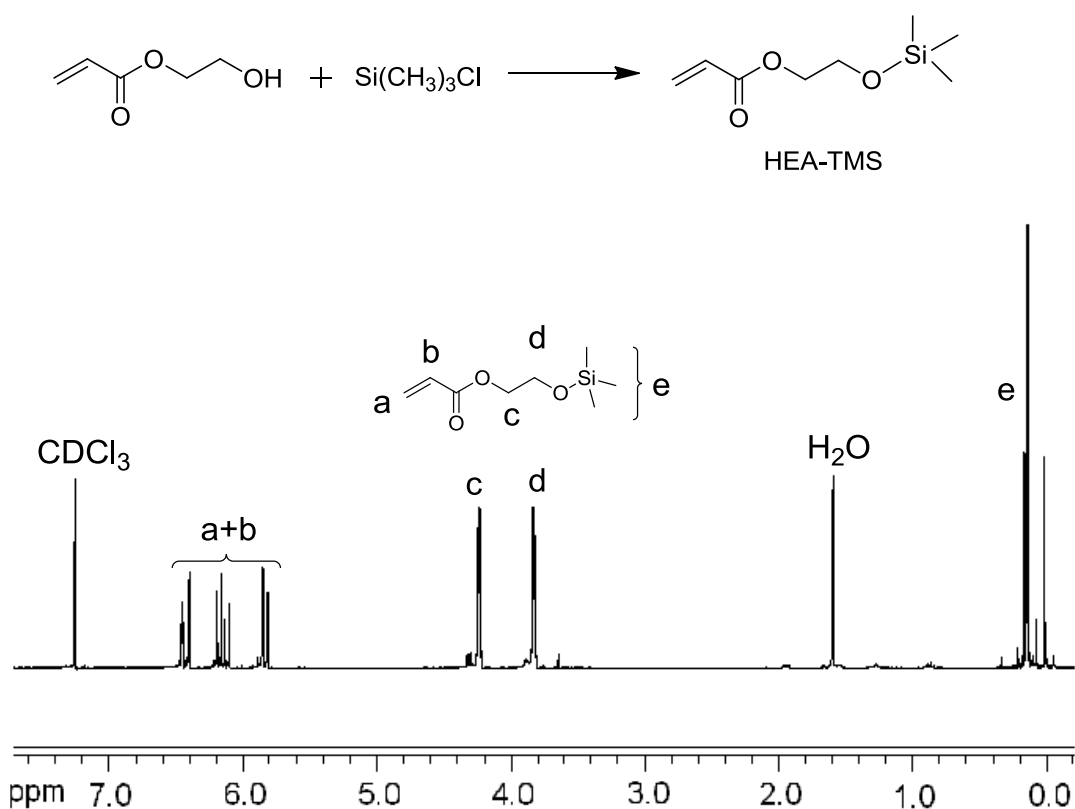
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## 1) Synthesis of copolymerization comonomer HEA-TMS.

In a dry round-bottom Schlenk flask with stirring bar, an amount of 11.6 g (0.1 mol) of 2-hydroxyethyl acrylate (HEA) was dissolved in anhydrous and degassed  $\text{CH}_2\text{Cl}_2$ . Then 13.6 g (0.2 mol) of imidazole, and 12.96 g (0.12 mmol) of  $\text{Me}_3\text{SiCl}$  in  $\text{CH}_2\text{Cl}_2$  solutions were added sequentially under the conditions of protection of  $\text{N}_2$  and  $0^\circ\text{C}$ . The reaction was stirred for overnight at room temperature. The organic solution was washed twice by water before dried over anhydrous  $\text{MgSO}_4$  overnight. The crude product was separated and purified by silica gel column chromatography, and pure HEA-TMS was obtained in yield 92%.



**Fig. S1**  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 300MHz) spectrum of HEA-TMS.

## 2) Synthesis of DPE-(OH)<sub>11</sub> by chain walking copolymerization of ethylene with HEA-TMS

In a typical procedure, a 300 mL Parr glass reactor with stirring bar was heated 3 h to 150 °C under vacuum and then cooled to room temperature. The flask was pressurized to 0.1 atm of ethylene and vented three times. The appropriate CH<sub>2</sub>Cl<sub>2</sub> solvent and HEA-TMS were introduced into the glass reactor under ethylene atmosphere at 35 °C. The system was maintained by continuously stirring for 10 min, and then 10 mL solution of palladium catalyst (300 μmol) in CH<sub>2</sub>Cl<sub>2</sub> were syringed into the well-stirred solution, and the total reaction volume was kept at 100 mL. The ethylene pressure was kept constant value of 0.1 atm by continuous feeding of gaseous ethylene throughout the reaction. The polymerizations were terminated by the addition of a large amount of methanol after continuously stirring for 24 h. Then the methanol was decanted off, the sticky polymer was redissolved in petroleum ether. The polymer solution was filtered through alumina and silica to remove catalyst residues. The resulting precipitated polymers were **condensed and collected**. The TMS protection groups of copolymer were removed to free all of the hydroxyl groups. The deprotection of TMS was done by treating the copolymers with tetrabutylammonium fluoride (10.0 equiv. of the calculated TMS group) in THF solution for overnight. After being concentrated in vacuum, the product was then precipitated out by adding a large amount of methanol, and dried under vacuum at 40 °C.

