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## **Self-assembly of large multimolecular micelles from hyperbranched star copolymers**

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### **S1. Materials**

Hyperbranched poly (3-ethyl-3-(hydroxymethyl)oxetane) (HBPO) with 37 functional hydroxyl groups was synthesized as reported before<sup>1</sup> (the degree of branching is 30%). 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97%, Aldrich) was used as received. 2-(dimethylamino) ethyl methacrylate (DMAEMA, 99%, Acros) was passed through a column of basic alumina to remove out the stabilizing agents. Copper( ) bromide (CuBr, C.P. Grade, Shanghai Chemical Reagent Co. Ltd) was purified by stirring over 24h in acetic acid, filtered, washed with ethanol, and then dried in vacuo. Tetrahydrofuran (THF, A.R. grade, Shanghai Chemical Reagent Co. Ltd) were refluxed with CaH<sub>2</sub> and then distilled. Other reagents were purchased from Shanghai Chemical Reagent Co. and used as received.

### **S2. Synthesis and Methods**

#### ***Synthesis of Macroinitiator HBPO-Br***

The ATRP initiators were synthesized by reacting the terminal hydroxyl groups of the HBPO precursors with 26% molar excess of 2-bromoisobutyryl bromide. Typically, in a one-neck flask, 6.00g (51.7 mmol hydroxyl groups) of HBPO was dissolved in 80mL dried

tetrahydrofuran (THF), after degassed for three cycles by pulling a vacuum and back-filling with nitrogen gas, then 0.73g (6.0 mmol) *N,N*-dimethylaminopyridine and 6.00g (59.2 mmol) triethylamine were added. At 0 °C, 2-bromo-isobutyryl bromide (15.0g, 65.2mmol) (diluted in 30 mL THF) was added drop-wise at a rate of 1 drop/3 S while stirring. Then it was reacted for approximately 72h. The resulting solution was filtered, then THF was removed under reduced pressure, the products were dissolved in CHCl<sub>3</sub>. Then the solution was washed twice with water, 0.5 mol/L hydrochloric acid and 0.5 M NaHCO<sub>3</sub>, and again washed with water. After dried with anhydrous magnesium sulfates and precipitated in cold methanol/water (v/v = 1/1) for 6 times. The product was dissolved in THF and then dried by anhydrous magnesium sulfate. After filtered, THF solvent was removed under reduced pressure, and then the resultant product was dried in vacuum for 24h to give a colorless solid.

### ***Synthesis of HBPO-star-PDMAEMAs***

A series of multi-arm star copolymers were synthesized in the presence of macroinitiator with CuBr as catalyst, HMTETA as ligand and THF as solvent. The general procedure was as follows. The macroinitiator and CuBr were placed into an oven-dried reaction tube, then it was sealed with a rubber septum, after degassed for three cycles by pulling a vacuum and back-filling with nitrogen gas, dried THF was added via a syringe. After the macroinitiator was dissolved completely, the solution was degassed for another three cycles. Then HMTETA was added by syringe. When the solution turned to light blue, DMAEMA monomer was added. The reaction was carried out at 60 °C until reaction solution had certain viscosity. The resultant sample was diluted with THF, passed through a column of basic alumina to remove copper salts, and then precipitated in cold *n*-hexane. The product was dried in vacuo over 48 hours at 40 °C.

## ***Measurement***

$^1\text{H}$  NMR spectra of the copolymers were recorded on a Varian Mercury Plus 400-MHz spectrometer with  $\text{CDCl}_3$  as solvent. The molecular weights and polydispersities of the copolymers were measured by SEC at 70 °C on a Perkin-Elmer Series 200 system (100  $\mu\text{L}$  injection column, 10  $\mu\text{m}$  PL gel 300 mm $\times$ 7.5 mm mixed-B columns) equipped with a RI detector. Dimethylformamide containing 0.01 mol/L lithium bromide was used as eluent at a flow rate of 1.0 mL/min. The column system was calibrated by mono-dispersed standard polystyrenes.