**Table S1** Results of chain walking copolymerization of ethylene with HEA <sup>a</sup>.

Sample	C <sub>HEA</sub>	Yield	HEA <sub>inc</sub> <sup>b</sup>	M <sub>n</sub> <sup>c</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>	N <sub>OH</sub> <sup>d</sup>	BD <sup>e</sup>	D <sub>g</sub> /D <sub>h</sub> <sup>f</sup>
	(M)	(g)	(mol%)	(kg/mol)				
DPE	0.02	19.5	0.32	95	1.38	11	102	0.76

<sup>a</sup> Polymerization conditions: catalyst  $3 \times 10^{-3}$  M, solvent CH<sub>2</sub>Cl<sub>2</sub>; temperature=35°C;  
time=24h;

<sup>b</sup> HEA Incorporation (mol%) established by <sup>1</sup>H NMR;

<sup>c</sup> Measured by GPC using a light scattering detector;

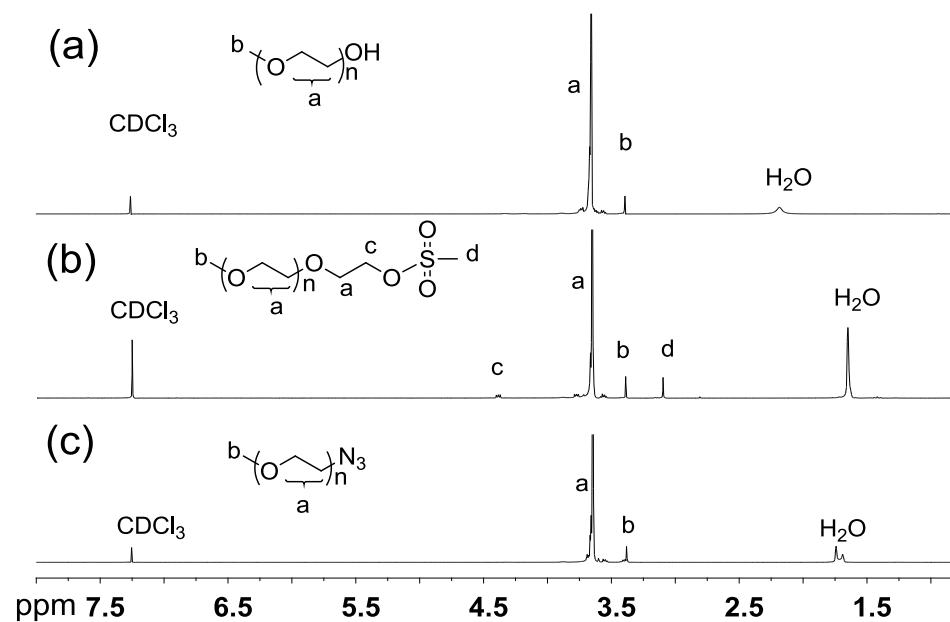
<sup>d</sup> Average number of hydroxyl per dendritic polyethylene molecular;

<sup>e</sup> Branch degree: Branches per 1000 C atoms determined by <sup>1</sup>H NMR spectroscopy;

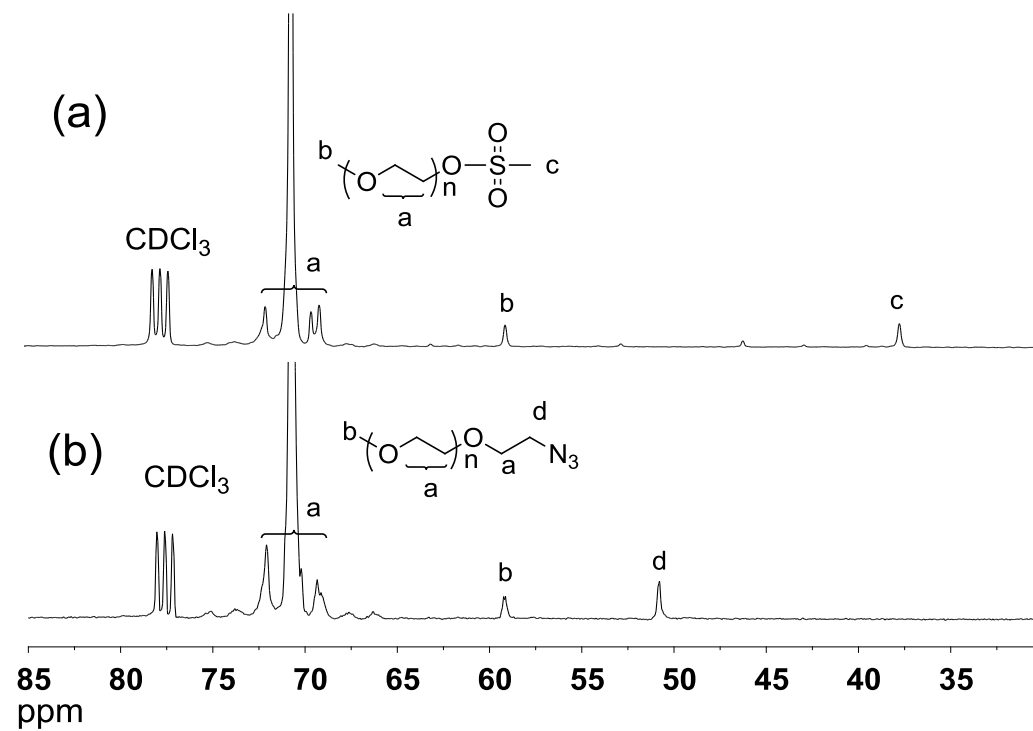
$$BD = \frac{2(I_{CH_3})}{3(I_{CH+CH_2+CH_3})} \times 1000$$

<sup>f</sup> D<sub>g</sub> was determined by GPC-LS, and D<sub>h</sub> was determined by DLS in THF.

### Characterization of azido-terminated PEO (PEO-N<sub>3</sub>)

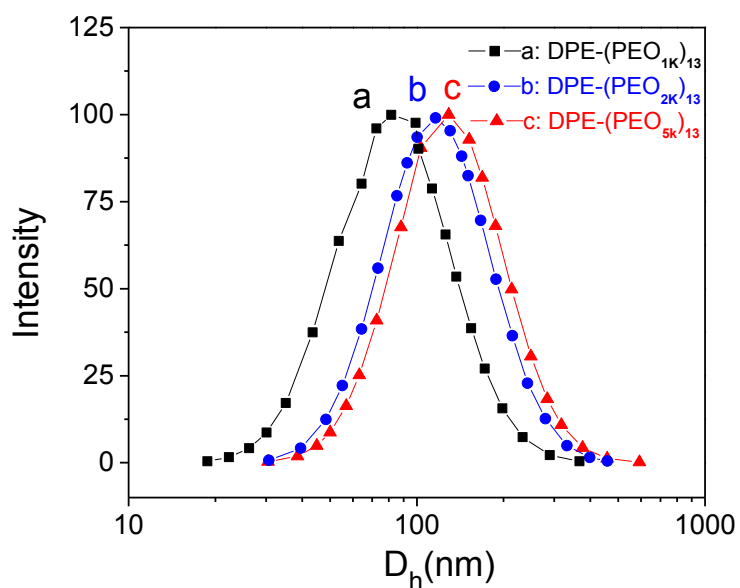


**Fig. S2** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz) spectra of (a) PEO-OH ( $M_n=1100$ ) (b) PEO-OSO<sub>2</sub>CH<sub>3</sub> and (c) PEO-N<sub>3</sub>.

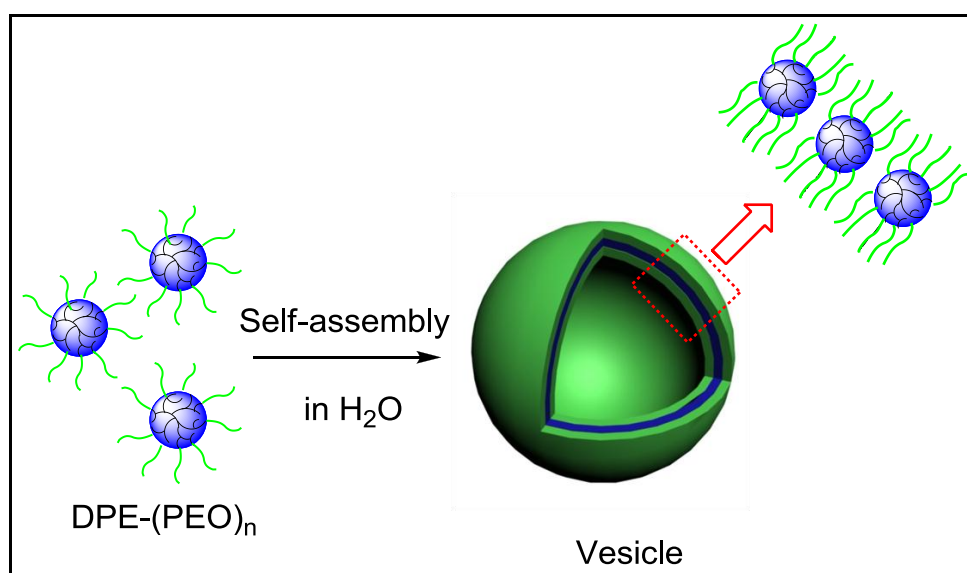


**Fig. S3** <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz) spectra of (a) PEO-OSO<sub>2</sub>CH<sub>3</sub> and (b) PEO-N<sub>3</sub> ( $M_n=1100$ ).