Fluorescence measurements were performed with pyrene and Nile red as the fluorescent probes to determine the critical micellization concentration (CMC). 1) Pyrene. HBPO-*star*-PDMAEMA sample was initially dissolved in pyrene containing water solution. Then the copolymer solution was prepared by diluting from a 10 mg/mL solution of HBPO-*star*-PDMAEMA to various desired concentrations (from 5 mg/mL to  $1\times 10^{-6}$  mg/mL) with a constant pyrene concentration of  $6\times 10^{-6}$  M. The excitation wavelength was set at 335nm. The  $I_1/I_3$  ratio values of all solutions were recorded. 2) Nile red. Different dilutions were prepared from a 2 mg/mL aqueous solution of HBPO-*star*-PDMAEMA to obtain samples with concentration ranging from 1 mg/mL to  $2\times 10^{-5}$  mg/mL. Then 5  $\mu\text{L}$  solution of Nile red in acetone (0.4 mg/mL) were added to 5mL of each sample. Emission spectra were recorded from 500 to 750 nm using a  $\lambda_{exc} = 557$  nm. The fluorescence spectra were both recorded on a LS-50B luminescence spectrometer (PERKIN ELMER Co., U.S.A.).

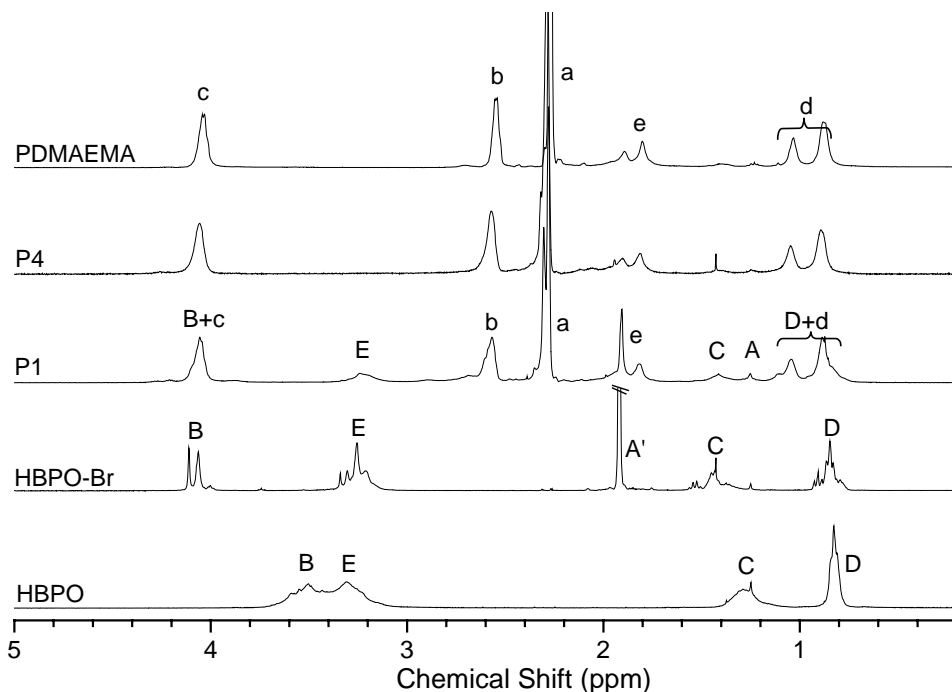
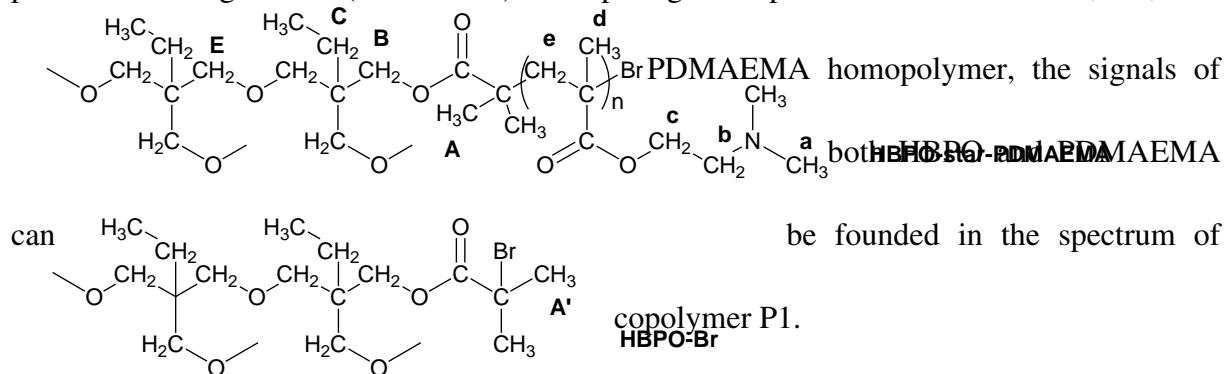
The DLS measurements with salt were also performed in aqueous solution at 20 °C with polymer concentrations of 10 mg/mL at a scattering angle of 173° using a Malvern Zetasizer Nano S apparatus equipped with a 4.0 mW laser operating at  $\lambda = 633$  nm. NaCl were added directly to the aqueous sample solution to achieve desired concentration (0.01 M, 0.1 M, 0.2M

and 0.5M).