### 3) Self-assembly in water

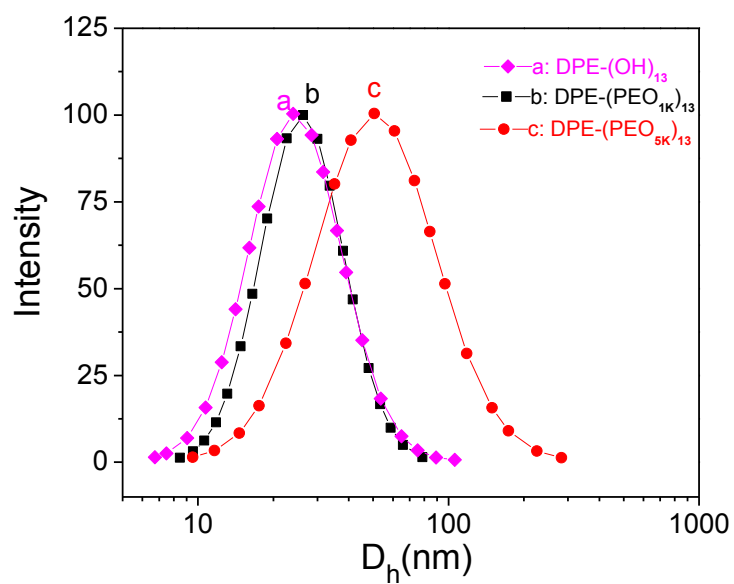


**Fig. S4** Hydrodynamic diameters ( $D_h$ ) of (a) DPE-(PEO<sub>1k</sub>)<sub>11</sub> (b) DPE-(PEO<sub>2k</sub>)<sub>11</sub> and (c) DPE-(PEO<sub>5k</sub>)<sub>11</sub> self-assembled in water at 0.5 mg/mL

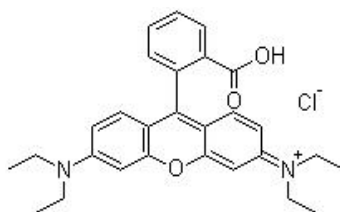


**Fig. S5** A possible self-assembly mechanism for the copolymers DPE-(PEO)<sub>11</sub> vesicle in water

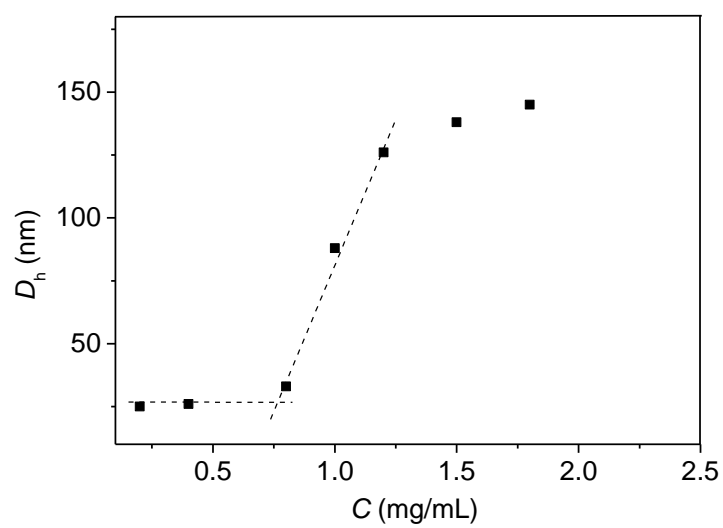
#### 4) Self-assembly in hexane



**Fig. S6** Hydrodynamic diameters ( $D_h$ ) of micelles (a) DPE-(OH)<sub>11</sub>, (b) DPE-(PEO<sub>1k</sub>)<sub>11</sub>, (c) DPE-(PEO<sub>5k</sub>)<sub>11</sub> self-assembled in hexane at 0.5 mg/mL



**Fig. S7** The molecular structure of Rhodamine B



**Fig. S8** Dependence of micelle size of DPE-(PEO<sub>1k</sub>)<sub>11</sub> copolymer in hexane on the polymer concentration