### S3. Characterization of HBPO-Br and HBPO-*star*-PDMAEMAs

The  $^1\text{H}$  NMR spectra of HBPO, HBPO-Br, HBPO-*star*-PDMAEMA and PDMAEMA are shown in Figure S1. Comparing the  $^1\text{H}$  NMR spectra of HBPO and HBPO-Br, the new signals appeared at 1.92 ppm attributed to the  $-\text{C}(\text{CH}_3)_2\text{Br}$  groups in the spectrum of HBPO-Br, which confirmed that macroinitiator was synthesized successfully. The conversion of hydroxyl groups can be obtained by comparing the  $-\text{C}(\text{CH}_3)_2\text{Br}$  signals (peak A') at 2.0 ppm with the  $-\text{CH}_3$  signals (peak D) of HBPO core at 0.9 ppm. The result shows that all hydroxyl groups have been reacted with 2-bromoisobutyryl bromide.

Typical  $^1\text{H}$  NMR spectra of HBPO-*star*-PDMAEMAs with assignments (symbols A-E represent the signals of HBPO core, and a-e denote the signals from PDMAEMA.) are also presented in Figure S1 (P1 and P4). Comparing the spectra of macroinitiator, P1, and



**Figure S1.**  $^1\text{H}$  NMR spectra of HBPO homopolymers, HBPO-Br macroinitiators, HBPO-*star*-PDMAEMA copolymers and PDMAEMA homopolymers.

Calculation of the  $\text{DP}_{arm}$  from NMR was done by subtracting the integral of the peak at 2.6 ppm ( $-\text{CH}_2\text{N}(\text{CH}_3)_2$ , **b** in Figure S1) from the peak at 4.0ppm ( $-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$  and  $-\text{CH}_2\text{CO}-$ , **c** and **B** in Figure S1), and then dividing the difference with the integral from the peak of  $-\text{CH}_2\text{N}(\text{CH}_3)_2$  ( $\text{DP}_{arm} = \mathbf{b}/(\mathbf{B}+\mathbf{c}-\mathbf{b})$ ). The calculation results of  $\text{DP}_{arm}$  calculation are listed in Table S1. In all cases, the  $\text{DP}_{arm}$  value is smaller than  $R_{feed}$ . Apparently, the intensities of HBPO core signals (see **E** peak, the  $-\text{CH}_2\text{O}-$  signals at 3.2-3.4 ppm) decreased and almost disappeared when  $\text{DP}_{arm}$  changed from 4 (P1) to 34 (P4), because the signals of HBPO cores become more and more difficult to be detected as the accretion of PDMAEMA length.

**Table S1.** Detail characterizations of HBPO precursors and HBPO-*star*-PDMAEMAs

Sample	$R_{feed}^a$	$M_n^b$	Polydispersity <sup>b</sup>	$\text{DP}_{arm}^c$	$M_n^c$
HBPO	--	4,300	2.16	--	--
HBPO-Br	--	6,900	1.93	--	9,800
P1	5	28,300	1.71	4	33,000

P2	7	39,900	1.71	6	44,700
P3	20	56,800	1.73	13	85,300
P4	50	91,800	1.69	34	207,300
P5	100	230,100	1.84	77	457,100
PDMAEMA <sup>d</sup>	--	30,300	1.27	--	--

<sup>a)</sup>  $R_{feed}$  is the feed ratio of DMAEMA to the initiate site of macroinitiator; <sup>b)</sup> determined by SEC, using linear polystyrene as standards; <sup>c)</sup>  $DP_{arm}$ , The number-average degree of polymerization of PDMAEMA arm on every initiating site, is determined by <sup>1</sup>H NMR; <sup>d)</sup> Initiated by ethyl 2-bromoisobutyrate.

The molecular weight obtained by SEC is listed in Table S1, and it is found to steadily increase with the increase of  $R_{feed}$ . The molecular weight distribution of HBPO precursors is relatively high with a polydispersity index of 2.16, however, after copolymerized with DMAEMA, the polydispersity index of copolymer decreases (<1.84).

Both the <sup>1</sup>H NMR and the SEC measurements prove that the HBPO-*star*-PDMAEMAs have been successfully synthesized by ATRP method.

## S4. Characterization of HBPO-*star*-PDMAEMAs micelles

### *Detailed analysis of the CMC measurement*

Both Figure 1a and 1b in the main text show two separate regions as polymer concentration increases. To be more detailed, in Figure 1a, the  $I_1/I_3$  ratio shows a slow decrease below CMC and then a sharp drop; similarly, the emission intensity of Nile red in Figure 1b undergoes a steady increase first, and then a quick rise at higher concentration. We consider that the first change stage below the CMC in both figures is attributed to the unimolecular micelles state of the HBPO-*star*-PDMAEMAs. The unimolecular micelles possess a hydrophobic HBPO core and many hydrophilic PDMAEMA arms, and can solubilize the hydrophobic dyes in the

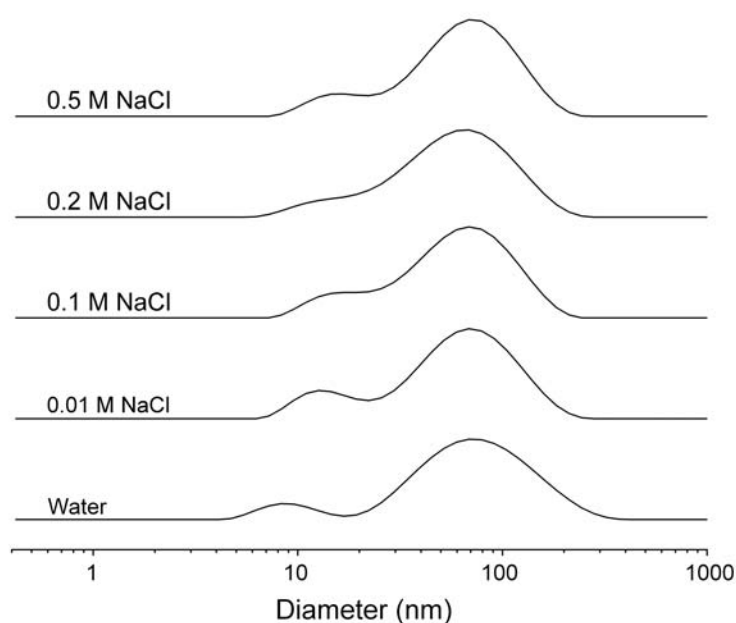
HBPO core to some extent. Thus, the solubility of the dyes increase monotonously with the increase of the polymer concentration, leading to the monotone decreasing of  $I_1/I_3$  ratio for pyrene and monotone increasing of emission intensity for Nile red. However, the HBPO cores are partially hydrated due to the formation of hydrogen bonds between the ether groups and water.<sup>1</sup> So, the solubility of the hydrophobic fluorescent dyes in the HBPO cores of the unimolecular micelles is greatly limited, which leads to the small variation of the  $I_1/I_3$  ratio for pyrene and the emission intensity for Nile red when the polymer concentration is below CMC.

Above CMC, the unimolecular micelles further aggregated together to form the multimolecular micelles as illustrated in Scheme 1b of the main text, thus the hydrated water in the HBPO cores were excluded to achieve the tight packing inside the large micelles, leading to the rapid increase of the hydrophobicity of the HBPO cores. As a result, the solubility of the dye molecules in the hydrophobic domains of the large multimolecular micelles increased quickly, giving rise to the rapid decrease of  $I_1/I_3$  ratio for pyrene in Figure 1a and the increase of emission intensity for Nile red in Figure 1b.

#### ***DLS studies in the presences of NaCl***

Figure S2 shows the intensity weighted size distributions of sample P5 in the presence of different concentration of NaCl. It should be noted that there are still processes with long correction time when NaCl was adding. Therefore, the detected process with long correction time is strictly attributed to the diffusion of large particles. The size of large particles decreased slightly when NaCl was added, more likely as a result of the decreased electrostatic repulsion of the charged PDMAEMA chains in the micelle corona due to the shielding of charges by salt, which tends to reduce the stretching of these chains and thus the size of the micelles.

As indicated in the main text, the hydrophobic interactions between the PDMAEMA arms are responsible for driving the micellar self-assembly of HBPO-*star*-PDMAEMA copolymers. Figure S2 has provided an additional evidence to support that the hydrophobic interactions are operative by the fact that addition of salt only slightly changes the aggregates dimensions.



**Figure S2.** The intensity weighted size distributions of sample P5 in the presence of different concentration of NaCl.

### Supporting reference

[1] Y. Y. Mai, Y. F. Zhou, D. Y. Yan, H. W. Lu. *Macromolecules* **2003**, 36, 9667.